Ion Management And Mass Transport For (photo-) Electrochemical Conversions

Zhifei Yan
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Ion Management And Mass Transport For (photo-) Electrochemical Conversions

Abstract

(Photop-) electrochemistry hold great potential for storing the surplus energy of renewably generated electrons in the form of energy-dense chemicals that can be stored for long periods of time at low cost. The efficiency of converting between electrical- and chemical- energy depends on the charge transfer kinetics at the anode and cathode, as well as ion and mass transport; the latter two have been shown to cause energy losses comparable to those of the electrode charge transfer processes. The first three chapters of the thesis explore the use of bipolar membranes (BPMs) for managing ion transport in CO2 electrolysis, fuel cells, and redox flow batteries, while focusing on understanding the fundamental aspects of BPMs. Chapter 1 introduces the potential of using electrolysis for renewable energy storage and summarizes recent progress in BPM research. In Chapter 2, we combine electrochemical impedance spectroscopy and finite element method based numerical modeling to elucidate the relation between the electric field and interfacial catalysis in enhancing water dissociation reaction in BPMs. Chapter 3 presents the results of managing interfacial protons in a BPM-based CO2 electrolyzer. The acidic local environment at the membrane/catalyst interface facilitates the competing hydrogen evolution reaction and leads to a low CO2 reduction efficiency. This problem was mitigated by coating the membrane with a weak acid polyelectrolyte film of ~ 50 nm, the local pH within which was monitored using ratiometric pH indicators covalently attached to the polyelectrolyte. Chapter 4 explores the forward-biased BPM in a redox flow battery that operates the positive/negative electrode in an alkaline/acidic environment. This unique configuration enables a battery potential that is ~ 0.7 V higher than the conventional ones using a single pH condition. The acid-base recombination reaction was found to be inefficient in forward-biased BPMs, being rate-limited by the narrow reaction zone in the junction region. In chapter 5, we designed a novel architecture for the catalyst layer in alkaline fuel cells, which allows for a better control of the microstructure and thus the study of mass transport in a membrane electrode assembly (MEA) configuration. The last chapter summaries the thesis and proposes future directions.

Degree Type
Dissertation

Degree Name
Doctor of Philosophy (PhD)

Graduate Group
Chemistry

First Advisor
Thomas E. Mallouk

Keywords
Bipolar membrane, Electrochemistry, Energy storage, Fuel cells, Ion transport

Subject Categories
Chemistry | Oil, Gas, and Energy

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ION MANAGEMENT AND MASS TRANSPORT FOR (PHOTO-) ELECTROCHEMICAL
CONVERSIONS
Zhifei Yan
A DISSERTATION
In
Chemistry
Presented to the Faculties of the University of Pennsylvania
in
Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy
2021

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ACKNOWLEDGMENT

A decade ago, when I first learned about ion exchange resins in organic chemistry and was left with the impression that the problem of ion exchange was simple and lame, I did not expect, five years later, to hear “Let’s start with bipolar (ion exchange) membranes” when discussing the first project with my advisor, Tom Mallouk. This was the first lesson that I learned from Tom: a seemingly easy idea is not necessarily a bad one. That’s why we had multiple such ideas afterward.

What we have witnessed in the past year or so reemphasized the fact that the world is full of problems urgently needing to be addressed. While some of these problems can be solved by chemistry alone, others require concerted efforts and thus an open mind – the second lesson Tom has taught me. As a student of Tom, I am always grateful that I was given the opportunity to think and work on a variety of topics that could potentially provide solutions to bigger problems, from the artificial photosynthesis to water purification, from water dissociation to fast ion conductors. Altogether, thanks to Tom, the past six years have been one of the most valuable times to me. My committee members have supported me tremendously as well: John Asbury, John Badding, and Mike Hickner at Penn State, and Chris Murray, Andrew Rappe, and James Pikul at Penn.

Graduate school would have been stressful without the support of friends. I would like to thank Chuanyu Yan, for teaching me how to appreciate the world and use that attitude towards people; Liqiang, Pengtao, Yande, and Yao for teaching me persistency and spending all the fun times in and outside lab; my mentor Chris for guiding me on conducting research projects. I would also like to acknowledge all the Mallouk group members, past and present: Luis, Shunta, Erik, Alyssa, Pratibha, Langqiu, Jeremy, Jarrett, Walter, Jeff, Linxi, Zichen, Yunhan, Mary, Kurt, Amy, and Colton. Over the years, I was also helped by a lot of excellent visiting scholars: Hongwei, Ketack, and Tiger.

I would also like to thank my girlfriend, Pho Bui, for her consistent support, who has shown me that life outside lab can be equally wonderful. Last but not the least, I want to show my appreciation to my family whose support made this journey enjoyable.
ABSTRACT

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The first three chapters of the thesis explore the use of bipolar membranes (BPMs) for managing ion transport in CO₂ electrolysis, fuel cells, and redox flow batteries, while focusing on understanding the fundamental aspects of BPMs. Chapter 1 introduces the potential of using electrolysis for renewable energy storage and summarizes recent progress in BPM research. In Chapter 2, we combine electrochemical impedance spectroscopy and finite element method based numerical modeling to elucidate the relation between the electric field and interfacial catalysis in enhancing water dissociation reaction in BPMs. Chapter 3 presents the results of managing interfacial protons in a BPM-based CO₂ electrolyzer. The acidic local environment at the membrane/catalyst interface facilitates the competing hydrogen evolution reaction and leads to a low CO₂ reduction efficiency. This problem was mitigated by coating the membrane with a weak acid polyelectrolyte film of ~ 50 nm, the local pH within which was monitored using ratiometric pH indicators covalently attached to the polyelectrolyte. Chapter 4 explores the forward-biased BPM in a redox flow battery that operates the positive/negative electrode in an alkaline/acidic
environment. This unique configuration enables a battery potential that is $\sim 0.7$ V higher than the conventional ones using a single pH condition. The acid-base recombination reaction was found to be inefficient in forward-biased BPMs, being rate-limited by the narrow reaction zone in the junction region. In chapter 5, we designed a novel architecture for the catalyst layer in alkaline fuel cells, which allows for a better control of the microstructure and thus the study of mass transport in a membrane electrode assembly (MEA) configuration. The last chapter summarizes the thesis and proposes future directions.
# TABLE OF CONTENTS

**ACKNOWLEDGMENT** ........................................................................................................... ii

**ABSTRACT** .......................................................................................................................... iii

List of Tables ............................................................................................................................... viii

List of Illustrations ...................................................................................................................... ix

**Chapter 1 Ion management for renewable energy storage** ..................................................... 1

1.1 Introduction ........................................................................................................................... 3

1.2 Electrolytic techniques ......................................................................................................... 7

1.2.1 Water Electrolysis ............................................................................................................ 7

1.2.2 CO₂ electrolysis ............................................................................................................... 11

1.2.3 Solid State Electrolytes .................................................................................................. 14

1.2.4 Electrochemical Nitrogen Reduction .............................................................................. 16

1.3 Ion management in BPMs .................................................................................................. 17

1.3.1 Free energy losses and reverse-biased BPMs ................................................................. 18

1.3.2 BPM based CO₂ electrolysis .......................................................................................... 21

1.3.3 BPM based fuel cells and redox flow batteries ............................................................... 24

1.4 Mechanism of the water dissociation reaction in BPMs ..................................................... 27

1.5 Conclusions and perspective .............................................................................................. 29

1.6 References .......................................................................................................................... 31

**Chapter 2 The balance of electric field and interfacial catalysis in promoting water**

dissociation in bipolar membranes ......................................................................................... 45

2.1 Introduction ........................................................................................................................... 47

2.2 Results and discussions ....................................................................................................... 50

2.2.1 BPM and self-assembly of the graphene oxide catalyst ............................................... 50

2.2.2 The balance between electric field and catalysis ........................................................... 51

2.2.3 Insights from the numerical model ................................................................................ 54
4.2.1 BPM under forward bias
4.2.2 BPM based acid-base redox flow battery
4.3 Conclusions
4.4 References

Chapter 5 Managing mass transport in alkaline fuel cells
5.1 Introduction
5.1 Results and discussion
5.2.1 The transport of H₂ gas in the aqueous RDE experiment
5.2.2 Design of the catalyst layers
5.2.3 Mass transport in the PTFE-supported catalyst layer
5.3 Conclusions
5.4 References

Chapter 6 Conclusions and perspectives
Appendix A Supporting information for chapter 2
Appendix B Supporting information for chapter 3
Appendix C Supporting information for chapter 4
Appendix D Supporting information for chapter 5
List of Tables

Table A.1. Parameters extracted from EIS and calculated values of capacitance and depletion layer thickness for 4GO BPM
.................................................................................................................................................. 143
Table A.2. Parameters extracted from EIS and calculated values of capacitance and depletion layer thickness for 1GO BPM
.................................................................................................................................................. 144
Table A.3. Parameters extracted from EIS and calculated values of capacitance and depletion layer thickness for 0GO BPM
.................................................................................................................................................. 145
Table A.4. Parameters extracted from EIS and calculated values of capacitance and depletion layer thickness for 3D BPM
.................................................................................................................................................. 146
Table A.5. Initial conditions of the numerical simulation ...................................................................... 149
Table C.1. Parameters for the simulation and initial conditions ......................................................... 177
Table D.1. Parameters for the numerical model ............................................................................... 191
Table D.2. Fitted data of modeled EIS spectra, with different diffusion coefficient, \( D_{O2} \) ............... 200
Table D.3. Fitted data of modeled EIS spectra, under different biases ............................................. 200
Table D.4. Fitted data of experimental EIS spectra, with 2 uL of ionomer (fitting scheme one) .......... 201
Table D.5. Fitted data of experimental EIS spectra, with 6 uL of ionomer (fitting scheme one) .......... 201
Table D.6. Fitted data of experimental EIS spectra, with 2 uL of ionomer (fitting scheme two) .......... 201
Table D.7. Fitted data of experimental EIS spectra, with 6 uL of ionomer (fitting scheme two) .......... 201
Table D.8. Fitted data of experimental EIS spectra, with 6 uL of ionomer (fitting scheme one) .......... 202
Table D.9. Fitted data of experimental EIS spectra, with 25 uL of ionomer (fitting scheme one) .......... 202
Table D.10. Fitted data of experimental EIS spectra, with 6 uL of ionomer (fitting scheme two) ........ 202
Table D.11. Fitted data of experimental EIS spectra, with 25 uL of ionomer (fitting scheme two) ....... 202
List of Illustrations

Fig. 1.1. Sustainable energy utilization. Schematics of energy storage and utilization based on electrolysis. Surplus electrical energy from renewable sources can be stored via electrolysis as chemical fuels. The energy is extracted to levelize demand on the short time scale and to meet the need for fuel in seasons when the renewable supply is less available. The intermittency plot (lower left) was obtained from ref. (6). ........................................................................... 4

Fig. 1.2. Schematics of electrolysis. (a) Reactants transport to the surface of an electrode where a cathodic reaction occurs. B) Comparison of the reaction pathways for the HER with and without catalyst. The catalyst stabilizes the intermediate and lowers the activation energy. (c) Electrolyzers in a gas-fed configuration. Gas-fed electrolysis exploits the fast diffusion of gaseous molecules, enabling high current density. Membrane electrolytes are usually required for ion management and gas separation. (d) Kinetics of the electrochemical HER. Transition state energy decreases as overpotential increases.......................................................................................................................... 6

Fig. 1.3. Water electrolysis. (a) HER volcano plot for catalytic elements. [Data obtained from (18)]. (b) Free energy diagram for the OER. The black curve refers to an ideal OER catalyst whereas the red curve represents a real catalyst (28). (c) Comparison between a low temperature PEM electrolyzer and a higher temperature solid oxide electrochemical cell (SOEC) [Data obtained from (52)] and (d) Electrolyzer and fuel cell mode performance of a SOCE using a proton conductor at intermediate temperatures. Increasing the temperature by 150 °C dramatically improved the cell current density. [Data was taken from (53)]. ........................................................................................................... 9

Fig. 1.4. CO₂ electrolysis. (a) The scaling relation between the adsorption strength of COOH and CO on various metal surfaces and in enzymes. [Reprinted with permission from (33), copyright (2013) American Chemical Society] (b) Comparison of current density and Faradaic efficiency of CO₂ reduction to ethylene (blue) and ethanol (red). Solid symbols refer to published stability tests. Higher current density is achieved in a triple phase boundary (TPB) configuration, compared to aqueous phase CO₂ reduction (Aq.). Data obtained from (35, 38–42) and (43–46),(50). (c) Enhanced mass transfer of CO₂ near a Au needle surface. The large electric field at the tip of the Au needle attracts hydrated K+, which concentrates CO₂ in its solvation shell. [Adapted with permission from Nature Publishing Group, (49)] (d) Construction of the triple phase boundary in gas-fed CO₂ electrolysis. The Cu catalyst is sputtered onto a PTFE porous support which provide a gas diffusion pathway. [From (50). Reprinted with permission from AAAS]. .................................................................................................................. 12

Fig. 1.5. pH gradient and potential losses in the membrane based electrolytic cells. (a) The formation of pH gradient as a function of time in a water electrolysis cell with an AEM (top) and CEM (bottom). (b) Schematics of ion transport in BPM under forward (top left) and reverse (top right) bias. (Bottom) Potential loss in phosphate buffer electrolyte with different membranes, at 25 mA/cm² current density. .......................................................................................... 19

Fig. 1.6. BPMs in water electrolysis. (a) Schematic of a BPM-based water electrolyzer with strong acid HClO₄ and base NaOH in the cathode and anode, respectively (top). Comparison of the overall J-E curves of two water splitting cells consisting of (middle) a BPM with 1M NaOH for OER and 1 M HClO₄ for HER and (bottom) a Nafion CEM with 1 M HClO₄ for both OER and HER. (b) Schematic of a perovskite photovoltaic-driven water splitting cells equipped with a BPM that enables the use of cheap metals as OER and HER catalysts due to the optimal pH conditions. (c) The use of BPM in a solar driven water splitting cell that has a pH 9.3 Kbi buffer in the anode and strong acid pH 0 the cathode. (d) Ion transport and crossover in reverse biased BPMs when a phosphate buffer is used as the catholyte and NaOH as anolyte. I Current density vs BPM cross-membrane potential with non-extreme pH conditions. . . . . 20

Fig. 1.7. BPMs in CO₂ electrolysis. (a) Schematic of a PV-CO₂ electrolyzer with a BPM separating the cathode and anode. (b) Coupling water oxidation and CO₂ reduction in a BPM-based electrolyzer with KHCO₃ aqueous electrolyte. (c) Schematic of a gas-fed BPM-based CO₂ electrolyzer (top). Comparison of the chronopotentiometric results between a BPM and a Nafion membrane in the electrolyzer. (d) Transport of neutral molecules is decreased in BPM-based CO₂ electrolyzers compared to the AEM, due to the outward H⁺/OH⁻ flux in reverse biased BPMs (top). The crossover of an anionic product (formate) is also suppressed with a BPM (red: BPM, green: 3D BPM, blue: AEM). .................................................................................................................. 22

Fig. 1.8. Interfacial proton management in the BPM-based CO₂ electrolyzers. (a) Incorporating a solid-supported aqueous NaHCO₃ buffering layer between the BPM and the cathode catalyst layer increases the CO₂ to CO FE. (b) The addition of a weak acidic LBL film on the BPM CEL suppressed the competing HER reaction in the CO₂ electrolyzer (top). The local pH in the LBL film was monitored using a ratiometric dye-tagged polyelectrolyte pH probe (bottom left). A larger peak ratio (560/510) corresponds to a lower pH. The higher local pH leads to increased faradaic efficiency compared to the pristine BPM (bottom right). ............................................................................. 24

Fig. 1.9. Forward-biased BPM for fuel cells and redox flow batteries. (a) Hybrid fuel cells with high/low pH for anode/cathode (left) and high/low pH for cathode/anode (right). (b) Theoretical BPM current density-voltage curves with different mechanisms for the acid-base recombination process. (c) The BPM-based acid-base redox flow battery where the positive/negative electrodes operate in the alkaline/acidic environment (top). Comparison of the cross-membrane potential vs current density of BPMs with and without interfacial catalysts under reverse and forward bias, via numerical modeling (bottom left) and experiment (bottom right). ............................................................................. 25
Fig. 1.10. The mechanism of water dissociation in BPMs and the modeling. (a) Correlation between the water dissociation overpotential and the PZC of the metal oxide catalysts in the BPMs. (b) Water dissociation reaction resistance (left) and the depletion layer thickness (right) as a function of the cross-membrane potentials, extrapolated from the electrochemical impedance spectroscopy measurements. (c) Numerical modeling of the I-V curves with pH 7-7 (left) and pH 0-14 (right). The catalytic effect was taken into account by an exponential effectiveness factor. (d) The distribution of H+/OH-, electric field, and charge density at the BPM junction from a comprehensive numerical model. The effect of the interfacial catalysis is incorporated explicitly using the protonation-deprotonation equilibria of the catalysts. ................................................................................................................................................27

Fig. 2.1. Schematic of the preparation of BPMs by LBL assembly, and a cross-sectional scanning electron micrograph (SEM) image of the 4GO BPM. The green and red lines span the CEL and AEL, respectively.....................................................50

Fig. 2.2. (a) J-E curves of BPMs prepared by the LBL technique, in 0.5 M KNO₃ at low reverse bias, which is also the bias range used in the EIS study. 0GO/1GO/4GO BPM correspond to BPMs with zero/one/four layers of GO catalyst; (b) Water dissociation rate constant k_d measured from the Gerischer element; (c) Water dissociation reaction resistance R_w; inset shows an enlarged view at lower voltage; (d) Depletion region thickness as a function of reverse bias voltage. Error bars in (a) and (c) are shown for cases where they are larger than the plot symbols.............. 52

Fig. 2.3. Numerical simulations of a BPM with catalyst. (a) Simulated J-V curve of a BPM with catalyst, and comparison with experimental results. The experimental J-V curve shown was obtained in 0.1 mM KNO₃ in order to match the conditions of the simulation; also shown are the current contributions from water dissociation products and from the electrolyte, KNO₃; (b) Potential distributions from the simulation; (c) Concentration profiles of the water dissociation products H⁺ and OH⁻ in the BPM; (d) Electrolyte KNO₃ ion distributions. Insets in (b) (c) and (d) are enlarged version of the AEL/CEL junction region................................................................................. 56

Fig. 2.4. Schematic drawings of (a) the depletion region for BPMs with and without catalyst and (b) an enlarged view of the junction region, showing the higher H⁺/OH⁻ flux in the BPM with catalyst. The black arrows indicate the higher electric field in the BPM without catalyst; the red/blue colors indicate the positive/negative fixed charges in AEL/CEL, respectively. Simulated (c) electric field intensity at the AEL/CEL interface and (d) depletion region thickness for BPMs with and without catalyst. ........................................................................................................ 58

Fig. 2.5. BPM with a 3D junction. (a) SEM image of the junction region, the scale bar corresponds to 20 µm; (b) (Left): schematic of the 3D junction BPM, with AEL (red), CEL (blue) and dual-fiber junctions. (Middle): enlarged view of the dual fiber junction. The mixture of AEL and CEL fibers in the junction region provide pathways for H⁺ and OH⁻ transport. Black arrows in the left and middle panels indicate the overall and local electric fields, respectively. (Right): enlarged view of the AEL/CEL interface in the junction region, where water dissociates into H⁺ and OH⁻ at the Al₂O₃ catalyst; (c) J-E curves of 3D junction and 4GO BPM in 0.5 M KNO₃ at lower reverse bias; (d) Water dissociation rate constant k_d; (f) Water dissociation reaction resistance R_w. (f) Depletion region thickness d as a function of reverse bias voltage.......................................................... 60

Fig. 2.6. (a) J-E curves of BPMs, measured with 0.5 M HCl and 0.5 M KOH in the cathodic and anodic chambers, respectively; (b) Steady-state performance of BPMs, measured under reverse bias of 100 mA/cm²; the dip in 4GO BPM is due to the removal of bubbles. ...........................................................................................................62

Fig. 3.1. An acidic cathode environment leads to low Faradaic efficiency for CO₂ reduction in a BPM-based electrolyser. (a) Schematic of the setup for visualising the cathode. 1 M KOH and humidified CO₂ gas (20 ml/min) were introduced at the anode and cathode, respectively. (b) CO and H₂: FE as a function of the overall cell voltage. The error bars represent one standard deviation of three independent measurements. (c) Photographs of the CEL surface under different cell voltages. Gas bubbles (enclosed in the green dashed circles) evolve faster at higher cell voltage. Scale bar corresponds to 250 µm. (d) Proposed mechanism for proton generation and the low FE for CO₂ reduction in a BPM-based CO₂ electrolyser. Blue dots represent electrons. .................................................................................. 80

Fig. 3.2. Modification of the BPM by LBL assembly. (a) Molecular structures of the polyelectrolytes and schematic drawing of the membrane structure. (b) Water contact angles measured after each step of the LBL assembly process. The first measurement at step 0 refers to the contact angle of the Nafion CEL. The variation of the contact angles indicates the alternative termination of the surface with PAA and PAH. The error bars represent one standard deviation of three independent measurements. ........................................................................ 81

Fig. 3.3. Attaching pH-responsive dyes to PAH and pH calibration. (a) Scheme for covalently attaching Oregon Green (OG) and tetramethylrhodamine (TMR) to PAH. (b) UV-Vis spectra of three dye-loaded PAH/PAH bilayers on a glass slide bathed in different pH solutions for calibration. The peak at 560 nm is due to TMR and the 480 and 510 nm peaks to OG. The spectra are normalized to the peak at 560 nm. The intensity ratio between the peaks at 560 nm to 510 nm (dash lines) is calibrated as a function of pH in Fig. 3.4g. ............................................................................................ 83

Fig. 3.4. Measurement of the local pH in the LBL film on the modified BPM. (a) Schematic of the UV-Vis measurement. (b) Schematic of the six samples (S1-S6) used for pH gradient measurements. Dye-PAH and PAH refer to the PAH polymer with and without dye attachment. Two or three bilayers of Dye-PAH/PAH are deposited as the probe layer. The location of the probe layer moves further away from the Nafion CEL in the LBL film with increasing sample number. (c) Photographs of the CEL surface of the Nafion BPM and LBL-modified BPM when bathed in 0.1 M KHCO₃ solution. The bubbles formed on the Nafion BPM indicate a lower surface pH. Scale bar represents 1 mm. UV-Vis spectra of sample (d) S1 and S4 at open circuit voltage and 4 mA reverse current (current density ~3.03 X
mA/cm²). (f) Intensity ratio of the peaks at 560 and 510 nm as a function of the average number of bilayers from the CEL in the LBL BPM. The ratio changes more rapidly within the first few layers compared with the remaining layers. The error bars represent one standard deviation of two independent measurements. (g) Calibrated peak intensity ratio as a function of pH. The smaller ratio at higher pH reveals a gradual pH increase in the LBL film as one moves away from the CEL. The error bars represent one standard deviation of three independent measurements.

Fig. 3.5. Electrochemical properties of the LBL-modified BPM and Nafion BPM. (a) Cross-membrane potential of the BPM with (LBL BPM) and without (Nafion LBL) LBL modification. Inset shows the four-electrode setup; the cross-membrane potential is recorded by the two reference electrodes placed directly against the faces of the BPM. Note that the results of the two samples are very similar. (b) Onset potential of the HER at a Pt catalyst with membranes of different compositions. An acidic Nafion CEM and a basic AEM were used as references. (c) CO faradaic efficiency as a function of cathode potential with the ionomer-free catalyst layer. (d) Hydrogen partial current density as a function of the cathode potential. The LBL BPM here contains 10 PAH/PAA bilayers. The decreasing CO current density for Nafion BPM at higher potentials could be caused by flooding in the ionomer-free catalyst layer. The error bars represent one standard deviation of two independent measurements.

Fig. 4.1. Schematic illustration of a BPM-based acid-base redox flow battery. (a) The charging process of the battery is shown, where ferrocyanide (Fe(CN)₆³⁻) in aqueous KOH is reduced and SPV (sulfonatopropyl) viologen, structure shown in Fig. 4.3a) in H₂SO₄ is oxidized at the positive and negative electrodes, respectively. The H⁺ and OH⁻ ions carry the charge in the bipolar membrane (BPM) that is composed of anion- and cation- exchange layers (AEL and CEL). The electrolytes are cycled through the cell using a peristaltic pump. (b) The transport of H⁺ and OH⁻ ions is coupled with the water dissociation and acid-base neutralization reactions during the charging and discharging processes, respectively. The AEL and CEL face the positive and negative electrodes, respectively. The BPM is subject to reverse bias when the flow battery is charging, and operates in forward bias during discharge.

Fig. 4.2. The effects of interfacial catalysis in BPM. (a) The experimental four-electrode setup for measuring the potential drop across the BPM. Using two reference electrodes eliminates the influence of the electrochemical reactions at the electrodes. KOH and HCl are used as the electrolytes on the AEL and CEL sides, respectively, of the BPM. The dashed box represents the region of interest that was modeled in numerical simulations. (b) The experimental setup was simplified as a one-dimensional model that includes four segments and two open boundaries (dashed box). This region corresponds to the region in a. To explore the effect of catalysis on the potential-current density relation under reverse and forward bias conditions, we compared three models. Model 1 simulates the experimental BPM without a catalyst, imposing constant k₀ and k_c. Models 2 and 3 assume the presence of a catalyst layer at the AEL/CEL interface, which increases k_c by three orders of magnitude; the neutralization rate constant k_c is also increased by the catalyst in Model 3, but not in Model 2. (c) Cross membrane potential-current density curves from the three models, compared to the experimental results shown in (d). Only model 3 with catalyzed k_c and catalyzed k_c can reproduce the trends observed in BPMs with and without catalyst layers (GO, graphene oxide) under both reverse and forward bias. The dashed lines indicate the open circuit condition. Error bars represent the standard deviation of three independent measurements. (d) Comparisons of the integrated reaction rates from Models 2 and 3. The neutralization reaction is rate-limited by the negligible amount of either H⁺ or OH⁻ in the AEL/CEL, resulting in a narrow reaction zone as shown in (f). (g) The integrated reaction rate of the dissociation, and (h), neutralization processes over the reaction zone. The neutralization rate increases to a maximum under a small reverse bias, even though the net reaction at that point is water dissociation. The dashed lines indicate the open circuit condition for Models 2 and 3.

Fig. 4.3. Performance of the acid-base redox flow battery. (a) Structures of the redox couples used at the negative electrode. SPV: 1,1'-bis(3-sulfonatopropyl)-4,4'-bipyridinium, DSAQ: 2,7-difluoronate-9,10-anthrquionine. 0.1 M ferrocyanide in 2 M KOH was used as the positive electrolyte for all the cell performance tests. (b) Cell performance with and without GO as the catalyst in the BPM. Improved performance can be achieved using BPMs with GO due to the increased dissociation and neutralization rate constants. Electrolyte: 0.1 M DSAQ (1M H₂SO₄) in the negative electrolyte. (c) Cyclic voltammogram (CV) of 0.1 M SPV in 1 M H₂SO₄ (magenta) or in 1 M KOH (blue), and 0.5 M ferrocyanide in 1 M KOH (red); and CV of 0.1 M DSAQ in 1 M H₂SO₄ (magenta) or in 1 M KOH (blue), and 0.1 M ferrocyanide in 1 M KOH (red). The SPV redox couple is pH-independent whereas the formal potential of DSAQ shifts positively at lower pH. (d) and (f) Potential and power density versus current density at ~100% state of charge. With the common positive electrode, operating SPV in acid (acid-base with BPM) increases the cell potential by ~0.66 V compared to a cell operated under a single alkaline condition (alkaline with CEM). The same comparison with the DSAQ redox couple shows ~0.35 V increase in the cell potential.

Fig. 4.4. Cell performance at different concentrations of ferrocyanide and cycling test. (a) Polarization and power density curves of cells operating at different concentrations of ferrocyanide in 2 M KOH; a negative electrolyte of 0.4 M DSAQ in 1M H₂SO₄ was used. The best cell performance was observed at intermediate concentrations (0.15 M). (b) Potential and current density versus time during the first ten charge-discharge cycles.

Fig. 5.1. EIS measurements of Pt/C electrode in RDE setup for the HOR process in 0.1 M KOH. (a) Bode plots at different rotating rate, at 0.03 V (vs RHE). (b) Bode plots at different applied potentials (vs RHE), with the rotating rate held at 400 rpm. The lower frequency peak (~ 0.5 Hz) shifts as a function of the rotating rate but not the potential, corresponding to the diffusion process.

Fig. 5.2. Catalyst layer with novel architectures. Scanning electron microscope (SEM) images of the (a) Ag/PTFE and (b) Pt/PTFE. The polarization and power density curves of the APEFCs using the (c) Ag/PTFE and (d) Pt/PTFE as
the ORR electrode. The anode: 0.4 mg PtRu/cm² PtRu/C (60 wt%); AEM and ionomers: quaternary ammonia poly (N-methyl-piperidine-co-p-terphenyl) (QAPPT). The cell was heated at 80 °C, humidified H₂ and O₂ gas are fed with a flow rate 500 mL/min.  

Fig. 5.3. The effects of ionomer loading on the fuel cell performance. (a) Polarization curves and (b) the power density curves. The testing conditions are the same as in Fig. 5.2, and can be found in the experimental section in the Appendix D.  

Fig. 5.4. Numerical modeling of the EIS spectra, phase shift analysis, and the equivalent circuit. Schematics of the Pt/ionomer/PTFE fiber in (a) 3D and (b) 2D, which can be simplified into a 1D model, consisting of a porous electrode and an electrolyte segment. Model 1 and 2 fixed the boundary oxygen concentration at the porous electrode and the electrolyte, respectively. Comparison of (c) the experimental EIS and modeled spectra from (i) model 1 and (j) model 2. The symbols are EIS data and the black lines represent fitted results to the equivalent circuit I. The arrows correspond to the frequencies in (d) (g) (i). Variation of the ac current and ac voltage in (d) experiment at 0.966 Hz, (h) from model 1 at 1 Hz, and (j) model 2 at 10 Hz. 10 Hz was chosen because the simulation failed to converge at < 10 Hz in model 2, but the capacitive current is sufficiently decreased at 10 Hz (Fig. D.11e). Time variations of (h) overpotential in model 1 and (k) oxygen concentration in model 2, both at x = 0.  

Fig. 5.5. Experimental Nyquist plots with different ionomer loadings (a) 2 uL/cm², (b) 6 uL/cm², and (c) 75 uL/cm². Modeled spectra in model 1 with oxygen diffusion coefficients decreased by (d) 10⁻¹, I 10⁻², and (f) 10⁻³ fold. D02 = 7.9 × 10⁻¹⁰ m²/s. The Nyquist plots become more suppressed with increased ionomer loadings, which is similar to the trends by reducing the diffusion coefficients of oxygen in the modeling.  

Fig. 5.6. Resistance values extracted from fitting the experimental EIS spectra to the equivalent circuit in Fig. 5.5e. (a) Comparison between 2 and 6 uL ionomers at cell voltage of 0.75 and 0.70 V. Smaller cell voltage corresponds to larger overpotential. (b) Resistance comparisons between 6 and 25 uL ionomers at DC current density of 0.208 and 0.333 A/cm². WR represents the diffusion resistance of the Warburg W1 element at ω → 0. Galvanostatic mode was used in (b) while potentiostat mode in (a), but the equivalency of the two modes was confirmed in Fig. D.9.  

Fig. A.1. Setup for measuring BPM performance. WE: working electrode, Pt wire (0.5 mm diameter), CE: counter electrode, Pt wire (0.5 mm diameter); RE1 and RE2: reference electrode, Ag/AgCl with 3 M NaCl filling solution. The membranes were arranged, from left to right: CEM (blue), BPM (blue and purple) and AEM (purple), with the cathode located on the left side. The two monopolar membranes were incorporated to minimize the effects of water splitting products (H₂ and O₂) generated at the working and counter electrodes.  

Fig. A.2. The equivalent circuit (EC) used to fit experimental EIS spectra.  

Fig. A.3. Experimental (black squares) and modelled (green lines) Nyquist plots of BPM with 4 layers of GO, 4GO BPM at different reverse bias potentials. The equivalent circuit is described in Fig. A.2.  

Fig. A.4. Experimental (black squares) and modelled (green lines) Nyquist plots of BPM with no GO, 0GO BPM at different reverse bias potentials. The red lines are modeled spectra with a fixed depletion layer thickness. Specifically, the depletion layer thickness at various potentials are averaged for the 0GO BPM. We then repeated the EIS modeling at the fixed (average) depletion thickness while other parameters were allowed to float freely. This fitting scheme (red lines) shows that the chi squared values are in the range of 0.03-0.6, which is much larger than that of the fitting at individually optimized depletion layer thicknesses (green lines).  

Fig. A.5. Experimental (black squares) and modelled (green lines) Nyquist plots 3D BPM at different reverse bias potentials.  

Fig. A.6. Concentration profiles of the ionic species obtained from simulation at all reverse biases, for the BPM with catalyst. (a) H⁺ (solid lines) and OH⁻ (dashed lines); (b) K⁺ (solid lines) and NO₃⁻ (dashed lines). The arrows indicate the profile evolution as the potential changes.  

Fig. A.7. Simulated results of BPMs without catalyst. (a) J-E curves with (hollow) and without (solid) catalyst; (b) potential distribution of a BPM without catalyst; (c) Water dissociation products H⁺ and OH⁻ concentration distribution in the BPM; (d) Electrolyte KNO₃ ion distribution. Insets in (b) (c) and (d) are enlarged versions of the AEL/CEL junction region.  

Fig. A.8. Simulated results of a BPM without catalyst under forward bias conditions. (a) J-E curve under forward and reverse bias conditions; (b) potential distribution under forward bias; (c) Water dissociation products H⁺ and OH⁻ concentration distributions in the BPM; (d) Electrolyte KNO₃ ion distribution. Note the absence of a depletion region under forward bias conditions. Insets in (b) (c) and (d) are enlarged version of the AEL/CEL junction region.  

Fig. A.9. Determination of the depletion region thickness from simulation. The distance from the point where charge density drops to half of the maximum in the AEL to its counterpart point in CEL is taken as the depletion region thickness. The magenta and orange boxes represent the depletion region on the AEL and CEL sides, respectively. The depletion thickness in this case is the distance between the left side of the magenta box and the right side of the
orange box. The two curves are for BPMs with and without catalyst at a reverse bias of 2 V, and the boxes representing the depletion layer are for BPM with catalyst. .............................................. 153

Fig. A.10. Comparison of the EIS spectra of the 1GO BPM taken in pH neutral (a-d) and asymmetric conditions l. (a-d): with the pH neutral electrolyte 0.5 M KNO₃, the gradual appearance of the intermediate semicircle as the reverse bias current increases is observed. (b) and (d) show an enlarged version of the intermediate semicircle in the square of (a)(c). From zero bias to 0.8 mA/cm² and above, the intermediate semicircle becomes more obvious, which confirms the gradual formation of the depletion region and the intensification of the water autodissociation reaction under the electric field. I Spectra taken under asymmetric conditions exhibit the intermediate semicircle even at open circuit, because of the intrinsic electric field across the AEL/CEL interface. The intrinsic electric field arises because of the acid-base neutralization reaction at the AEL/CEL interface, which leaves the fixed membrane charge near the interface unbalanced, i.e. the formation of a depletion region. As such, even though the asymmetric condition is more relevant to standard operating conditions for BPMs, it doesn’t provide information on the depletion layer thickness and water dissociation kinetics below the open circuit voltage (ideally 0.834 V, assuming 1 M fixed charge density in the AEL and CEL). Thus, the asymmetric pH spectra do not inform us about the trend in the water dissociation reaction during the early stages of formation of the depletion region. ................. 154

Fig. B.1. Characterization of the Ag catalyst on a GDL. (a) SEM image of the Ag NP/C mixture deposited on the carbon paper GDL. (b) TEM image of the Ag nanoparticles. .......................................................................................................................... 158

Fig. B.2. (a) Overall current density of the CO₂ electrolyser used for the visualization experiment. (b) The CO Faradaic efficiency of a control experiment with the same configuration, except that there is no hole in the center of the carbon paper.................................................. 158

Fig. B.3. Visualisation of the cathode side of the BPM-based CO₂ electrolyser. Different parts of the cathode are indicated in the optical micrograph. The upper left shows a conducting copper foil that connects the carbon paper GDL to the external circuit; the hole made in the center of the GDL allows direct access of the light beam to the CEL side of the BPM. Figures shown in the main text are zoomed-in views of the CEL region................................. 159

Fig. B.4. TEM images of the LBL-BPM. (a) HAADF image. EDS mapping of F (b) Br (c) and their overlap map (d). The F element signal is from the Nafion polymer and Br comes mainly from the eosin-labeled PAH. A thin layer of Br (~50 nm) can be seen on the Nafion surface.............................................. 160

Fig. B.5. (a) UV-Vis spectra of the Nafion BPM without dye-PAH under open circuit voltage (OCV) and 4 mA reverse current conditions. (b) The difference between the spectra at 4 mA and OCV shown in (b)............................................. 161

Fig. B.6. (a) Original UV-Vis spectra of the sample S1, under OCV and 4 mA, before baseline correction, with OCV of the Nafion BPM as background. (b) The same experiment was done with 4 mA reverse current applied to the Nafion BPM as background. (c)(d) UV-Vis spectra after baseline correction. The 560/510 ratios are 0.957 (OCV) and 1.24 (4 mA) in (c), 0.968 (OCV) and 1.20 (4 mA) in (d).................................. 162

Fig. B.7. UV-Vis spectra of sample (a) S2 and (b) S3, under OCV and 4 mA reverse current............................... 163

Fig. B.8. UV-Vis spectra of sample (a) S5 and (b) S6 under OCV and 4 mA reverse current.................. 164

Fig. B.9. UV-Vis spectra of the S1 at OCV (black), followed by 4 mA reverse current (red) for 10 minutes, followed by OCV again (blue). The almost overlapped absorbance at 510 nm and 560 nm in the OCV after applying 4 mA reverse current confirms the reversibility of the test. .................................................. 164

Fig. B.10. UV-Vis spectra of LBL modified Nafion, under OCV and 4 mA current. Two bilayers of dye-PAH/PAA are deposited onto the Nafion. Compared to the S1 sample, Fig. 3.4d, the negligible difference between the OCV and 4 mA indicates the increased 560/510 ratio in the S1 sample under 4 mA is likely the result of decreased pH under reverse bias, which is absent in the Nafion membrane................................. 165

Fig. B.11. UV-Vis results using spectral modeling. The three prominent absorption peaks are fitted as Gaussian functions. The spectra are then obtained by overlapping the simulated peaks. (a) Simulated spectra as a function of pH. (b) Calibration of intensity ratio. (b) Simulated intensity ratios of the S1-S6 samples. The values and the overall trends are consistent with those without modeling, as reported in the main text. .................................................. 166

Fig. B.12. H₂ partial current density as a function of cathode potential (a) with ionomer-free catalyst layer and (b) with Nafion ionomer. The suppressed H₂ current density can be seen in both cases. .................................................. 166

Fig. B.13. Comparison of (a) the CO FE and (b) CO partial current density, between the Nafion BPM and LBL BPM as a function of cathode potential, in the Nafion ionomer-containing configuration. Compared to Fig. 3.5c and 3.5d, the same trend that LBL BPM increases the CO FE but retains similar CO current density can be observed. ...... 167

Fig. B.14. Overall current density vs cell potential curve for the Nafion- and LBL- BPMs in the configuration with ionomer. .................................................. 167

Fig. C.1. EIS tests of the BPMs with and without GO catalysts. (a) Nyquist plots of the BPM with GO catalyst. (b) Nyquist plots of the BPM without GO, the inset shows enlarged view of the results at 2 and 10 mA/cm². The samples with GO catalyst show smaller resistance semicircles, indicating faster reaction kinetics. The difference between the two samples is much larger in reverse bias (negative current density) than in forward bias. ...................... 178
Fig. C.2. Concentration distributions of ionic species in Model 3. (a) Concentration profiles of OH⁻ and H⁺ as a function of position at open circuit (500 mV), and under forward (200 mV) and reverse bias (800 mV). (b) Enlarged view at the AEL/CEL interface, where the depletion layer containing minimal amounts of both ions can be seen. The thickness of the depletion layer decreases at lower potentials. (c) Distribution of K⁺ and Cl⁻ ions that are excluded from the BPM because perfect permselectivity was assumed. ......................................... 178

Fig. C.3. Electric potential distribution in Model 3. A large portion of the potential drop occurs across the AEL/CEL interface. .................................................................................................................. 179

Fig. C.4. The distribution of dissociation reaction rates in Model 3. A significant dissociation rate is seen only within a narrow region of ~3 nm, i.e. the reaction zone. .................................................................................................................. 179

Fig. C.5. Effect of electric field as a function of potential in Model 3. (a) The strength of the electric field in different models. (b) The effect of the electric field on the dissociation process; the expression for f(b) is shown in equation C.6. .................................................................................................................. 180

Fig. C.6. Changes in water concentration. (a) The distribution of water concentration in Model 3. There is a net increase/decrease in water concentration under forward/reverse bias conditions. Most of the change happens within the BPM. (b) The net water concentration change as a function of potential. The overall shape of the curve resembles those in Fig. 4.2c. The integrated water concentration refers to the integrated net water concentration changes over the reaction region (~25 μm to ~25 μm). .......................................................... 180

Fig. C.7. Effect of the catalytic power on the concentration of water splitting in Model 3. Increasing the catalytic effect in Model 3 from 0 to 10² induces a much larger increase for the forward bias current than in the reverse bias current. However, reverse bias current is enhanced more when the catalytic factor is increased from 10³ to 10⁵. ... 181

Fig. C.8. EIS tests of the BPM-based acid-base redox flow battery with 0.05 M ferrocyanide in 2 M KOH at the positive electrode. (a) Nyquist plots and (b) Bode plots at different current densities. Three components of the impedance can be identified: the ohmic resistance (~10⁻⁹ Ω), the reaction kinetics of the dissociation and neutralization processes (~10⁻³ Ω), and the transport resistance (~0.1 Ω). The resistance ascribed to transport increases under forward bias (40 mA/cm²), while the semicircle associated with the reaction process does not change significantly. .................................................................................................................. 181

Fig. C.9. EIS tests of the BPM-based acid-base redox flow battery with 0.3 M ferrocyanide in 2 M KOH at the positive electrode. (a) Nyquist plots and (b) Bode plots at different current densities. Large increases in the kinetic processes can be observed due to the migration of the anions Fe(CN)₆⁴⁻/Fe(CN)₃³⁻ into the AEL in competition with OH⁻. The latter is involved in the acid-base neutralization process. .................................................................................................................. 182

Fig. C.10. EIS tests of the BPM-based acid-base redox flow battery with 0.1 M ferrocyanide in 2 M KOH at the positive electrode. (a) Nyquist plots and (b) Bode plots at different current densities. A balance between the transport and kinetic processes is achieved with an intermediate concentration of ferrocyanide, which results in the best cell performance as shown in Fig. 4.4a. .................................................................................................................. 182

Fig. C.11. Influence of water splitting. (a) Cyclic voltammogram of the acid-base configuration with 2 M KOH and 1 M H₂SO₄ at the positive and negative electrodes, respectively. (b) Current density versus time at a given cell potential. The low current density (~3 mA/cm²) at 1.8 V suggests negligible influence of the water splitting reaction on the acid-base redox flow battery, as the highest potential during charging was set to 1.6 V. .................................................................................................................. 183

Fig. D.1. Nyquist plots the Pt/C electrode in RDE setup during the alkaline HOR process at different potentials. ........ 192

Fig. D.2. EIS measurements of the Pt/C RDE electrode during the acidic HOR process. (a) Bode plots at different rotating rate, at 0.01 V (vs RHE). (b) Bode plots at different applied potentials (vs RHE). The shifting of the peak position with the rotating rate but not potential indicates that it relates to the diffusion process, which is similar to the alkaline HOR (Fig. 5.1). .................................................................................................................. 192

Fig. D.3. Polarization curves of the Pt/C RDE electrode in the (a) alkaline and (b) acidic HOR process. Much faster reaction kinetics were observed in the acidic electrolyte. .................................................................................................................. 193

Fig. D.4. (a) Polarization and power density curve of the APEFCs with the conventional MEA configurations for both the cathode and anode. (b) Nyquist plot of the cell at 0.1 A/cm² applied current density. Testing conditions are the same as those in Fig. 5.2 and 5.3. .................................................................................................................. 193

Fig. D.5. Photographs of the Pt/PTFE cathode to be assembled into the APEFC. Two pieces of copper foil cover the top and bottom edge of the Pt/PTFE to connect the catalyst film and the carbon plate. Ionomers were deposited only to the active area (the purple box). .................................................................................................................. 194

Fig. D.6. Polarization and power density curves of the Ag/PTFE with and without AEM ionomers. The ionomer loading is 75 μL/cm². In contrast to the Pt/PTFE electrode (Fig. 5.3), no significant difference was observed. ........ 194

Fig. D.7. Polarization and power density curves of the Pt/PTFE without ionomer and with Nafion ionomer. Incorporating the Nafion ionomer leads to decreased performance. .......... 195

Fig. D.8. Polarization and power density curves of the Pt/PTFE electrode with different thickness of the Pt electrode.... 195
Fig. D.9. (a) Nyquist and (b) Bode plots of the experimental EIS measurements with potentiostat and galvanostat modes. No significant difference was noted, suggesting the equivalency of the two modes. 25 uL ionomer were used.

Fig. D.10. Comparison of the modeled EIS spectra between the time- (red triangle) and frequency- (black line) domain for a simple system coupling an electrochemical reaction and a diffusion process. The similar Nyquist (a) and bode plots (b) indicate the two methods are equivalent.

Fig. D.11. The time variation of input voltage and overall current response for (a) the experiment at 876 Hz (Fig. 5.4c) and (b) the model 1 at 10000 Hz (Fig. 5.4f). Current leads voltage in both cases. The time variation of the input voltage and the capacitive current response for the model 1 at (c) 1 Hz and (d) 10000 Hz. Much smaller capacitive current was seen at the lower frequency. I Capacitive current and (f) overpotential as a function of time in model 2 at 10 Hz.

Fig. D.12. (a) Nyquist plots of the experimental EIS at cell potentials 0.81, 0.76, and 0.70 V. Smaller cell potential means larger reaction overpotential. (b) The negative of the imaginary impedance as a function of frequency. The peak position of the higher frequency arc shifts to larger values and the lower frequency inductive loop remains unaffected.

Fig. D.13. (a) Nyquist plots of the modeled EIS at -0.20 and -0.25 V. More negative potential means larger reaction overpotential and the thermodynamic equilibrium potential is set to 0 V. (b) The negative of the imaginary impedance as a function of frequency. The peak position shift is consistent with the experiments shown in Fig. D.12.

Fig. D.14. Extracted resistance values by fitting the (a) experimental and (b) modeled (model 1) EIS at different overpotentials. Applying a larger overpotential leads to decreased values.

Fig. D.15. Extracted resistance values from fitting the simulated EIS spectra in model 1 with different diffusion coefficients for the oxygen gas. Decreasing the $D_{O_2}$ mainly affects the transport resistance $WR$. 
Chapter 1

Ion management for renewable energy storage

Abstract

Electrolysis converts electrical energy into chemical energy by storing electrons in the form of stable chemical bonds. The chemical energy can be used as a fuel or converted back to electricity when needed. Water electrolysis to hydrogen and oxygen is a well-established technology, whereas fundamental advances in CO₂ and/or N₂ electrolysis are still needed to enable short term and seasonal energy storage in the form of liquid fuels.

For an electrochemical reaction to proceed with high efficiency, rapid charge transfer kinetics across the electrode/electrolyte interface and robust ion management in the electrolyte are needed. The ion transport, in isolation, can be sufficiently described by the Nernst-Planck equation, while at system level care must be taken when the ionic transport is coupled to other processes such as homogenous chemical reactions and electrode polarization. This consideration has led to our analysis of the polarization losses due to the ionic concentration gradient in water splitting photoelectrochemical cells with various buffer-membrane combinations.

To mitigate the concentration gradients, we and other groups proposed the use of reverse-biased bipolar membranes (BPMs) in electrolytic cells. A BPM consists of a cation exchanger layer (CEL) laminated with an anion exchange layer (AEL), usually equipped with a catalyst layer deposited in between to enhance the water dissociation reaction. When strongly acidic/basic aqueous solutions are placed next to the CEL/AEL, a negligible cross-membrane overpotential is observed under prolonged operation because the neutral water molecules at the CEL/AEL interface dissociate into proton and hydroxide ions, which replenish those consumed at the cathode and
anode. BPM electrolyzers provide the unique advantage of operating the cathode and anode under different pH conditions, which is desirable considering the different pH-dependence of the efficiency of electrocatalytic reactions.

This chapter discusses the electrolytic reactions that can potentially enable renewable energy storage, including water and CO₂ electrolysis, fuel cells and redox flow batteries. Recent progress and major obstacles associated with electrocatalysis and mass transfer management at the system level are reviewed. We then review our current understanding of the working mechanisms of BPMs, and how can we use BPMs to effectively manage ions for various (photo-) electrochemical applications. We conclude that knowledge and strategies are transferable between these different electrochemical technologies, although there are also unique complications that arise from the specifics of the reactions involved.
1.1 Introduction

Building sustainable, clean energy systems is one of the most critical problems that the world faces in this century. Population growth and economic development in the coming decades will inevitably result in a substantial increase in global energy consumption.\textsuperscript{1-3} Traditional fossil sources of energy are carbon-positive and contribute substantially to climate change. Various alternative sources of carbon-neutral power exist, including nuclear fission, biofuels and electricity generation from renewable resources such as wind and solar energy.\textsuperscript{1} It is projected that renewable electricity can provide a dramatic decrease in carbon dioxide intensity, defined as carbon dioxide emissions per unit of energy output, despite the projected increase in overall energy consumption.\textsuperscript{4}

Electricity from renewable sources such as wind and solar has become economically competitive due to years of cost decline and advances in technology. The globally averaged levelized cost of electricity (LCOE) for utility-scale solar photovoltaic (PV) power has fallen 73\% since 2010, while the LCOE from onshore wind has reached 0.03 USD/kWh in some part of the world.\textsuperscript{5} The price of renewable electricity from all currently commercial sources is projected to be comparable to or lower than that of fossil fuel-derived electricity by 2020.\textsuperscript{5} One of the major contributors to the falling LCOE for solar and wind power electricity comes from the sharp reduction in installation costs. The global capacity weighted average total installation cost of newly commissioned utility scale PV projects has decreased by 68\% to around 1600 USD/kW since 2010. The construction costs of the new nuclear- and coal fired- power plants are very uncertain and are subject to various factors; however, total costs between 5500 to 8100 USD/kW and 3500 USD/kW, respectively, have been suggested and are expected to increase in the future.\textsuperscript{6,7}

Despite of the rapid growth of renewable electricity, the current fraction of power generated from renewable sources in the electric energy mix remains low, with a much greater proportion of electricity being produced from gas, oil, and coal. However, based on a reference case prediction, electricity from renewable resources is expected to increase from 18\% to about 31\% between 2018 to 2050.\textsuperscript{4} One of the issues with solar electricity is the intermittent nature of the diurnal solar cycle,
which is not well matched with demand and thus requires excess generation capacity at the grid level or backup power on the consumer end. For example, Fig. 1.1 shows the net electrical load fluctuation as a function of time for a spring day in California. Starting from around 4 pm a supply of an additional 13000 MW of electricity from non-solar resources such as natural gas and nuclear within 3 hours is needed to replace the electricity shortfall of solar power.8

![Fig. 1.1. Sustainable energy utilization. Schematics of energy storage and utilization based on electrolysis. Surplus electrical energy from renewable sources can be stored via electrolysis as chemical fuels. The energy is extracted to levelize demand on the short time scale and to meet the need for fuel in seasons when the renewable supply is less available. The intermittency plot (lower left) was obtained from ref. (8).](image)

The fluctuating power from solar and wind thus requires massive energy storage, both on the short and long terms.9 There are multiple ways that electrical energy can be stored including physical approaches such as pumped hydroelectric, and compressed air energy storage (CAES), large-scale batteries such as lead-acid, lithium, sodium sulfur batteries, and flow batteries, and electrolysis, with pumped hydroelectric being the current leading technology in the energy storage sector.10,11 Most of these methods suffer from being only suitable for short term storage or are
limited by particular geographic requirements. Electrolysis stands out as a means of storing electric energy in the form of stable chemical bonds. The potentially enormous energy capacity, negligible self-discharge rate, existing infrastructure, and low capital cost of containing renewably generated carbon-based fuels make them ideal for seasonal storage, a feature that is highly desirable given the seasonality of renewable energy sources. The need for such a technology will be increasingly acute with the larger anticipated penetration of the low-cost renewable electricity into the power grid, as illustrated in Fig. 1.1.

While water electrolysis to hydrogen and oxygen is a well-established technology, an efficient and cost-effective means of storing electrical energy in the form of liquid fuels does not yet exist. In order for such a technology to become economically competitive with abundant fossil fuels, one has to start with very cheap electricity. A technoeconomic analysis of CO$_2$ electrolysis indicates that a renewable electricity price below 0.04 USD/kWh will be needed for electrolysis-derived fuels to be competitive with fossil-derived fuels.$^{12}$ This is a target that renewable electricity is well on its way to reaching based on the IRENA renewable cost database.$^5$

In Fig. 1.1, we illustrate how a sustainable energy cycle can be achieved by coupling electrolysis with electricity generated from solar and wind among other renewable sources. Electrolysis can produce both commodity chemicals and hydrogen, mitigating the intermittency of the renewable power. In this scenario, hydrogen-air fuel cells can be used to convert energy that is transiently stored as hydrogen back to electricity. High energy density liquid fuels are the preferred form for seasonal storage and can form a green energy cycle if CO$_2$ in the air can be concentrated enough to electrolyze efficiently. There is research currently working to capture carbon from the atmosphere and even a few startup companies like Climeworks.$^{13}$ The electrolysis of CO$_2$ to CO and hydrogen (syngas) has been achieved with a variety of different electrocatalysts and provides a feedstock for hydrocarbon fuels via the Fischer-Tropsch process. Alternatively, C-C coupled products including ethylene and ethanol can be made directly by electrolysis at copper-containing catalysts, but the efficiency, selectivity, and throughput of those reactions need to be improved. Not shown in the figure is the electrochemical reduction of N$_2$ to ammonia for the
production of fertilizers. In this case electrolysis takes advantage of an unlimited chemical feedstock as the earth’s atmosphere provides the nitrogen and water needed for the reaction. In addition to making fuels and fertilizers from electrolysis, thermochemical methods provide a promising route to hydrogenate CO and N\textsubscript{2} using renewable hydrogen and could produce carbon neutral products as well. Two examples are the Fischer-Tropsch and Haber-Bosch processes, which are already well developed at scale. The former is used to make liquid hydrocarbons from CO and H\textsubscript{2} and the latter is used to make ammonia from N\textsubscript{2} and H\textsubscript{2}. It should be noted that ~80% of the energy consumed in ammonia synthesis is for the formation of reactants, mainly hydrogen production via steam reforming and the water-gas shift reaction.
and the rate at which the product can be removed, as shown in Fig. 1.2a. The electron transfer rate and the mass transport flux are coupled as they both are proportional to the current. Active catalysts are needed to lower the activation barrier by binding and stabilizing certain transition states, Fig. 1.2b. Increasing the overpotential for one or both electrode processes accelerates the reaction kinetics by effectively lowering the activation barrier, but the extra energy cost lowers the power conversion efficiency, as illustrated in Fig. 1.2d. When the electron transfer kinetics are sufficiently fast, the highest current density is achieved by accelerating the supply of reactant. In the case of CO₂ electrolysis, this can be accomplished by supplying the reactant and removing the products in the gas phase, taking advantage of the faster diffusion coefficient of gases and avoiding the low solubility of CO₂ in liquid water, as shown in Fig 1.2c.

1.2 Electrolytic techniques

1.2.1 Water Electrolysis

Water electrolysis has a long history, the first published demonstration dating to 1789, and it is now a well-established commercial technology.¹⁵ For example, a large installation of alkaline electrolyzers by Norsk Hydro (1948-1990) at a hydroelectric plant was capable of generating about 70,000 kg H₂/day.¹¹ The largest wind-hydrogen plant was installed in Norway in 2004 by Norsk Hydro and Enercon, coupling a 600 kW wind turbine with a 48 kW electrolyzer.¹⁶

There has been increasing interest in water electrolysis over the past two decades because of its potential role in a hydrogen-based energy economy involving electrolytic production, storage, transport, and use of hydrogen as fuel.³ Current research focuses on water electrolyzers that can be categorized according to their electrolytes: alkaline electrolytes, proton exchange membranes (PEM), and solid-state proton or oxide ion conductors. Commercial PEM electrolyzers achieve the best performance (~70% energy efficiency at current densities of 1.7 A/cm², Giner Inc.)¹⁷ but the large overpotential of the anodic water oxidation reaction and the corrosive acidic environment...
necessitate the use of precious metal catalysts. The solid membrane electrolyte and manufacture of the bipolar plates also add significantly to cost. Alkaline electrolyzers are the oldest technology with somewhat lower system efficiency (~64% efficiency, at current densities of 1 A/cm², GHW) and lower cost (800 USD/kW). Alkaline electrolytes enable the use of non-precious metal catalysts such as Ni and Fe. A common issue associated with current commercial PEM and alkaline water electrolyzers is manufacturability that current units are built mostly by hand. With a large-scale production, dramatic capital cost reduction of manufacture is possible, leaving the electricity, current efficiency and maintenance of the units to be the dominating contributors to the total cost.

There has been recent interest in developing better catalysts to lower the cost and increase the efficiency of water electrolysis. In acidic PEM electrolyzers, the cathodic hydrogen evolution reaction (HER) follows a relatively simple mechanism. A proton is adsorbed on the electrocatalyst surface, followed by either a catalytic or electrochemical desorption of the adsorbed H. A plot correlating HER catalytic activity with metal-hydrogen bond strength on various metal catalysts goes through a maximum, and is thus termed volcano plot, Fig. 1.3a. A simple explanation for the volcano shape is that metals that bind hydrogen too weakly cannot stabilize the M-H intermediate, whereas those that make very strong M-H bonds fill most of the binding sites leaving little room for a new adsorption event. While the M-H bond strength is a good descriptor for most catalysts, some metals with particular facets, such as Pt (111), exhibited 20-200 times higher HER exchange current density in acid than base even though the H-binding energy is similar. Mechanistic studies point to the role of hydroxide adsorption or water reorganization under interfacial electric field during the HER process. Precious metals (Pd and Pt) are the best catalysts but their cost and low natural abundance present obstacles to use of this technology on a very large scale. Thus, an appealing strategy is to replace pure Pt with core-shell, over- and sub-layer, doped and supported structures. Further reduction in precious metal loading is possible by using single atom catalysts, which have emerged in recent few years. The high surface energy of single atoms favors their coalescence and requires supports that can anchor them strongly. N-doped graphene is a widely
used motif, providing nitrogen atoms for coordinating metal atoms.\textsuperscript{20} Electrocatalyst supports can also stabilize catalytic metal atoms and modulate their reactivity by donating or accepting electrons. For instance, there is evidence of d-electron transfer between late transition metal (oxide) and early transition metal layered supports in the strong metal-support interaction.\textsuperscript{21} Similar considerations may be applicable to alloys containing metals with different electron negativities.

One of the important geometric factors is the catalytically active surface area, the measurement of which is vital for meaningful comparisons of catalyst activity. One well-known case are Raney catalysts, made by etching an active metal from an alloy to generate a high surface area form of the less active metal. Current density normalized to the active surface area often reveals similar site turnover rates and activation energies to the planar counterpart, even though the current

Fig. 1.3. Water electrolysis. (a) HER volcano plot for catalytic elements. [Data obtained from (18)]. (b) Free energy diagram for the OER. The black curve refers to an ideal OER catalyst whereas the red curve represents a real catalyst (28). (c) Comparison between a low temperature PEM electrolyzer and a higher temperature solid oxide electrochemical cell (SOEC) [Data obtained from (52)] and (d) Electrolyzer and fuel cell mode performance of a SOCE using a proton conductor at intermediate temperatures. Increasing the temperature by 150 °C dramatically improved the cell current density. [Data was taken from (53)]
can differ by orders of magnitude. For metals such as Au or Pt, under potential deposition (UPD) is a good way to measure the active surface area in the electrolyte of the actual electrocatalytic experiment. Potential relaxation, AC impedance and capacitance measurements from cyclic voltammetry are other effective methods. However, uncertainties can arise from experimental conditions including electrolyte conductivity, surface coverage and time scales. A complementary set of measurements by different techniques is thus helpful in obtaining an accurate surface area. Also, due to the fast electron transfer kinetics compared to the mass transport in acidic aqueous electrolyte, the HER activity is usually mass transfer limited and would require forced convection or microelectrode design to measure the intrinsic activity.

Recently, a number of non-precious metal HER catalysts have been discovered. Inspired by the MoFe cofactor of nitrogenase, which has a hydrogen binding energy close to that of Pt, the edge sites of MoS$_2$ as well as several metal phosphide catalysts have been shown to be active towards HER. Recent studies have shown that S vacancies and strain engineering are also effective ways to improve HER performance.

The four-electron, four-proton oxygen evolution reaction (OER) is more mechanistically complex and invariably involves substantial (250-300 mV) onset overpotentials in acidic media. The reaction is thought to proceed via an adsorbed M-OH species, followed by a deprotonation step. Oxygen gas is formed either from a surface hydroperoxy intermediate, M-OOH, or by bimolecular recombination of M-O. For oxide-based OER catalysts with rocksalt, rutile, spinel and perovskite structures, volcano plots have been developed from theoretical considerations. An ideal OER with optimal binding energies has free energy difference between M-OOH and M-OH ($\Delta G_{\text{OH}} - \Delta G_{\text{OOH}}$) of 2.46 eV, requiring an onset potential of 1.23 V, Fig. 1.3b. Onset potential of real catalysts, however, are significantly higher because ($\Delta G_{\text{OH}} - \Delta G_{\text{OOH}}$) deviates from the ideal case and is proposed to be regulated by the free energy of M-O bonding. A universal average ($\Delta G_{\text{OH}} - \Delta G_{\text{OOH}}$) value of 3.2 eV was suggested and found to be consistent with several groups of catalysts because the binding strength of OH scales linearly with that of OOH. Although the scaling relation is generally considered valid, further complication to experimental investigation comes from the fact
that the properties of catalyst surfaces may change during electrochemical operation, particularly under anodic conditions. Metal oxidation states, for example, vary with the applied potential, and this effect can lead to dramatic changes in catalytic activity, conductivity and stability. The transition from Ni$^{2+}$ to Ni$^{3+}$ is typically a prerequisite for high OER activity in alkaline nickel-based catalysts as the former is insulating. Pretreatment of the catalyst surface before testing is important for meaningful evaluation and comparisons. Metal oxides with high solubility at higher oxidation states are often unstable in acid media and a tradeoff between the stability and activity of Pt, Pd, Au and Ru has been observed. Currently iridium oxide is the only known stable catalyst for oxygen evolution in acidic media, and it is used only in pure form in the catalyst layer.

Conductive supports can be used to reduce the precious metal loadings leading to lower costs and a better utilization of catalysts. However, while carbon can be used as a conductive support for both half reactions in a fuel cell, it can only be used on the hydrogen side in a PEM electrolyzer, on the oxygen side it quickly corrodes. Oxide support such mesoporous tin oxide doped with indium has shown high conductivity (0.3 S/cm) and promising electrochemical stability under repetitive voltammetric scans at anode potentials. Two of the key research topics for acid electrolysis are thus finding a more abundant, lower-cost alternative catalyst to iridium oxide for oxygen evolution and/or discovering a conductive support that also has long-term stability under oxygen evolution conditions in acidic media.

1.2.2 CO$_2$ electrolysis

Electrochemical reduction of CO$_2$ to liquid fuel and value-added chemicals represents a possible solution for carbon-neutral seasonal storage of renewable electricity. CO$_2$ can be reduced to various C1 products including carbon monoxide (CO), formate, methane, methanol and C2+ products including ethylene and ethanol. CO$_2$ reduction with high selectivity to CO and formate has already been realized since these reactions are a two-electron transfer process. It is more challenging to obtain a C2+ product with high selectivity as the process requires transferring more
than two electrons and multiple protons, thus requiring multiple reaction intermediates, some of which are shared with different possible products. The high overpotential required for most CO₂ reduction catalysts also suggests a low energy conversion efficiency, < 50% (compared to the 60%-70% for water electrolyzers).¹²

Fig. 1.4. CO₂ electrolysis. (a) The scaling relation between the adsorption strength of COOH and CO on various metal surfaces and in enzymes. [Reprinted with permission from (33), copyright (2013) American Chemical Society] (b) Comparison of current density and Faradaic efficiency of CO₂ reduction to ethylene (blue) and ethanol (red). Solid symbols refer to published stability tests. Higher current density is achieved in a triple phase boundary (TPB) configuration, compared to aqueous phase CO₂ reduction (Aq.). Data obtained from (35, 38–42) and (43–46), (50). (c) Enhanced mass transfer of CO₂ near a Au needle surface. The large electric field at the tip of the Au needle attracts hydrated K⁺, which concentrates CO₂ in its solvation shell. [Adapted with permission from Nature Publishing Group, (49)] (d) Construction of the triple phase boundary in gas-fed CO₂ electrolysis. The Cu catalyst is sputtered onto a PTFE porous support which provide a gas diffusion pathway. [From (50). Reprinted with permission from AAAS]

As discussed for the OER, the efficiency of CO₂ reduction on metallic catalysts is limited by linear scaling relations. For example, Fig. 1.4a plots a correlation of the free energy (calculated by density functional theory, DFT) of two intermediates in the reduction of CO₂ to CO, E(COOH) and E(CO). A lower free energy and more stable M-COOH bond is desired, whereas weaker binding to CO is necessary to optimize desorption of the product.³³ This is challenging for a single metal
catalyst if the intermediates bind to the same site because the M-C bond strengths scale linearly. Multi-metallic catalysts take inspiration from the active site of the CO dehydrogenase enzyme CODH, in which cooperative binding to two metal atoms stabilizes a CO$_2^\cdot$ transition state.$^{34,35}$ Cu is a unique CO$_2$ reduction catalyst because it favors C2+ products, including some like ethanol that are ideal for seasonal storage. Cu makes a moderately strong bond to CO but no so strong as to poison the surface, allowing sufficient coverage for C-C coupling or protonation steps.$^{36,37}$ The catalytic pathways leading to hydrocarbons or oxygenates on Cu are complicated and highly coupled, as evidenced by the relatively low Faradaic efficiency (FE) for producing ethylene and ethanol, Fig. 1.4b. Alloying Cu with other metals$^{35,38-42}$ and building nanostructures that modulate the chemical environment of the CO binding site$^{43-46}$ are interesting strategies for steering the C2+ product distribution. Given the complexity of this problem, there is a need for better spectroscopic probes and microscopies that can characterize the structure of the electrocatalytic sites. Systematic high throughput screening guided by computation and machine learning are also emerging as effective means of attacking electrocatalytic problems of this nature.$^{47,48}$

There are also acute system-level problems for CO$_2$ electrolysis. The low solubility of CO$_2$ in water under acidic conditions creates a mass transfer limitation, and at high overpotentials the HER reaction becomes dominant. Strategies for concentrating CO$_2$ at the electrode surface can mitigate this problem to a certain extent, Fig. 1.4c $^{49}$ and mass transfer is dramatically improved when CO$_2$ is supplied in the gas phase. In this case, construction of a high surface area triple-phase boundary (TPB) where catalyst, electrolyte and gaseous reactant meet, is essential. Fig. 1.4d shows a TPB made by sputtering a Cu catalyst layer onto a PTFE substrate that prevents system flooding, on top of which is deposited a carbon conductive layer. Gaseous CO$_2$ diffuses through the porous PTFE layer and the hydrogen evolution reaction (HER) is suppressed by using an alkaline electrolyte.$^{50}$ Lessons from biological systems such as the C4 plants (plants with alternative photosynthetic pathway incorporating CO$_2$ into a C4 intermediate, oxaloacetate) may inspire other strategies for concentrating CO$_2$ in a TPB configuration. Photosynthetic organisms have evolved the ability to channel CO$_2$ to ribulose-1,5-bisphosphate (RuBP) as carbon source for the Calvin
cycle. C4 plants acquire extra concentration by trapping CO$_2$ in a four-carbon compound and passing it to bundle sheath cells for decarboxylation, resulting in a local supply of CO$_2$ for fixation.$^{51}$ Analogous CO$_2$ storage and delivery would be addressing a major problem of gas-fed CO$_2$ electrolyzers, because the single-pass conversion rate in current electrolyzers is low. One can imagine equipping the diffusion layer in an electrolyzer with gradient-localized “bundle sheath cells” that salvage the unreacted CO$_2$ gas from the TPB and pass it down to reactive sites, achieving higher conversion rates.

A number of lessons learned from water electrolyzers can be applied to the CO$_2$ electrolysis problem, although some problems are CO$_2$-specific. pH gradients developed across the membrane electrolyte cost energy in water electrolyzers that operate in neutral or near neutral solution, and for this reason all water electrolyzers operate under strongly acidic or strongly basic conditions. The use of buffered solutions in CO$_2$ electrolysis creates pH gradients and proton management problems at high current density. For water electrolyzers, a bipolar membrane (BPM) addresses this problem by operating the cathode and anode in acid and base, respectively. This arrangement minimizes the membrane polarization loss because water autodissociation in the BPM provides H$^+$ and OH$^-$ ions to the cathode and anode, respectively. This strategy can be applied to CO$_2$ electrolysis, but with some modification since CO$_2$ reduction requires a different optimal pH from the hydrogen evolution reaction. The use of BPM also mitigates the crossover problem of both anionic and neutral products.

**1.2.3 Solid State Electrolytes**

Because chemical reaction rates rise exponentially with temperature, intermediate and high temperature electrolyzers are effective in lowering electrode overpotentials for both the anode and cathode reactions. Fig. 1.3c compares the polarization curves of PEM cell at 60 °C with a solid oxide electrolysis cell (SOEC) at 800 °C,$^{52}$ and Fig. 1.3d shows data from a cell containing a solid state proton conducting electrolyte.$^{53}$ The electrode reactions in Intermediate (250-500°C) and high
temperature (600-800°C) electrolyzers are slightly different than in polymer electrolyzers depending on the type of electrolyte used. For example, in an SOEC, water vapor or CO$_2$ is reacted at the cathode to produce H$_2$ or CO, respectively, and O$^2-$ in a 2-electron process. At the anode, O$^2-$ ions combine to form O$_2$ gas.

$(\text{La}_{1-x}\text{Sr}_x)_{1-y}\text{MnO}_3$ is one of the best studied catalysts for the SOEC anode but has trouble with delamination from the electrolyte, causing an increase in polarization.$^{54,55}$ At the cathode, nickel and other late transition metals are frequently used as SOEC catalysts but usually are not very stable at the temperatures required.$^{56}$ Tests have been done using perovskites including La$_{0.6}$Sr$_{0.4}$VO$_3$ and $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_3$ as catalysts at the cathode as well with promising results.$^{57,58}$ $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$ has oxide ion conductivity five times higher than typical zirconia electrolytes, but its stability in a SOEC has not been studied in detail yet.$^{59}$ One study using $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$ in a solid oxide fuel cell found the output voltage to decay at 1 mV/h$^{60}$ which is not viable for a commercial system. Proton conducting electrolytes are also very promising because they can achieve higher conductivity than oxygen conducting materials at relatively low temperatures due to the lower activation energy of proton conduction.$^{61}$ The most studied type of proton conducting electrolytes are BaZrO$_3$ and BaCeO$_3$ perovskites, where the former is more stable and the later more conductive.$^{62-64}$ A nice compromise between the two came from combining them to make BaCe$_{0.9}$Zr$_{0.1}$Y$_{0.2}$O$_{3-δ}$ which resulted in an impressive 830 mA/cm$^2$ current density at 1.5 V.$^{65}$ The downside to ceramic proton or oxide ion conductors is that the ion conductivities are not as high as polymer electrolytes and the high operating temperatures cause even the electrode and electrolyte materials to degrade over time. One way that researchers have tried to minimize the degradation is to lower the temperature of operation. Recently, solid acids have been shown to be good proton conductors at intermediate temperatures. For example, CsHSO$_4$, CsH$_2$PO$_4$, and Cs$_2$(HSO$_4$)(H$_2$PO$_4$) have shown high proton conductivity as well as a few others including Rb$_3$H(SeO$_2$)$_2$, (NH$_4$)$_2$H(SO$_4$)$_2$ and K$_3$H(SO$_4$)$_2$. These materials achieve conductivities at temperatures as low as 120–300°C, but are limited by their brittle mechanical properties.$^{66}$ Future research should focus on improving how the electrolyte and catalyst interface
is made to minimize delamination. Another interesting development has been to use electrolytes that can conduct both protons and oxide ions. One group made a hybrid SOEC, using BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-d}$ as the electrolyte, that could produce 3.16 A/cm$^2$ at 1.3 V and 750°C. This performance is much better than that reported for single ion conducting electrolytes.\textsuperscript{67} Research on solid state systems for both water splitting and CO$_2$ electrolysis is showing steady progress and is promising for the generation of fuel and chemical feedstocks (H$_2$ and CO) from electrical energy. Halder-Topsoe already produces SOECs for large scale, on-demand CO production from CO$_2$ with purities as high as 99.999\%.\textsuperscript{68}

\subsection*{1.2.4 Electrochemical Nitrogen Reduction}

The electrosynthesis of ammonia (ESA) is being studied to better understand electrocatalytic activation of dinitrogen and its limitations. This has been done at a range of temperatures by reacting N$_2$ gas at a cathode and water at an anode that are separated by a proton conducting electrolyte or reacting both N$_2$ and water at the cathode using an anion-conducting electrolyte. Because of the 6-electron nature of the N$_2$ reduction reaction, the Faradaic and energy efficiencies for combining water oxidation and nitrogen reduction tend to be very low. A more commonly studied approach is to use higher temperatures and feed H$_2$ to the anode. This can increase the Faradaic efficiency at the cost of oxidizing the H$_2$ but high temperatures risk decomposing any NH$_3$ formed.\textsuperscript{69} In low temperature ESA, the most commonly studied membrane is Nafion because of its high conductivity and stability, although one of the highest Fes so far reported (41\%) came from anion exchange polymer membrane with an iron cathode.\textsuperscript{70} Other catalysts tested include Pt, Ru and conducting metal oxides with similar results.\textsuperscript{71} Several attempts to use molten salts at 300-400°C with N$^3-$ as mobile ion in the electrolyte and Ni or Al as the catalysts reported FE as high as 80\% and a synthesis rate faster than any solid oxide conductor.\textsuperscript{72,73} In this case, the electrocatalysts are typically late transition metals such as silver, nickel or palladium and the electrolytes are often the same as those used in water splitting SOECs.\textsuperscript{71} One research group also used CH$_4$ as a hydrogen
source instead of H₂ with similar results.⁷⁴ Low FE and low current density are persistent challenges for ESA research. At higher temperatures, the FE ranges from <1-80% but the current densities are too low for practical purposes, ranging from <1-23 mA/cm². For temperatures below 100°C, the FE is typically only 1-2% although there are a few reports that have been considerably higher and may show promise if the current density can be improved.⁷⁰ Density functional theory (DFT) calculations have helped to clarify the challenges in nitrogen electrocatalysis. Most notably, one group found that the differences in adsorption energies for NHₓ* intermediates are far from the optimal values for the desired reaction and that a catalyst should have two different absorption sites in order to produce ammonia at a reasonable rate.⁷⁵⁷⁶

1.3 Ion management in BPMs

(Photo-) electrochemistry stores the surplus electron from renewable sources in chemical bonds that can be stored for both short and long terms, potentially mitigating the intermittency problem of renewable energy.²⁷⁷ While many studies have focused on studying the charge transfer kinetics on the electrode, the understanding of ion transport is equally important as ions carry the current inside the cell and can cause significant energy loss.⁷⁸–⁸⁰ Ion exchange membrane separators are usually needed to separate gaseous reactants/products and to allow the gas products to build up and be collected at above 1 atm pressure.

Water electrolyzers and fuel cells operate under either strongly acidic or alkaline conditions to minimize ohmic resistance loss. Bipolar membranes (BPM) consisting of an acidic cation exchange layer (CEL) and a basic anion exchange layer (AEL), on the other hand, use both protons and hydroxide ions as charge carriers and thus offer the possibility of different pH conditions for the cathode and anode. This feature enables the coupling of electrochemical reactions with different pH-dependences.⁸¹–⁸³ The transport of protons and hydroxide ions is coupled to water dissociation (reverse bias) and acid-base neutralization (forward bias) reactions at the AEL/CEL interface. Mechanistic studies of the reactions at the molecular level have so far been limited, and future
efforts are needed to better understand the effects of catalysis on the reaction kinetics. This will not only help to design BPMs with higher performance, but will also provide useful insights into electrochemical conversions that involve equilibria between protons, hydroxide ions, and water.84

This subsection starts by reviewing early studies on the free energy losses in buffer-membrane based photoelectrochemical cells, followed by the solution to the problem using reverse-biased BPMs. BPMs operating under non-extreme pH conditions have important implications for (photo-) electrochemical conversions, and could exhibit different behaviors than their counterparts in strongly acidic/basic environments. Forward-biased BPMs for fuel cells and redox flow batteries are then reviewed. We finally discuss theoretical treatments of the BPM junction and our current understanding of the mechanism of the water dissociation reaction at the AEL/CEL interface.

1.3.1 Free energy losses and reverse-biased BPMs

The polarization losses in a water splitting photovoltaic cell (PEC) include those from the electrode overpotential, series resistance from the solution and membrane, and the cross-membrane pH gradient. While it has been known that the first loss (~250-400 mV) highly depends on the operating conditions of the electrode material, the pH-gradient loss was found to evolve with time and could contribute up to 300-600 mV.78 Starting with a near neutral phosphate buffer electrolyte (1.0 M, pH=6.73) and an anion exchange membrane (AEM), the pH values in the cathode/anode chambers were observed to increase/decrease after applying a current density of 25 mA/cm² (Fig. 1.5a). The hydroxide ion/protons generated electrochemically during the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER) result in progressive pH changes that cannot be effectively mitigated by the buffer species. A pH gradient of ~ 6 units forms within 6 hours of operation (24 hours at higher concentration), corresponding to a free energy loss of ~354 mV (59 mV/ΔpH). The pH change is more severe for the cathode than for the anode due to the electromigration of phosphate anions from the cathode to the anode, which lowers the buffer capacity of the catholyte. When operating with a cation exchange membrane
(CEM), the cations of the buffer carry the charge and more symmetric pH changes were observed (Fig. 1.5a). Even though the pH-gradient can be partially depolarized during the off-current period, in a realistic PEC device, a solution that lifts the constraint on the buffer types to manage pH gradients was called for.

This has led to the use of BPMs for water electrolysis. A BPM consists of a CEL laminated onto an AEL, where orienting the CEL/AEL to the cathode/anode sides of the cell subjects the BPM to reverse bias, and vice versa (Fig. 1.5b). Under sufficiently large reverse bias, the water dissociation reaction produces protons and hydroxide ions as the principal charge carriers within the BPM. These ions migrate towards the cathode/anode electrodes, respectively, to compensate for the electrochemical consumption of H⁺ and OH⁻ (Fig. 1.6a). Compared with conventional monopolar membranes (CEM and AEM), the BPM shows negligible changes in the cross-membrane potential under prolonged reverse-bias operation (Fig. 1.5b).

![Fig. 1.5. pH gradient and potential losses in the membrane based electrolytic cells. (a) The formation of pH gradient as a function of time in a water electrolysis cell with an AEM (top) and CEM (bottom). [Reprinted with permission from 78] (b) Schematics of ion transport in BPM under forward (top left) and reverse (top right) bias. (Bottom) Potential loss in phosphate buffer electrolyte with different membranes, at 25 mA/cm² current density. [Reprinted with permission from 81]]
In addition to effectively managing ions in the electrolyte, the different pH conditions offered by BPMs can also benefit the electrochemical conversions at the electrodes. The configuration with strong acid/base placed next to the CEL/AEL allows the HER/OER to occur in their optimal pH environments. Thermodynamically, the potential due to pH gradient across the BPM is exactly balanced out by the Nernstian shift in the thermodynamic potentials of the HER/OER reaction, resulting in the same overall potential requirement as with monopolar membranes (Fig. 1.6a).82 However, the HER proceeds much faster in acid and the basic environment enables the use of earth-abundant materials for the OER reaction. For example, a BPM-based perovskite photovoltaic-driven water splitting cell employed CoP for the HER in acid and NiFe LDH for the OER in base, achieving an overall 12.7 % solar to hydrogen (STH) efficiency at ~ 10 mA/cm² photocurrent density (Fig. 1.6b).86

Fig. 1.6. BPMs in water electrolysis. (a) Schematic of a BPM-based water electrolyzer with strong acid HClO₄ and base NaOH in the cathode and anode, respectively (top). Comparison of the overall J-E curves of two water splitting cells consisting of (middle) a BPM with NaOH for OER and HClO₄ for HER and (bottom) a Nafion CEM with HClO₄ for both OER and HER. [Reprinted with permission from 82] (b) Schematic of a perovskite photovoltaic-driven water splitting cell equipped with a BPM that enables the use of cheap metals as OER and HER catalysts. [Reprinted with permission from 86] (c) The use of BPM in a solar driven water splitting cell that has a pH 9.3 Kbi buffer in the anode and strong acid pH 0 the cathode. [Reprinted with permission from 89] (d) Ion transport and crossover in reverse biased BPMs when a phosphate buffer is used as the catholyte and NaOH as anolyte. (e) Current density vs BPM cross-membrane potential with non-extreme pH conditions. [Reprinted with permission from 88]
For integrated PECs, non-extreme pH conditions are beneficial as certain types of light absorbers are not stable in strong acid or base. A configuration consisting of a GaAs/InGaP/TiO$_2$/Ni photoanode in a potassium borate (KBI) buffer (pH = 9.3) and a Pt cathode in a pH 0 electrolyte, separated by a BPM, was able to operate continuously for over 100 hours with ~ 10% STH efficiency (Fig. 1.6c). When a BPM is used with a high concentration of buffer electrolyte, the crossover of buffer species could become significant, and this could eventually lead to dissipation of buffering capacity just as in the case of monopolar membranes discussed above. The crossover rate of ions generally diminishes with increasing reverse bias and can be limited to below a few mA/cm$^2$. Buffer species, however, can contribute up to 10s of mA/cm$^2$ if they are charge neutral. The neutral H$_3$PO$_3$ species in the cathode chamber can diffuse into the CEL and is deprotonated at the AEL/CEL interface, which facilitates its transport (now as a negatively charged ion) through the AEL to the anode chamber (Fig. 1.6d). The polarization curves of BPMs exhibit similar trends at higher reverse bias, consistent with H$^+$ and OH$^-$ being the major charge carriers under these conditions. The different behaviors at lower current density could be related to the ion crossover, and the concentration polarization at the BPM/electrolyte interface (Fig. 1.6e). The latter phenomenon has been known to occur in monopolar membranes if the transference number in the bulk of the membrane is larger than in the adjacent electrolyte. This is plausible for BPMs that contain a higher concentration of H$^+$/OH$^-$ in the CEL/AEL than in the contacting electrolyte solutions at non-extreme pH. Understanding the potential losses at the BPM/electrolyte interface can be aided by characterizing the potential- and concentration-gradients in the diffusion boundary layer (DBL), which has been done for AEMs and electrode surfaces.

1.3.2 BPM based CO$_2$ electrolysis

The BPM-generated proton source under reverse bias can be used for electrochemical reactions other than HER, such as the CO$_2$ reduction reaction (CO2RR). The CO$_2$ reactant can be fed into the system either in the dissolved form with an aqueous electrolyte (aqueous CO2RR, Fig.
1.7a and 1.7b) or in the gaseous state by using a porous gas diffusion layer (GDL) (gas-fed CO2RR, Fig. 1.7c). The ion transport process in the aqueous CO2RR case is similar to that in water electrolysis. To suppress the competing HER, the cathode usually contains a near-neutral or basic buffer electrolyte, such as bicarbonate, which is also involved in the chemical equilibria with the BPM-generated protons (Fig. 1.7b). Compared with a conventional CEM, more robust CO2RR performance can be achieved using BPMs. For example, when KHCO₃ was used with a Nafion CEM, the transport of K⁺ from the anode to the cathode chamber changed the local environments of both electrodes and lowered the CO2RR efficiency. A similar effect exists in the gas-fed CO₂ electrolyzer, which shows a higher cell potential after the anode is drained of K⁺ (Fig. 1.7c). The use of a BPM also decreases the crossover of CO2RR products (Fig. 1.7d). The transport of charged products such as formic acid (formate under neutral or alkaline conditions) is inhibited dramatically compared to the AEM separator because the CEL of the BPM electrostatically repels anions. The crossover of neutral species such as ethanol is also mitigated, albeit to a lesser degree, mainly through the electroosmotic drag created by the outward proton and hydroxide fluxes under reverse bias (Fig. 1.7d).

Fig. 1.7. BPMs in CO₂ electrolysis. (a) Schematic of a PV-CO₂ electrolyzer with a BPM separating the cathode and anode. [Reprinted with permission from 95] (b) Coupling water oxidation and CO₂ reduction in a BPM-based electrolyzer with KHCO₃ aqueous electrolyte. [Reprinted with permission from 96] (c) Schematic of a gas-fed BPM-based CO₂ electrolyzer (top). Comparison of the chronopotentiometric results between a BPM and a Nafion membrane in the electrolyzer. [Reprinted with permission from 97] (d) Transport of neutral molecules is decreased in BPM-based CO₂ electrolyzers.
compared to the AEM, due to the outward H\(^+\)/OH\(^-\) flux in reverse biased BPMs (top). The crossover of an anionic product (formate) is also suppressed with a BPM (red: BPM, green: 3D BPM, blue: AEM). [Reprinted with permission from 100]

Gas-fed electrolyzers achieve higher limiting current density as molecules generally diffuse faster in gas than in liquids. CO\(_2\) electrolyzers equipped with BPMs that attain 100s of mA/cm\(^2\) current density have been reported, but usually suffer from the acidic local cathode environment that favors the competing HER reaction\(^{97,101}\) The resulted low faradaic efficiency (FE) requires proper management of ions at the BPM/catalyst interface. Incorporating an aqueous NaKCO\(_3\) layer between the BPM and the cathode increases the local pH and thus CO FE (Fig. 1.8a),\(^{101}\) with ion transport being similar to the case of a buffered electrolyte in the aqueous CO2RR as discussed above.

The electrochemical reactions in a gas-fed system happen exclusively in the catalyst layer that has a mixture of catalyst/support, ionomers, and pores. The local environment of the catalyst is determined by the membrane surface (for catalyst molecules or nanoparticles in contact with the membrane) and by the ionomer for those far away from the membrane. Considering the former scenario, we modified the surface pH of a BPM that contained a strongly acidic CEL with a weak acid cation exchanger using polyelectrolyte layer-by-layer (LBL) assembly (Fig. 1.8b).\(^{102}\) The local pH within the LBL film (~50 nm thick) was measured, at a resolution of ~10 nm, by ratiometric pH indicator molecules covalently attached at low loading to one of the polyelectrolytes. A sharp increase in pH from the CEL surface to the outer edge of the LBL film was observed, which helped to suppress the HER side reaction and led to improved CO FE in the modified BPM (Fig. 1.8b). The mechanism of ion transport within the LBL film has been studied intensively for the monopolar membranes in electrodialysis and water treatment applications,\(^{103,104}\) whereas the behavior of the LBL film in the gas-fed electrochemical device might deviate from those cases due to the absence of bulk water that solvates the ions and swells the membrane. For catalysts that are farther away from the membrane surface, ion conductive polymers (ionomers) are required, and are used routinely in H\(_2\)-O\(_2\) fuel cells.\(^{105}\) Designing functional ionomers that are compatible with the
environment for the CO2RR could be a promising way to resolve the problem of proton management in BPM-based CO2 electrolyzers.

Fig. 1.8. Interfacial proton management in the BPM-based CO2 electrolyzers. (a) Incorporating a solid-supported aqueous NaHCO3 buffering layer between the BPM and the cathode catalyst layer (top) increases the CO2 to CO FE (bottom). [Reprinted with permission from 101] (b) The addition of a weak acidic LBL film on the BPM CEL suppressed the competing HER reaction in the CO2 electrolyzer (top). The local pH in the LBL film was monitored using a ratiometric dye-tagged polyelectrolyte pH probe (bottom left). A larger peak ratio (560/510) corresponds to a lower pH. The higher local pH leads to increased faradaic efficiency compared to the pristine BPM (bottom right). [Reprinted with permission from 102]

1.3.3 BPM based fuel cells and redox flow batteries

H2-O2 fuel cells operating with BPMs under both reverse and forward bias have been proposed by the Kohl group. Reverse and forward bias correspond to a high/low pH for the anode/cathode, and high/low pH for the cathode/anode, respectively (Fig. 1.9a).106–108 The forward-biased BPM was found to be a better configuration for fuel cells because the protons and hydroxide ions recombine to form water that self-humidifies the device. This configuration allows the hydrogen oxidation reaction (HOR)/oxygen reduction reaction (ORR) to occur in the preferred acidic/basic environments, greatly expanding the catalyst candidate pool. As in the water electrolyzer, the use of a BPM, in either forward or reverse bias, doesn’t change the overall thermodynamic cell potential in the H2-O2 fuel cell, because the potential difference across the BPM (830 mV for ΔpH = 14) is exactly balanced out by the Nernstian shift of the two half reactions, i.e. both the hydrogen and
oxygen electrodes have a 59 mV/pH slope between pH 0 and 14 in their Pourbaix diagrams. This scenario changes for redox reactions that exhibit slopes deviating from 59 mV/pH within any pH range between 0-14. An increase/decrease in the potential difference between the two electrodes occurs if the slopes are smaller/larger than 59 mV/pH. For example, the formal potential of the sulfonated propylviologen (SPV) (~0.58 V, vs Ag/AgCl) is unaffected by the electrolyte pH between pH 0 and 14 (i.e. 0 mV/pH slope). Coupling SPV in acid and ferrocyanide in base, separated by a BPM, creates a redox flow battery with an open circuit voltage (OCV) of ~1.6 V, an increase of ~0.7 V compared to the same battery operating with both molecules under alkaline conditions (Fig. 1.9). The Pourbaix diagram of 1,7-disulfonate anthraquinone (DSAQ), on the other hand, shows slopes of ~59 mV/pH, ~30 mV/pH and ~0 mV/pH within the pH ranges of ~0-7, ~7-10 and ~10-14, resulting in an OCV increase of ~350 mV, close to the theoretical value (323 mV = 29 mV/pH*3+59 mV/pH*4).

The kinetic behaviors of the acid-base H₂-O₂ fuel cells and discharging redox flow batteries depend critically on the properties of BPMs under forward bias. The net reaction at the AEL/CEL interface in a forward-biased BPM is the strong acid - strong base neutralization reaction, which is
among the fastest uncatalyzed reactions (rate constant $\sim 1.3 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$), but the kinetics of this reaction have been proven to limit the performance of both fuel cells and redox flow batteries.$^{107,109}$

A bimolecular $\text{H}^+$ and $\text{OH}^-$ recombination mechanism requires an appreciable concentration of $\text{H}^+$ and $\text{OH}^-$ within the same spatial region. This requirement means that the neutralization reaction occurs at a significant rate only in the narrow region (a few nanometers wide) at the AEL/CEL interface, where the distributions of $\text{H}^+$ and $\text{OH}^-$ overlap. Further, this reaction must proceed quasi-reversibly (i.e., the water autodissociation reaction must also occur at an adequate rate) in order for the potential of the cell to approach its open-circuit value. The neutralization reaction is rate-limited by the concentration of minority species ($\text{H}^+/\text{OH}^-$ for the AEL/CEL, respectively). Lowering the ion exchange capacity (IEC) of the interfacial ionomers has been predicted to increase the minority ion concentration in numerical modeling, but that modification may complicate other processes such as the ionic conduction and water retention.$^{107,108}$

Considering the extremely narrow reaction zone, increasing the rate constant of the neutralization reaction (and also the rate of the autodissociation reaction, which is connected by the equilibrium constant $K_w$) is critical to the efficient operation of the cell. Making direct analogy to the electronic p-n junction theory, Grew et al proposed a trap-assisted acid-base recombination process in the forward-biased BPM for fuel cells.$^{107}$ The model predicted a four to five orders of magnitude increase in the current density compared to a bimolecular mechanism (Fig. 1.9b).$^{107}$ The traps were rationalized to be associated with the fixed charge of the membranes (or defects) within the space charge region that provide local Coulombic interactions. This concept is reminiscent of the mobile ion pairs in the Onsager’s weak electrolyte theorem.$^{111}$ Alternatively, we experimentally observed a dramatic increase for the acid-base neutralization rate in the BPM by equipping the interface with a graphene oxide (GO) catalyst.$^{109}$ This effect was confirmed by comparing the experimental data to numerical models, in which the observed potential-current density curves could be fully reproduced only if both the water dissociation and acid-base neutralization reactions were enhanced by interfacial catalysis (Fig. 1.9c). Understanding the mechanism at the microscopic level would further inform the design of BPMs under forward bias.
Specific requirements on BPMs may apply to both fuel cells and redox flow batteries. For example, crossover of ions and redox species is a major concern for redox flow batteries, while the availability of water content might be essential for H₂-O₂ fuel cells in which water is supplied in vapor form.

1.4 Mechanism of the water dissociation reaction in BPMs

Compared with acid-base neutralization, the water dissociation reaction has been subjected to more intensive studies. The autoionization of a liquid water molecule to a H⁺/OH⁻ pair is a slow process with the dissociation rate constant of ~2.5×10⁻⁵ s⁻¹, translating to a current density of about 10⁻⁵ mA/cm². Experimentally, however, BPMs can sustain current densities up to ~ 1 A/cm². The dissociation reaction can be enhanced by the interfacial electric field and by catalysis in order to achieve these high current densities.

![Fig. 1.10. The mechanism of water dissociation in BPMs and the modeling. (a) Correlation between the water dissociation overpotential and the PZC of the metal oxide catalysts in the BPMs. [Reprinted with permission from 84] (b) Water dissociation reaction resistance (left) and the depletion layer thickness (right) as a function of the cross-membrane potentials. [Reprinted with permission from 124] (c) Numerical modeling of the I-V curves with pH 7-7 (left) and pH 0-14 (right). [Reprinted with permission from 125] (d) The distribution of H⁺/OH⁻, electric field, and charge density at the BPM junction from a comprehensive numerical model. The effect of the interfacial catalysis is incorporated explicitly using the protonation-deprotonation equilibria of the catalysts. [Reprinted with permission from 121]

Accessing the transient species that are involved in water dissociation has been a challenge in experiments, but it is well suited for computational methods that employ advanced sampling techniques. Molecular dynamics simulations have suggested the major pathways for the
water autoionization process. Local solvent fluctuation leads to a transient electric field that initiates the separation of a pair of H\(^+\) and OH\(^-\) ions next to each other, followed by ion transfer along a hydrogen-bonded water wire in either a stepwise or concerted fashion.\(^{114,117}\) A stable H\(^+\)/OH\(^-\) pair will be produced if a recombination event doesn’t occur. This can happen if the ions have been transported far enough, a process assisted by the solvent electric field or by configurational changes of the water wire connecting the ion pair.\(^{114,117}\) This picture provides the molecular basis for the effect of electric field, which participates in both the initiation and ion transfer process, on the water dissociation reaction.\(^{115,118}\) Regardless of the microscopic mechanism, the electric field perturbs the distribution between the ion pairs and the neutral species, as described by the Onsager’s weak electrolyte theorem that accounts for the enhanced dissociation rate constant of weak electrolytes in electric fields.\(^{111,119}\) The model assumes a Coulombic potential of point-charge type between the ion pairs due to the low concentration of free ions, a situation that is likely to be encountered in the junction region of BPMs. The recombination rate constant, on the other hand, is presumed to be unaffected by the electric field, the validity of which needs to be assessed by tracing the electric field fluctuation in the recombination event.

The effect of the electric field alone is not sufficient to explain the dramatic performance increase of BPMs equipped with interfacial catalysts. The protonation-deprotonation mechanism has been widely used to explain the catalytic water dissociation process.\(^{120–123}\) According to the theory, the rate constants of the protonation and deprotonation scale oppositely with the pKa of the active sites, suggesting an optimal pKa of near 7 for the best catalysts.\(^{120,121}\) A recent study by Oener et al. attempted to correlate the water dissociation activity and the pH of zero charge (PZC) of a series of metal oxides in BPMs. They found that creating catalyst layers with graded PZC’s gave superior performance to BPMs that used a single PZC.\(^84\) The correlation between the PZC and the water dissociation overpotential was observed not to be completely monotonic (Fig. 1.10a), which could be related to the stability, surface area, and distributed pKas of the metal oxides. While the mechanism of the catalyzed water dissociation could be different from that of the homogenous autoionization in free solutions, the microscopic picture discussed above for liquid water raises the
question of whether the pKa alone is sufficient to account for all the factors that affect the initiation and proton transfer step. The relationship between these two mechanisms, the electric field and catalysis effect, is also of interest. The depletion of ions in the junction region gives rise to interfacial electric fields that can be diminished by the catalytic regeneration of H⁺/OH⁻ ion. This points to the counterbalanced role of electric field and interfacial catalysis in enhancing the water dissociation reaction, as found in electrochemical impedance spectroscopy (EIS) studies of BPMs with controlled interfacial catalyst layers (Fig. 1.10b). A statistical model predicting an exponential dependence of the dissociation rate constant on the electric field assumes that the catalyst donates (or accepts) protons and that the electric field aligns the water dipoles to assist the proton transfer, implying the sequential operation of the two mechanisms.

Coupling the water dissociation/acid-base neutralization reactions with the transport of ionic species can be done through numerical modeling. By analogy to the modeling of transport in monopolar membranes, the Poisson and Nernst-Planck (PNP) equations can be combined to describe the electric field and transport phenomena. The electric field can be included using either the exponential form or Onsager’s derivations, while the catalytic effect is accounted for by increasing the rates constants within the reaction zone by a certain factor that is either extrapolated from experiments (Fig. 1.10c), or deduced from material properties such as the pKa (Fig. 1.10d). These models can reproduce the overall trends of the polarization curves (Fig. 1.10c) and reveal useful information that details the distributions of ions, space charge density and potential across the BPM junction (Fig. 1.10d).

1.5 Conclusions and perspective

The growth in renewable energy capacity from solar, wind, and other carbon-neutral sources is limited by the lack of adequate solutions for short- and long-term energy storage. Carbon-based liquid fuels are ideal for long-term energy storage because of their high energy density and the well-developed infrastructure for their transport, storage, and use. Electrolysis provides a key link
between electrical energy and liquid fuel, either by direct electrosynthesis from CO\textsubscript{2} and water, or through the generation of feedstocks for fuel synthesis, such as hydrogen and syngas. The latter electrolytic processes, which involve two-electron, two-proton cathode reactions, are already well developed from the scientific and technological point of view. Water electrolysis using alkaline electrolyzers has been commercialized in parts of the world where hydroelectric power is cheap and abundant. Technology demonstrations for the production of CO and syngas have been successful with both low temperature polymer electrolyte-based systems and high temperature solid state electrolyzers.

The direct electrolytic production of liquid fuels such as ethanol or ammonia requires us to master electrocatalytic reaction cascades beyond simple one-electron intermediates. While the reduction of CO\textsubscript{2} to C-C coupled products on copper-containing catalysts has been known since the 1980’s, the detailed mechanism has only recently been understood by combining electronic structure theory with experimental electrochemical and spectroscopic experiments. Encouraging progress has been made in the search for catalysts and electrolytes that enable the selective production of C\textsubscript{2} products such as ethylene and ethanol, but high cathode and anode overpotentials limit the efficiency of these processes. In addition to the study of catalysis, strategies for improving the transport of reactants, products, and ions are also important for the development of efficient electrolyzers for CO\textsubscript{2} and N\textsubscript{2}.

Our understanding of well-developed technologies such as water electrolysis provides a useful guide for other problems in electrochemical energy conversion. The principles of catalysis in multi-electron reactions, for example linear scaling relations, are transferable from one reaction to another. Lessons at the system level are also common to different electrolytic systems. For example, proton management using BPMs addresses system-level issues for both water and CO\textsubscript{2} electrolysis. For BPM based fuel cells and redox flow batteries, water management and molecular crossover needs further investigation. The lowering of electrode overpotentials at elevated temperatures is effective for water and CO\textsubscript{2} electrolysis to produce H\textsubscript{2} and CO, and might in the future be applied to reactions that directly produce liquid fuel. Natural enzymatic systems also
provide inspiration to develop new strategies for pre-concentrating and delivering reactants, and also controlling the environment of catalytically active sites to improve both the selectivity and efficiency of electrocatalysts for the production of liquid fuels.

1.6 References


(55) Jiang, W.; Wei, B.; Lv, Z.; Wang, Z. H.; Zhu, L.; Li, Y. Q. Performance and Stability of Co-Synthesized Sm$_{0.5}$Sr$_{0.5}$CoO$_3$–Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ Composite Oxygen Electrode for Solid Oxide Electrolysis Cells. *Int. J. Hydrog. Energy* **2015**, *40*, 561–567.


(57) Yang, X.; Irvine, J. T. S. (La$_{0.75}$Sr$_{0.25}$)$_{0.95}$Mn$_{0.5}$Cr$_{0.5}$O$_3$ as the Cathode of Solid Oxide Electrolysis Cells for High Temperature Hydrogen Production from Steam. *J. Mater. Chem.* **2008**, *18*, 2349–2354.


(62) Fabbri, E.; D’Epifanio, A.; Di Bartolomeo, E.; Licoccia, S.; Traversa, E. Tailoring the Chemical Stability of Ba(Ce$_{0.8-x}$Zr$_x$)$_{0.2}$O$_{3-δ}$ Protonic Conductors for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs). *Solid State Ion.* **2008**, *179*, 558–564.


(65) He, F.; Song, D.; Peng, R.; Meng, G.; Yang, S. Electrode Performance and Analysis of Reversible Solid Oxide Fuel Cells with Proton Conducting Electrolyte of BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.2}$O$_3$–δ. J. Power Sources 2010, 195, 3359–3364.


(69) Vasileiou, E.; Kyriakou, V.; Garagounis, I.; Vourros, A.; Manerbin, A.; Coors, W. G.; Stoukides, M. Electrochemical Enhancement of Ammonia Synthesis in a BaZr$_{0.7}$Ce$_{0.2}$Y$_{0.1}$O$_{2.9}$ Solid Electrolyte Cell. Solid State Ion. 2016, 288, 357–362.


615.
(112) Strathmann, H.; Rapp, H.-J.; Bauer, B.; Bell, C. M. Theoretical and Practical Aspects of
(113) Shen, C.; Wycisk, R.; N. Pintauro, P. High Performance Electrospun Bipolar Membrane with
(115) Saitta, A. M.; Saija, F.; Giaquinta, P. V. Ab Initio Molecular Dynamics Study of Dissociation
(116) Moqadam, M.; Lervik, A.; Riccardi, E.; Venkatraman, V.; Alsberg, B. K.; van Erp, T. S. Local
E4576.
(117) Hassanali, A.; Prakash, M. K.; Eshet, H.; Parrinello, M. On the Recombination of Hydronium
(118) Mafé, S.; Ramírez, P.; Alcaraz, A. Electric Field-Assisted Proton Transfer and Water
Dissociation at the Junction of a Fixed-Charge Bipolar Membrane. Chem. Phys. Lett. 1998,
294, 406–412.
(119) Onsager, L.; Fuoss, R. M. Irreversible Processes in Electrolytes. Diffusion, Conductance
and Viscous Flow in Arbitrary Mixtures of Strong Electrolytes. J. Phys. Chem. 1932, 36,
2689–2778.
(120) Strathmann, H.; Krol, J. J.; Rapp, H.-J.; Eigenberger, G. Limiting Current Density and Water
(121) Mareev, S. A.; Evdochenko, E.; Wessling, M.; Kozaderova, O. A.; Niftaliev, S. I.;
Pismenskaya, N. D.; Nikonenko, V. V. A Comprehensive Mathematical Model of Water


Chapter 2

The balance of electric field and interfacial catalysis in promoting water dissociation in bipolar membranes

Abstract

The lamination of a cation exchange layer (CEL) and an anion exchange layer (AEL) to form a hybrid bipolar membrane (BPM) can have several unique advantages over conventional monopolar ion exchange membranes in (photo-) electrolysis. Upon application of a reverse bias, the ordinarily slow water dissociation reaction at the AEL/CEL junction of the BPM is dramatically accelerated by the large electric field at the interface and by the presence of catalyst in the junction. Using electrochemical impedance spectroscopy (EIS), we have found a counterbalanced role of the electric field and the junction catalyst in accelerating water dissociation in a BPM. Experimental BPMs were prepared from a crosslinked AEL and a Nafion CEL, with a graphite oxide (GO) catalyst deposited at the junction using layer-by-layer (LBL) assembly. BPMs with an interfacial catalyst layer were found to have smaller electric fields at the interface compared to samples with no added catalyst. A comprehensive numerical simulation model showed that the damping of the electric field in BPMs with a catalyst layer is a result of a higher water dissociation product (H+/OH-) flux, which neutralizes the net charge density of the CEL and AEL. This conclusion is further substantiated by EIS studies of a high-performance 3D junction BPM that shows a low electric field due to the facile catalytic generation and transport of H+ and OH-. Numerical modeling of these effects in the BPM provides a prescription for designing membranes that function at lower overpotential. The potential drop across the synthetic BPM was lower than that of a commercial BPM by more than 200 mV at
> 100 mA/cm$^2$ reverse bias current density, with the two membranes having similar long-term stability.

2.1 Introduction

Much of current (photo-)electrolysis research focuses on developing efficient and cost-effective catalysts to lower the over-potential for water splitting\textsuperscript{1-5} and CO\textsubscript{2} reduction.\textsuperscript{6-15} Relatively little attention has been paid to mass transfer management of reactants, ions and products, the understanding of which is essential for a robust and stable electrolysis system.\textsuperscript{16-18} Proton transport, in particular, is a vital process in an electrolysis cell because cathodic electron transfer is accompanied by the consumption of protons, for example in the hydrogen evolution reaction (HER) and in CO\textsubscript{2} reduction.\textsuperscript{7,19} Membrane separators are typically incorporated into the electrolysis system to allow for selective passage of electrolyte ions and the separation of the cathodic and anodic products.\textsuperscript{17,20} Mass transfer in membrane separators can induce additional resistance and can result in a transmembrane pH gradient, compromising the energy efficiency of the system.\textsuperscript{21-23} Although commercial electrolyzers normally operate under strongly acidic or basic conditions to minimize series resistance,\textsuperscript{24} pH neutral electrolytes are advantageous for some oxygen evolution reaction (OER) catalysts that contain only earth-abundant elements.\textsuperscript{16,20,21} Previous studies of electrolytic cells with buffer-based electrolytes and commercial anion- and cation exchange membranes (A/CEM) have suggested that a > 300 mV pH gradient develops across conventional A/CEM separators under DC polarization, which is only partially mitigated by back diffusion if electroneutral buffers are used.\textsuperscript{20}

Bipolar membranes (BPM) have been proposed as an alternative to the conventional A/CEM separators and have been shown to circumvent many system-level challenges associated with coupling earth-abundant catalyst materials and membrane separators in electrolytic cells.\textsuperscript{25-36} BPMs composed of two oppositely charged ion exchange layers are beneficial in several respects. First, incorporating a BPM into the cell allows for the separation of acidic and basic solutions in the cathode and anode compartments, respectively, thus providing optimal pH conditions for HER and oxygen evolution reaction (OER) catalysts.\textsuperscript{2,3} Second, under reverse bias, i.e., with the cation exchange layer (CEL) facing the cathode, the water dissociation reaction that occurs in the
membrane replenishes the cathode and anode with H\(^+\) and OH\(^-\), respectively, minimizing electrolyte adjustments.\(^{25,32}\) Finally, the pH gradient at the BPM/electrolyte interface is mitigated due to the predominance of H\(^+\)/OH\(^-\) species inside the CEL/AEL, which match the principal charge carriers in the electrolyte. As a result, most of the cross-membrane potential drop occurs at the CEL/AEL interface, justifying the focus on tailoring the interfacial structure of the BPM in much of the current research on this problem.\(^{37-40}\) A BPM with a 3D interfacial junction has recently been shown to enable water electrolysis at a current density of 1 A/cm\(^2\) in 0.5 M Na\(_2\)SO\(_4\) solution at membrane potential drop of 2 V.\(^{39}\) The incorporation of different water dissociation catalysts into the interfacial layer has also been intensively studied.\(^{37,38,40,41}\) At the interface, water molecules dissociate into H\(^+\) and OH\(^-\) ions, and that reaction is critical to the overall performance of the BPM.

It is widely accepted that the large electric field created under reverse bias and the catalyst in the interfacial region of the BPM dramatically enhance the rate of water dissociation at the AEL/CEL junction, but the relative importance and correlation of these two factors remains unknown. Two effects, namely the second Wien effect, in which an electric field increases the water dissociation rate by orders of magnitude relative to its value in a field-free solution, and a catalytic effect involving proton transfer to a weak base, have been investigated in various models.\(^{42-48}\) By making an analogy to a p-n junction, an abrupt junction model considers the electric field according to absolute rate theory with the field increasing the generation rate in the forward direction.\(^{42,46}\) Based on Onsanger’s weak electrolyte theorem and assuming that water can be viewed as a weak electrolyte, the forward dissociation rate constant is simplified to be an electric field-dependent variable.\(^{49}\) Even though the abrupt junction model correctly predicts the DC polarization behavior of the BPM and the existence of one semicircle in the complex plane of impedance spectra at high reverse bias current,\(^{42,43,50-53}\) it has been speculated that an unrealistically high electric field would be required if the field-enhanced effect were the sole mechanism for water autodissociation.\(^{46}\) The treatment of catalyst’s role follows the reasoning of Simons, where the catalyst participates in the water dissociation reaction via a protonation-deprotonation mechanism.\(^{43,44,46,47}\)
In principle, a model that couples ionic transport, electrostatics and the field-dependent water dissociation reaction should represent the BPM system realistically and shed light on the correlation between the electric field and the catalyst in accelerating the water dissociation reaction. Unfortunately, unlike its monopolar ion exchange membrane counterpart, an analytical solution to equations of such complexity in the BPM system is not available at this time. Attempts at numerical simulations of the BPM have shown only certain aspects of BPM behavior because of the lack of one or more of the factors mentioned above. More importantly, an experimental investigation of the roles of the electric field and junction catalyst has been challenging due to the coexisting nature of the two and the sensitivity of the water dissociation reaction to the structure of the interfacial layer.

In the present study, we explore the correlation between the electric field and the junction catalyst in promoting the water dissociation reaction in BPMs. To systematically and controllably adjust the interfacial structure, we prepared a lightly crosslinked AEL with a flat surface and modified it with graphite oxide (GO) as the catalyst using layer-by-layer (LBL) assembly, followed by deposition of a Nafion thin film from a solution in dimethylformamide (DMF) as the CEL. BPMs with one layer and four layers of GO as the junction catalyst were tested by using electrochemical impedance spectroscopy (EIS) and compared against a BPM without a GO catalyst. Interestingly, we observed a counterbalanced role of the electric field and the catalyst in promoting water dissociation. Incorporating the catalyst decreases the electric field intensity across the BPM junction. A numerical simulation model taking into account the ionic transport, electrostatics and electric field-dependent dissociation reaction confirmed our experimental findings. Furthermore, EIS measurements on a BPM with a 3D junction substantiate the conclusions from the numerical model. Finally, the as-prepared BPM shows a significantly lower cross-membrane potential drop than a commercial BPM at > 100 mA/cm² current density and has comparable stability over a 10 hour test.
2.2 Results and discussions

2.2.1 BPM and self-assembly of the graphene oxide catalyst

BPMs were prepared from a lightly crosslinked AEM and Nafion dissolved in DMF and deposited at 120 °C as the CEL. The relatively high processing temperature and the DMF solvent alleviate the rod-like aggregation that occurs in lower temperature alcohol/water Nafion dispersions. GO layers were deposited as the junction catalyst with poly-dialkyldimethylammonium (PDDA) as the polycation using LBL assembly to allow for precise control over the interfacial structure (Fig. 2.1). From cross-sectional SEM images of the BPM, an AEL of about 100 μm and CEL of about 40 μm thickness can be clearly distinguished, whereas the GO interfacial layer is too thin to be imaged by this technique.

![Fig. 2.1. Schematic of the preparation of BPMs by LBL assembly, and a cross-sectional scanning electron micrograph (SEM) image of the 4GO BPM. The green and red lines span the CEL and AEL, respectively.](image-url)
2.2.2 The balance between electric field and catalysis

BPMs with one and four layers of GO were prepared by LBL assembly. EIS measurements were performed while systematically varying the reverse bias on the 1GO and 4GO BPMs and compared with results from a BPM fabricated without catalyst as a control, 0GO BPM. EIS measurements were carried out in a four-electrode cell (see Fig. A.1) in which current was applied through outer Pt working and counter electrodes and the potential was measured between Ag/AgCl (3M NaCl) reference electrodes (RE) positioned close to the faces of the BPM via Haber-Luggin capillaries. This arrangement minimized the effects of solution resistance and eliminated the overpotentials for the HER and OER, as well as the electrode double-layer capacitance at the Pt working (WE) and counter electrodes (CE) in the EIS measurements and the J-E curves. An extra CEM was also incorporated between the WE and one of the Res to prevent interference from electrolysis products (Fig. A.1). An AEM was placed between the CE and the other Res for the same reason.

A DC current was initially applied via the working and counter electrodes to reach steady-state conditions, and EIS data were then acquired by applying a small amplitude AC signal. The typical Nyquist plots exhibit two semicircles in which the lower frequency semicircle contracts with increasing reverse bias (Fig. A.2, A.3 and A.4). An equivalent circuit developed from the neutral layer model was used to fit all the experimental spectra as we believe that (1) the incorporation of the GO catalyst layer into the BPM can be better described by a model that treats the BPM interfacial layer explicitly and (2) an abrupt junction is unlikely to exist in BPMs prepared by the method shown in Fig. 2.1,42,44,53 The overall impedance was then modeled by the series connection of a Gerischer element, an Ohmic resistor representing the membrane and bulk electrolyte, and a block consisting of a resistor and a capacitor (Fig. A.2). A detailed discussion of what each element represents physically is found in the ESI†. The quality of the EIS fitting to the equivalent circuit was confirmed by noting the parameter $\chi^2$, showing a value of $\sim 0.01$ and $\sim 0.003$ for the 4GO and 0GO BPM (Fig. A.3 and A.4), respectively.
Fig. 2.2. (a) J-E curves of BPMs prepared by the LBL technique, in 0.5 M KNO$_3$ at low reverse bias, which is also the bias range used in the EIS study. 0GO/1GO/4GO BPM correspond to BPMs with zero/one/four layers of GO catalyst; (b) Water dissociation rate constant $k_d$ measured from the Gerischer element; (c) Water dissociation reaction resistance $R_w$; inset shows an enlarged view at lower voltage; (d) Depletion region thickness as a function of reverse bias voltage. Error bars in (a) and (c) are shown for cases where they are larger than the plot symbols.

Fig. 2.2a compares J-E curves of the BPMs under reverse bias ranging from 0.6 V to 1.5 V. All BPMs had similar co-ion leakage current density, which is below 0.5 mA/cm$^2$, as indicated by the flat portion of the J-E curve between 0.6 and 0.7 V. Above 0.75 V the current increases significantly as the dominant current-carrying ions in the CEL and AEL become H$^+$ and OH$^-$, respectively. The dissociation of water, reaction (2.1), has a formal potential (at unit activity of H$^+$ and OH$^-$) of 0.83 V at room temperature, close to observed onset bias. Beyond the onset potential, the 4GO BPM has the lowest overpotential at a given current density, followed by the 1GO BPM, which has much higher current density than the 0GO BPM within the studied reverse bias range.

$$\text{H}_2\text{O (l)} = \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$$  \hspace{1cm} (2.1)
The water dissociation rate constants, $k_d$, of all BPMs increase with increasing bias (Fig. 2.2b). This suggests that water dissociation is enhanced by the electric field, irrespective of the presence of a catalyst. To be specific, the 0GO and 1GO BPMs show appreciable increases in $k_d$ at voltages between 0.8 to 0.9 V (Fig. 2.2b). In contrast, $k_d$ for the 4GO BPM is relatively large at low reverse bias and increases with increasing voltage. Our attempts to extract accurate values of $k_d$ at reverse bias potentials > 1.1 V were not successful because the lower frequency semicircles in the EIS spectra become very small and noisy (Fig. A.3 and A.4).

Fig. 2.2c shows the reaction resistance, $R_w$, as extracted from the electric double layer (EDL) in the EIS equivalent circuit (Fig. A.2). The BPMs fabricated from the AEL plus Nafion share the same trend in $R_w$, i.e., that it decreases as voltage increases and gradually converges to a plateau (Fig. 2.2c). The flat portion of the curve corresponds to a quasi-equilibrium region for the water dissociation reaction, where the forward dissociation and backward neutralization reaction rates cancel each other and are equal to the exchange current. Before reaching the quasi-equilibrium region, the dissociation reaction is largely suppressed because of the fast backward acid-base neutralization reaction. An increase in reverse bias helps promote the dissociation reaction, thus decreasing $R_w$. The 4GO BPM exhibited the lowest $R_w$ within the studied voltage range, compared to the 0GO and 1GO BPMs, indicating that the forward dissociation reaction is promoted more efficiently with more added catalyst (Fig. 2.2c). The dependence of $R_w$ on voltage is much weaker for the 1GO/4GO BPMs, suggesting a lower electric field in BPMs that contain catalyst layers. It is noteworthy that the different reaction resistances, $R_w$, between these synthetic BPMs cannot be simply attributed to the co-ion leakage effect, since all BPMs had similar leakage current density (Fig. 2.2a), but very different values of $R_w$.

In the neutral layer model, a reaction layer in which the water dissociation reaction becomes prevalent and produces nearly the total amount of $H^+$ and $OH^-$ required for a given current density is sandwiched by an EDL formed from the unbalanced fixed charge density on the CEL and AEL sides. This unbalanced charge is a consequence of the depletion of ions under reverse bias.
conditions, resulting in the formation of a depletion region. The depletion layer thickness can be calculated from equation (2.2):

\[ d = \frac{\varepsilon_0 \varepsilon_r A}{C} \]  

(2.2)

where \( \varepsilon_0 \) and \( \varepsilon_r \) are respectively the vacuum electric permittivity and the dielectric constant in the reaction layer (80 was taken for pure water), and \( C \) and \( A \) are the capacitance and active membrane area (1 cm\(^2\)). The capacitance \( C \) was calculated based on equations A.7 and A.8. The values of the capacitance and the depletion layer thickness as a function of reverse current are recorded in Table A.1, A.2 and A.3 for 4GO, 1GO and 0GO BPM, respectively, along with other parameters from the EIS fitting. The validity of calculating the depletion layer thickness from EIS fitting scheme is further confirmed by repeating the modeling process of the EIS spectra for the 0GO BPM with a fixed (average) depletion thickness (other parameters were allowed to float freely). The resulting \( \chi^2 \) value of 0.03-0.6 was much larger than those from the fitting where depletion layer thickness was optimized, 0.001-0.003 (red v.s. green lines, Fig. A.4).

With the method outlined above, we obtained a depletion layer thickness, \( d \), on the scale of hundreds of nanometers for the 0GO BPM and tens of nanometers for the 1GO and 4GO BPMs (Fig. 2.2d). As shown in Fig. 2.2d, the depletion thickness \( d \) is much smaller for the 1GO and 4GO BPMs than it is for the 0GO BPM. The key findings from this analysis are the thinner depletion region and weaker dependence on electric potential with increasing catalyst loading. This indicates that there is a smaller electric field acting on the reaction layer in BPMs that contain water dissociation catalysts, which will be evident from the results of the numerical modeling below.

2.2.3 Insights from the numerical model

To gain further insight into the experimental data, we constructed a numerical model that takes into account ionic transport, electrostatics, and the rates of the water dissociation/recombination reactions.\(^{45,61,62}\) In order to fully address the characteristics of BPMs, it is necessary to identify the mechanisms that participate in the ionic transport of both the electrolyte and water dissociation
products under bias as well as the water dissociation/recombination reaction. A large body of previous work devoted to the theoretical understanding of various phenomena in ion exchange membranes is based on the Nernst-Planck-Poisson equations (NPP), where the Nernst-Planck equation (equation A.9) describes ionic transport and maintains species continuity and the Poisson equation describes the fixed charge and the ion permselectivity (equation A.10). Incorporating the water dissociation reaction is achieved by adding a flux term in the transport equation for H⁺ and OH⁻, which also affects the whole system electrostatically by modifying the bulk charge density. The reaction rate can be obtained from a kinetic model for the dissociation and recombination of H⁺ and OH⁻, with a forward rate constant that depends on the electric field and a field-independent recombination rate constant (equation A.11 and A.12). Two diffusion boundary layers were added at the two faces of the BPM in order to better match the experimental conditions, and this turns out to be important in modeling the BPM under higher reverse bias.

The analysis of the model begins with predictions of the J-E curve and potential distribution profile at equilibrium. Fig. 2.3a shows the current density at a given reverse bias and its comparison with experiment. The agreement of the overall current density between experiment and simulation is satisfactory at low reverse bias, whereas the deviation increases under higher bias. This deviation could be caused by the static boundary conditions employed in the model, which result in unrealistic concentration profiles, as will be discussed below. The overall current density is decomposed into the contributions from water dissociation products H⁺/OH⁻ and from supporting electrolyte K⁺/NO₃⁻. As expected, the H⁺/OH⁻ flux surpasses that of K⁺/NO₃⁻ only after a certain reverse bias threshold, 2V (Fig. 2.3a), after which the water dissociation reaction is enhanced dramatically by the electric field according to the second Wien effect. It has been shown that hysteresis develops in the J-E curve of BPMs that are subjected to a time-periodic reverse voltage due to the incomplete depletion of mobile ions at the junction, and the magnitude of the hysteresis depends on the scan rate. The absence of hysteresis in the J-E curve (Fig. 2.3a), is consistent with these observations as the current model simulates the steady-state response. Under a reverse bias less than 5V, more than 90% of the potential drop occurs across the BPM junction (Fig. 2.3b).
At larger reverse bias of 5V, there is an appreciable potential drop in the region of electrolyte close to the boundary (Fig. 2.3b). We attribute this potential drop to the low H⁺/OH⁻ concentration at the two boundaries, which limits the achievable H⁺/OH⁻ flux under higher reverse bias (Fig. 2.3c). This also gives rise to an underestimate of the H⁺/OH⁻ contribution to the overall current density as shown in Fig. 2.3a. Improvement of the model may be possible by using dynamic boundary conditions.

Fig. 2.3. Numerical simulations of a BPM with catalyst. (a) Simulated J-E curve of a BPM with catalyst, and comparison with experimental results. The experimental J-V curve shown was obtained in 0.1 mM KNO₃ in order to match the conditions of the simulation; also shown are the current contributions from water dissociation products and from the electrolyte, KNO₃; (b) Potential distributions from the simulation; (c) Concentration profiles of the water dissociation products H⁺ and OH⁻ in the BPM; (d) Electrolyte KNO₃ ion distributions. Insets in (b) (c) and (d) are enlarged version of the AEL/CEL junction region.

Fig. 2.3c and 2.3d show the concentration profiles of H⁺/OH⁻ and K⁺/NO₃⁻ at reverse biases of 0.3V, 2.5 V and 5 V. These concentration profiles were found to be representative of the overall concentration distributions as the reverse bias varies (Fig. A.6). At lower reverse bias, the
supporting K⁺/NO₃⁻ ions are the major charge carriers inside both the BPM and diffusion layers. In contrast, water dissociation products H⁺ and OH⁻ become the dominant ionic species under higher reverse bias, expelling K⁺ and NO₃⁻ from the bulk of the membrane and accumulating in the diffusion boundary layers. The insets in Fig. 2.3c and d illustrate the formation of a depletion region at the AEL/CEL interface, the thickness of which increases with increasing reverse bias.

In order to assess the effectiveness of the catalyst, results from the model without the catalytic effect (Fig. A.7), were compared with the BPM with catalyst, which enhances the dissociation rate constant by two orders of magnitude (Fig. 2.3). Lower current density is observed at a given reverse bias compared with the BPM with catalyst (Fig. A.7a). As expected, the H⁺/OH⁻ flux is also smaller than that of the BPM with catalyst due to the lower reaction rate constant. The onset reverse bias at which the H⁺/OH⁻ flux start to dominate over that of K⁺/NO₃⁻ is lower for the BPM with catalyst, i.e. 2 V vs. 4.5 V. The potential and concentration distribution profiles for BPMs with and without catalyst resemble each other. Furthermore, to check the consistency of the model, results for the BPM without catalyst were subjected to forward bias conditions, as shown in Fig. A.8. Current contributed from H⁺/OH⁻ flux is marginally small for the studied voltage range, and the BPM shows typical Ohmic resistance (Fig. A.8a). The predominant charge carriers in the BPM and diffusion boundary layers are those from the supporting electrolyte at all voltages (Fig. A.8c and A.8d). One striking difference from BPMs under reverse bias is the absence of the depletion region, which is replaced by a smooth transition of one type of charge carrier to another. These results are in good agreement with recent theoretical reports on BPMs in fuel cell applications where forward bias and the backward recombination reaction are more relevant. Interestingly, most of the potential drop under forward bias conditions happens across the diffusion layer (Fig. A.8b), rather than at the AEL/CEL junction, due to the high concentration of ions present.

Having established the validity of the numerical model, we extracted the electric field intensity at the AEL/CEL interface and calculated the depletion region thickness based on the method outlined in Fig. A.9. Fig. 2.4 compares the electric field intensity and depletion layer thickness for BPMs with and without catalyst. Consistent with the experimental observations (Fig. 2.2d), a thinner
depletion region is found for the BPM with catalyst (Fig. 2.4d), leading to a smaller electric field across the AEL/CEL interface (Fig. 2.4c). The difference can be understood as a result of the counterbalanced roles of electric field and catalyst in promoting water dissociation (Fig. 2.4a and 2.4b). Under reverse bias, mobile ions in the BPM are driven out so that a depletion region forms due to the unbalanced fixed charge on the CEL and AEL layers. The resulting electric field enhances water dissociation and produces overwhelmingly a flux of $\text{H}^+$ and $\text{OH}^-$ ions towards the CEL and AEL of the BPM, respectively. As such, the unbalanced fixed charge density is partially neutralized by the respective counter ions, i.e. $\text{H}^+$ for the CEL and $\text{OH}^-$ for the AEL, hence shrinking the depletion region. Since the $\text{H}^+$/OH$^-$ flux for the BPM with catalyst is much larger than that without catalyst (Fig. A.7a), a larger portion of the fixed charge is rebalanced (Fig. 2.4b), causing the electric field across the reaction layer to decrease.

Fig. 2.4. Schematic drawings of (a) the depletion region for BPMs with and without catalyst and (b) an enlarged view of the junction region, showing the higher $\text{H}^+$/OH$^-$ flux in the BPM with catalyst. The black arrows indicate the higher electric field in the BPM without catalyst; the red/blue colors indicate the positive/negative fixed charges in AEL/CEL, respectively. Simulated (c) electric field intensity at the AEL/CEL interface and (d) depletion region thickness for BPMs with and without catalyst.
2.2.4 High H⁺/OH⁻ flux achieved through a 3D junction

Pintauro et al. recently reported a novel type of BPM with a diffuse 3D junction by combining single and dual polymer fiber electrospinning. The BPM has been shown to sustain at 1 A/cm² reverse-bias current density with less than 2 V of transmembrane potential drop in 0.5 M Na₂SO₄. The low membrane impedance has been attributed to the 3D extended junction region for the water dissociation reaction. Fig. 2.5 shows an SEM image of the 3D junction region with intertwined AEL and CEL fibers (Fig. 2.5a), a schematic of the 3D BPM (Fig. 2.5b left), and an enlarged schematic of the junction region (Fig. 2.5b middle and right). The intimate contact between the AEL/CEL fibers enabled by DMF vapor treatment and hot pressing in the junction provides multiple transport pathways for water dissociation products H⁺ and OH⁻ and greatly facilitates their removal from the junction region (Fig. 2.5b, middle). Consequently, a large H⁺/OH⁻ flux and faster water dissociation are expected in the 3D junction of the BPM, which was experimentally confirmed below. As shown above, a large ion flux from water dissociation should compensate for the unbalanced fixed charge in the AEL and CEL and decrease the electric field across the junction region. In addition, unlike in the planar junction BPM, in which the electric field is applied perpendicular to the depletion layer plane, the 3D junctions span a range of angles to the membrane plane, as evidenced in the SEM image of the junction (Fig. 2.5a). This effect lowers the local electric field across the dispersed AEL/CEL fiber interface and thus further reduces the overall electric field (Fig. 2.5b, left and middle).

Developing an accurate model for the 3D BPM is challenging due to the interpenetrating structure within the junction region. However, the same neutral layer model was taken to interpret the EIS data in the 3D BPM. On the one hand, the basic working principle of the 3D junction BPM is the same as that of the 2D BPM (Fig. 2.5b). It is the intimate local contact between the AEL and CEL that distinguishes the 3D interface from its 2D counterpart. However, the neutral layer model does not take into account the microstructure of the reaction region. On the other hand, the EIS spectra collected for 3D junction BPM do resemble its 2D counterpart, Fig. A.5, except for the detailed shape at higher frequency region.
Fig. 2.5. BPM with a 3D junction. (a) SEM image of the junction region, the scale bar corresponds to 20 μm; (b) (Left): schematic of the 3D junction BPM, with AEL (red), CEL (blue) and dual-fiber junctions. (Middle): enlarged view of the dual fiber junction. The mixture of AEL and CEL fibers in the junction region provide pathways for H\(^+\) and OH\(^-\) transport. Black arrows in the left and middle panels indicate the overall and local electric fields, respectively. (Right): enlarged view of the AEL/CEL interface in the junction region, where water dissociates into H\(^+\) and OH\(^-\) at the Al\(_2\)O\(_3\) catalyst; (c) J-E curves of 3D junction and 4GO BPM in 0.5 M KNO\(_3\) at lower reverse bias; (d) Water dissociation rate constant \(k_d\); (e) Water dissociation reaction resistance \(R_w\); (f) Depletion region thickness \(d\) as a function of reverse bias voltage.

Under steady-state galvanostatic polarization, the 3D junction BPM exhibits a similar co-ion leakage current as the 4GO BPM at lower reverse bias in a pH neutral electrolyte (Fig. 2.5c). The 3D junction BPM shows a nearly constant \(k_d\) up to a reverse bias of ~0.9 V (Fig. 2.5d). It is noteworthy that the observed lower overpotential of the 3D junction BPM does not stem from catalysis of the water dissociation reaction because the 4GO BPM exhibits a relatively larger rate constant \(k_d\). In stark contrast to the 4GO BPM, the reaction resistance, \(R_w\), for the 3D junction BPM does not show obvious convergence to a plateau but rather remains almost constant, and is much
smaller within the studied voltage range (Fig. 2.5e). The lower reaction resistance for the 3D junction BPM is attributed to facilitate water dissociation made possible by the rapid removal of H\(^+\)/OH\(^-\) through the interpenetrating AEL/CEL fibers, which results in a larger H\(^+\)/OH\(^-\) flux in the junction region relative to flat interface BPMs. The independence of \(R_w\) on the transmembrane voltage indicates a small electric field in the 3D junction BPM as a result of the large H\(^+\)/OH\(^-\) flux. The smaller electric field is also verified by the thinner depletion thickness \(d\) compared with that of the 4GO BPM (Fig. 2.5f).

Finally, it is tempting to consider carrying out EIS measurements of the BPMs under normal operating conditions as in Fig. 2.6, i.e. with acid and base in the cathode and anode compartments, respectively, in order to correlate the water autodissociation kinetics with cell performance under practically relevant conditions. For the purpose of studying the mechanism of water autodissociation and the effects of electric field and catalysis, the pH neutral electrolyte allows us to monitor the gradual formation of the depletion region and the resulting electric field. This was found to be difficult with asymmetric electrolytes, as shown in Fig. A.10.

2.2.5 Performance evaluation of BPMs at high reverse bias

Fig. 2.6a compares BPMs with no GO/four layers of GO (0GO/4GO BPM), and the 3D junction BPM with a commercial Fumatech BPM in terms of the potential drop across the membrane at a given reverse bias current density. At low current density, the cross-membrane potential is similar for all membranes except the 0GO BPM, whereas at current densities greater than 100 mA/cm\(^2\), the 4GO and 3D junction BPMs show significantly lower potential drop than the Fumatech BPM. The characteristics of the BPM current density-voltage (J-E) curve have been thoroughly discussed in the literature.\(^{37,40}\) Galvanostatic measurements at a reverse-bias current density of 100 mA/cm\(^2\) were performed and the results (Fig. 2.6b) suggest that both membranes were stable for at least 10 hours of continuous operation. The moderate increase in the cross-membrane potential for the 4GO BPM may be associated with degradation of GO in the interfacial layer during operation.
Compared with the BPM with no catalyst, 0GO BPM, the cross-membrane potential of the 4GO BPM is much lower at all studied reverse bias values (Fig. 2.6a) due to the smaller water dissociation reaction resistance, $R_w$, of the latter (Fig. 2.2c). The depletion layer thickness and thus the electric field in the 0GO BPM are larger than those of the BPM with catalyst, 4GO BPM, and show a clear dependence of increasing as the reverse bias increases (Fig. 2.2d). For the 0GO BPM, a wider depletion region gives rise to a stronger electric field, which promotes water dissociation to a larger extent so that the produced $\text{H}^+$/OH$^-$ flux matches the higher current density at an increased reverse bias. However, for the 4GO BPM, the catalyst provides an alternative means of enhancing the rate of water dissociation. As such, the depletion region and electric field do not need to be as enlarged in order to achieve the same current density.

Similarly, the electric field in the 3D junction BPM is also shown to be small (Fig. 2.5f). Two origins for the small electric field in the 3D junction BPM are: (1) the large $\text{H}^+$/OH$^-$ flux due to the facile transport of the charged species because of the interpenetrating AEL/CEL dual fiber structure, compared to the incorporation of an effective catalyst as considered in the 4GO BPM and (2) the wide range of angles spanned by the AEL/CEL interfaces with respect to the overall electric field. Because of this effect, improving the membrane fabrication process so that the
AEL/CEL interfaces are more perpendicular to the membrane plane would be expected to impart a larger role to the electric field in 3D junction BPMs.

2.3 Conclusions

In summary, BPMs were prepared from a crosslinked AEL and Nafion CEL with a GO catalyst deposited in between by LBL assembly, allowing for precise control of the interfacial structure. By adjusting the GO catalyst layers, a balance between the second Wien effect and the catalytic effect in promoting water dissociation has been discovered. A comprehensive numerical simulation model elucidated that the electric field enhancement for water dissociation may be compromised by incorporating catalysts into the BPM junction, as that produces a larger H⁺/OH⁻ flux that partially mitigates the net fixed charge on AEL and CEL of the BPMs. This conclusion is further corroborated by testing a 3D junction BPM, which exhibits a large H⁺/OH⁻ flux because of facilitated ionic transport through the interpenetrating junction. This quantification of the balancing role of electric field and catalyst in promoting water dissociation implies a crucial rule of the catalyst layer under higher reverse bias conditions and should help guide the design of higher performance BPMs. In particular, the diminished role of the second Wien effect at higher reverse bias for BPMs with catalyst layers implies that for applications in which high current density is desirable, increasing the effectiveness of the catalysis is the best solution. For the 3D BPM, modifying the fabrication procedure to orient the AEL/CEL interface perpendicular to the membrane plane would enable the electric field to play a larger role in accelerating water dissociation.

2.4 References


(11) Rogers, C.; Perkins, W. S.; Veber, G.; Williams, T. E.; Cloke, R. R.; Fischer, F. R. Synergistic Enhancement of Electrocatalytic CO\textsubscript{2} Reduction with Gold Nanoparticles Embedded in


66


(54) Zhu, L.; Pan, J.; Christensen, C. M.; Lin, B.; Hickner, M. A. Functionalization of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)s with Hindered Fluorene Side Chains for Anion Exchange Membranes. Macromolecules 2016, 49, 3300–3309.


Chapter 3

Improving the efficiency of CO$_2$ electrolysis by using a bipolar membrane with a weak acid cation exchange layer

Abstract

The conversion of electricity to chemicals is needed to mitigate the intermittency of renewable energy sources. Driving these electrochemical conversions at useful rates requires not only fast charge transfer kinetics, but also rapid mass and ion transport in the cell. However, little is known about the effect of local environments on the ionic flows that are managed by solid polymer electrolytes. Here, we show that it is possible to measure and manipulate the local pH in membrane electrolyzers with tens-of-nanometers resolutions. In bipolar membrane-based gas-fed CO$_2$ electrolyzers, the acidic environment of the cation exchange layer results in low CO$_2$ reduction efficiency. By using ratiometric indicators and layer-by-layer assembly of polyelectrolytes, the local pH could be measured and controlled within a weak acid layer of ~50 nm thickness. When incorporated into a gas-fed CO$_2$ electrolyser, the weak acid layer suppresses the competing hydrogen evolution reaction without compromising the CO$_2$ reduction efficiency. The method of probing and controlling the local membrane environment can be useful in other electrochemical devices including electrolyzers, fuel cells and flow batteries, and the operando study of ion distributions within solid electrolytes.

3.1 Introduction

Population growth and continuing economic development over the coming decades, coupled with the environmental consequences of increased fossil fuel use, will necessitate the large-scale utilization of renewable and carbon-neutral energy sources such as wind and solar.\textsuperscript{1–3} Electrical energy derived from renewable resources can in principle meet the terawatt challenge while minimizing the release of carbon to the atmosphere. One of the major obstacles to the large-scale deployment of renewable electricity is its intermittent and seasonal generation, which requires that surplus energy be stored economically for long periods of time.

The electrolysis of carbon dioxide (CO\textsubscript{2}) offers the possibility of carbon-neutral seasonal storage of renewable electricity. CO\textsubscript{2} can be electrochemically reduced to various carbon-containing products depending on the type of catalyst and reaction conditions. High temperature electrolyzers based on solid-state oxide ion conductors typically reduce CO\textsubscript{2} to CO, which is a feedstock for the synthesis of methanol and the Fischer-Tropsch synthesis of hydrocarbon fuels.\textsuperscript{4} Low temperature electrolyzers based on aqueous electrolytes can produce CO, formate, ethylene, and alcohols directly from CO\textsubscript{2}.\textsuperscript{5} Due to the low solubility and slow diffusion of CO\textsubscript{2} in aqueous media, the mass transfer-limited current density is typically low. In contrast, gas-fed CO\textsubscript{2} electrolyzers that utilise the high density triple phase boundary enable fast diffusion of the reactants and products, and an order of magnitude higher current density.\textsuperscript{6–8} As a well-developed technology, water electrolysis provides a useful guide for CO\textsubscript{2} electrolyzer design. By mimicking the proton exchange membrane (PEM) electrolyser, an early example of a gas-fed CO\textsubscript{2} electrolyser employed a highly conductive Nafion proton exchange membrane.\textsuperscript{7} While high current densities could be achieved, the Faradaic efficiency (FE) of CO\textsubscript{2} reduction was very low due to the acidic environment of the Nafion, which favors the competing hydrogen evolution reaction (HER). This problem could be temporarily mitigated by inserting a buffering layer between the acidic Nafion membrane and the cathode catalyst. Similarly, alkaline CO\textsubscript{2} electrolyzers have shown high FE for CO\textsubscript{2} reduction as the rate of the HER is suppressed in base.\textsuperscript{9,10} However, system-level problems including product...
crossover and poor CO₂ utilization prevent the practical operation of anion exchange membrane-
based CO₂ electrolyzers for certain products.¹¹

Bipolar membranes (BPMs) have been studied as an alternative membrane separator for both fuel cells and electrolyzers.¹²⁻¹⁷ A BPM is composed of a cation exchange layer (CEL) and an anion exchange layer (AEL), usually with a water dissociation catalyst in between. Assuming ideal permselectivity of the CEL and AEL, no ions can pass through the BPM because cations will be rejected by the AEL and anions by CEL, unless the ions are generated (as in reverse bias) or combined (in forward bias) at the AEL/CEL interface. The recombination of H⁺ and OH⁻ to form water in the BPM was employed in a self-humidified fuel cell that works best at a much lower humidifying level than a conventional PEM fuel cell.¹² In water electrolyzers with BPMs, the dissociation of water to H⁺ and OH⁻ sustains the acidic and basic environments of the cathode and anode chambers, respectively, enabling stable performance and the use of earth-abundant oxygen evolution reaction (OER) catalysts at the alkaline anode.¹³,¹⁶

The benefit of using a BPM to manage ion transport in electrolytic cells has been explored in CO₂ electrolysis.¹⁶,¹⁹ Unique to CO₂ electrolyzers is the capability of the BPM to mitigate neutral and anionic product crossover.¹¹ Anionic products such as formate electromigrate to the anode where they are oxidised, unless a bipolar configuration is used in either forward or reverse bias mode.²⁰,²¹ Crossover also occurs with charge-neutral products such as methanol via diffusion and electroosmosis. This effect is mitigated in a reverse-biased BPM-based electrolyser by the outward flux of H⁺ and OH⁻ ions towards the cathode and anode, respectively.¹¹

While a reverse-bias BPM can effectively manage ion transport in the bulk of the membrane, a high concentration of protons is generated at the CEL/catalyst interface, and the role of these ions is not well understood in gas-fed CO₂ electrolyzers. It has been shown that zero-gap electrolyzers with a Nafion CEM alone lead to essentially zero FE for CO production.⁷,⁸ In contrast, a BPM equipped with a Nafion CEL has a low (30 %) but nonzero FE,¹⁸ even though in both cases a similarly acidic cathode environment might be expected. Most of the proposed CO₂ reduction mechanisms involve a protonation reaction to remove surface bound CO or two-carbon species.²²—
and protons also react with CO$_2$-generating molecules such as carbonate and bicarbonate. Our understanding of the role of protons in CO$_2$ reduction is further complicated by the difficulty in monitoring the local pH. Several recent studies have employed pH-responsive reporters, such as the ratio of acid and base forms of a buffer$^{25,26}$ or a non-Faradaic probe reaction,$^{27,28}$ to measure the local surface pH in-situ under aqueous electrolysis conditions. Ratiometric pH indicators are widely used in molecular biology to measure local intracellular pH.$^{29}$ A pH-sensitive ratiometric probe typically has two or more absorption or emission bands that respond differently to the proton concentration. Within a certain pH range, there is a one-to-one correspondence between the ratio of the intensity of the absorption peaks at different wavelengths and the pH. Ratiometric dyes have the advantage of minimal interference from parameters that are difficult to control, such as the local probe concentration and optical path length, making them attractive candidates for local pH monitoring at electrochemical interfaces.

Previous studies have found low FE for CO$_2$ reduction in BPM-based electrolysers, but the reason remains unclear.$^{18}$ The experiments described here use a direct optical probe of the BPM CEL surface during the reaction in a spectroelectrochemical cell. These observations highlight the role of protons that are generated by the BPM and migrate to the CEL/cathode interface. Layer-by-layer (LBL) assembly was then used to deposit weak acid polyelectrolyte layers on the strongly acidic CEL. Quantitative measurements of the membrane near-surface pH could then be made by covalently binding a ratiometric pH indicator to the polyelectrolyte chains in an individual layer. Ag nanoparticles (NP) were chosen as a model catalyst for the electrochemical reduction of CO$_2$ to CO. We observed that the CO production FE was increased due to the suppressed HER current density in LBL film modified BPM-based electrolysers.

3.2 Experimental methods

3.2.1 BPM fabrication
BPMs were prepared according to the procedure described elsewhere. To prepare BPMs with thin AEL (~10 μm) with minimal background, the opposite process was conducted. Briefly, activated Nafion membrane was taped to the glass slides to leave an area of 3 cm by 3 cm, followed by dipping it in PDDA solution (1 mg/ml) and GO suspension each for 20 minutes, with water raising in between. 100 uL of brominated PPO solution (5 wt%, degree of functionalization 60%) and 1.25 uL of NNNN-tetramethyl-hexanediamine were added to 1 mL of NMP. This solution was sprayed onto the PDDA/GO modified Nafion on a hot plate heated at ~ 150 °C.

3.2.2 Electrode preparation

5 mg of Ag NP and 5 mg of carbon powder were added to a vial containing 0.75 mL nanopure water, 0.25 mL isopropanol and 0.04 mL Nafion solution (5 wt% in alcohol/water mixture). For ionomer-free configuration, no ionomer was added. The mixture was placed in a bath sonicator for one hour. The catalyst ink was then air-sprayed onto four pieces of carbon paper (1 x 1 cm²) at room temperature. The metal loading was ~ 1.0 mg/cm².

3.2.3 Visualisation of the cathode GDL

Fuel cell hardware was used for the visualization experiment. A graphite flow field with Ni foam were used on the anode side of the cell. For the cathode, a hole (~2 mm in diameter) was punched into the Ag-deposited GDL to allow for optical access. A cubic cut was made to the cathode flow plates in the center. A transparent quartz window was inserted on the side close to the cathode GDL. On top of the quartz window was a patterned serpentine flow field. A visualization camera was oriented to point towards the CEL of the BPM. In a typical experiment, 1 M KOH was cycled through the anode flow field using a peristaltic pump and humidified CO₂ gas was passed through the cathode flow field.
3.2.4 LBL assembly of PAH/PAA bilayers

LBL assembly was carried out manually at room temperature, using a procedure similar to that described by Kaschak et al.\textsuperscript{31} The Nafion side of the BPM was rinsed with water a few times before being air dried. The first layer of PAA (2 mg/ml, in water, pH adjusted to 3 using 1 M HCl) was deposited directly onto the Nafion surface for 20 minutes, followed by rinsing the surface with water three times. The first PAH layer (2 mg/ml, in water pH ~6.0) was deposited in another 20 minute step. After these first two adsorption steps, the entire Nafion BPM was sequentially dipped into the PAA and PAH solutions for 5 minutes, with water rinsing and air drying repeated three times between each deposition. The AEL was attached to a glass slide so that only the CEL side was exposed to the polyelectrolyte solutions. In order to monitor the local pH within the LBL film, dye-labeled PAH (see below) was deposited at targeted location for samples S1-S6.

3.2.5 Covalent modification of PAH

Dye 76errocyanide76tion of PAH followed the method of Kaschak et al.\textsuperscript{31} 100 mg of PAH was dissolved in 5 mL water containing 50 mg KHCO\textsubscript{3}. The slightly alkaline environment maintains most of the amine groups in their deprotonated form so that the conjugation of the dye to free amine groups can take place. 5.0 mg of Oregon Green (OG) and 4.5 mg TMR were dissolved in 15 mL DMF. The dye mixture was slowly added to the PAH solution while solution was swirled. The reaction mixture was incubated at room temperature in the dark for 3 hours. 0.8 mL 1 M HCl was added to the mixture and the dye labeled PAH (dye-PAH) was precipitated with acetone. The dye-PAH was redissolved in water and then precipitated with acetone again. The resulting polymer was dried at 70 °C and stored in the dark. To obtain the TEM images of the LBL layers on the Nafion BPM, Eosin-5-isothiocyanate was attached to the PAH because the dye has four Br atoms that provide the LBL layer better contrast with the fluorocarbon backbone of the Nafion layer.
3.2.6 In-situ monitoring of the membrane pH

Ultraviolet-visible (UV-Vis) absorption spectra were collected using a Varian Cary 6000i spectrophotometer from 400-800 nm. A customized cell with a cathode and anode chamber, clamped by two quartz glass windows, was used. A BPM was inserted between the cathode and anode chambers. Pt wires were used as cathode and anode electrodes. A piece of BPM without added LBL layers was used as the background reference. 0.1 M KHCO$_3$ was used as the electrolyte. For the spectra at -4 mA reverse current, at least 10 minutes of a stabilization run was performed before taking the spectra.

3.2.7 Electrochemical characterization

DC polarization curves were measured in a four-compartment and double-reference electrochemical cell. The BPM was placed in the center of the cell and an extra CEM and AEM were positioned in the outer chambers to minimize the influence of electrochemical products. Two Pt wires and two Ag/AgCl electrodes fixed in the two central chambers using Haber-Luggin capillaries, were used as working/counter and reference electrodes. The electrolyte was 1 M KNO$_3$. For measurements of the HER onset potential on Pt, a water vapor-fed water electrolyser configuration was employed. Water vapor carried by Ar gas was fed in at the cathode and 1 M KOH was cycled through the anode. Both the cathode and anode were Pt NP sprayed onto carbon paper (~1mg/cm$^2$ metal loading). An Ag/AgCl reference electrode, made from silver foil anodized in HCl solution, was positioned next to the Pt working electrode. The reference electrode was calibrated against a standardized reference electrode each time before the experiment. An acidic CEM and basic AEM were taken as reference membranes, as they represent the low and high pH extremes for ionomer membranes. Before the measurements, the CEM and AEM were bathed in 0.5 M H$_2$SO$_4$ and 1 M KOH overnight, respectively. For the Nafion BPM and LBL-modified BPM, membranes were subjected to 50 mA reverse bias current in 0.1 M KHCO$_3$ for at least one hour to
ensure the complete replacement of counter ions in the CEL and AEL with protons and hydroxide ions, followed by thoroughly rinsing with water.

### 3.2.8 CO₂ electrolysis experiments

Two graphite flow plates were used to deliver gaseous CO₂ and act as the current collector. A three-electrode setup was used. The cathode contained a carbon paper GDL with deposited Ag NP and the anode contained Pt NP on a carbon GDL. An in-house constructed Ag/AgCl foil was used as the reference electrode. The cell configuration was as shown in Fig. 3.1a, with the exception that there was no hole in the GDL and the Ag/AgCl reference electrode was placed next to but not touching the cathode GDL. BPMs were used to separate the cathode and anode chambers. CO₂ gas was passed through a water bubbler at a rate of 20 mL/min, adjusted by a mass flow controller. 1 M KOH was pumped through the anode flow field by means of a peristaltic pump. The gas mixture from the electrolyser was sent to a gas chromatograph (PerkinElmer Clarus 580) for analysis. The electrochemical experiments were done using an EZStat Pro Potentiostat-Galvanostat (Nuvant Systems). The cell was stabilized for ~15 mins at constant potential before the gas samples were taken for injection into the GC.

### 3.3 Results and discussion

#### 3.3.1 Visualisation of the cathode

In order to understand the causes of the low FE in the BPM-based CO₂ electrolyser, a cell with a transparent quartz window was fabricated. A hole was made in the center of the Ag nanoparticle (NP) (Ag NP is ~ 50 nm in diameter, Fig. B.1) covered gas diffusion layer (GDL) to allow optical access to the membrane surface (Fig. 3.1a). An overall cell current density of ~ 80 mA/cm² was measured at 3.5 V cell potential, as shown in Fig. B.2. However, the FE for CO₂
conversion to CO was lower than 40% at all the applied potentials studied here, with the remaining part of the current arising from reduction of water or protons to gaseous hydrogen, Fig. 3.1b. This is consistent with previous reports of BPM-based CO$_2$ electrolyser$^{18}$ and not affected appreciably by the presence of the hole in the GDL, Fig. B.2. Images of the BPM CEL surface at different times and at various cell potentials are shown in Fig. 3.1c. At a cell potential of 2.5 V, small isolated gas bubbles were identified and remain static within 3 seconds. When the cell potential was increased to 3.0 V, the gas bubbles evolved much faster during the same time interval. In contrast to a previous visualization study of a water electrolyser in which oxygen gas bubble nucleation was observed only at the rims of the pore where the triple phase boundary sites are located,$^{32}$ the gas bubbles here were dispersed evenly over the CEL surface. The fact that gas bubbles emerge on the CEL surface rules out electrochemical generation as a possible mechanism for the bubble formation because the catalyst was deposited on the GDL, rather than on the membrane surface as in a conventional membrane-electrode assembly (MEA) configuration.

A plausible explanation for the observed bubbles is the formation of CO$_2$ gas resulting from the lower solubility of CO$_2$ in aqueous microphase of the strongly acidic CEL, Fig. 3.1d. In reverse bias, the rate of water dissociation into H$^+$ and OH$^-$ at the AEL/CEL interface of the BPM is increased by the local electric field and by catalysis.$^{30}$ The H$^+$ produced in this way migrates towards the cathode and creates an acidic environment at the CEL/cathode interface. The low pH leads to the relatively insoluble CO$_2$ species near the CEL/GDL region and the continuous formation of CO$_2$ bubbles. The high proton concentration at the CEL results in a low FE for CO$_2$ reduction, either by promoting the competing HER reaction or by removing the CO$_2$ reactant from the triple-phase boundary. A recent study has employed the acidic environment at the CEL to generate CO$_2$ gas from a bicarbonate electrolyte in an electrochemical cell that combines CO$_2$ capture and reduction, which supports our proposed mechanism.$^{33}$
Fig. 3.1. An acidic cathode environment leads to low Faradaic efficiency for CO$_2$ reduction in a BPM-based electrolyser. (a) Schematic of the setup for visualising the cathode. 1 M KOH and humidified CO$_2$ gas (20 ml/min) were introduced at the anode and cathode, respectively. (b) CO and H$_2$ FE as a function of the overall cell voltage. The error bars represent one standard deviation of three independent measurements. (c) Photographs of the CEL surface under different cell voltages. Gas bubbles (enclosed in the green dashed circles) evolve faster at higher cell voltage. Scale bar corresponds to 250 µm. (d) Proposed mechanism for proton generation and the low FE for CO$_2$ reduction in a BPM-based CO$_2$ electrolyser. Blue dots represent electrons.

3.3.2 Layer-by-layer (LBL) modification of the BPM

BPMs were fabricated by air-spraying a Nafion CEL onto a graphene oxide (GO)-modified AEM, as described previously. The Nafion membrane is strongly acidic because of its sulfonic acid groups. The most widely used weak acid cation exchangers are based on acrylic acid (-COOH, pKa ~ 4-6) in combination with divinylbenzene and crosslinkers that provide chemical and mechanical stability in liquid environments. Polyelectrolytes can also be grown as nanometer-thick layers by LBL assembly, which offers a simple and precise way of tailoring the local chemical environment of the membrane surface. A weak acid cation exchange layer was thus prepared by alternately exposing the Nafion CEL surface to solutions of poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH), with rinsing steps in between as illustrated in Fig. 3.2a. Contact angle measurements during the LBL assembly process, Fig. 3.2b, showed that the
hydrophilic Nafion face of the BPM was gradually modified by growth of the PAH/PAA layers. After 3-4 bilayers of PAH/PAA were deposited, the contact angle alternated with each deposition step, with a higher contact angle for PAA termination. Because this trend was not observed for the first three bilayers, we hypothesize that the polyelectrolyte film is initially patchy but eventually covers the entire membrane surface. Characterization of the LBL layers by electron microscopy is challenging because of the low contrast between the PAA, PAH and Nafion. However covalent attachment of the Br-containing molecule Eosin to PAH enables STEM imaging of the Nafion/10 bilayer LBL interface by EDS mapping of fluorine (Nafion layer) and Br (PAH in the LBL layer), Fig. B.4. An LBL layer of approximately 50 nm can be discerned on the Nafion CEL surface. Taken together, the contact angle measurements and STEM images confirm the growth of a relatively uniform PAH/PAA multilayer film by the LBL process.

Fig. 3.2. Modification of the BPM by LBL assembly. (a) Molecular structures of the polyelectrolytes and schematic drawing of the membrane structure. (b) Water contact angles measured after each step of the LBL assembly process. The first
measurement at step 0 refers to the contact angle of the Nafion CEL. The variation of the contact angles indicates the alternative termination of the surface with PAA and PAH. The error bars represent one standard deviation of three independent measurements.

3.3.3 Measurement of the local surface pH using ratiometric dyes

A ratiometric dye has two or more absorption or emission signals that respond differently to an analyte such as H⁺. By calibrating the ratio of signal intensities against the external pH, one can measure pH in-situ without knowing the precise local concentration of the dye. In order to measure the pH at the CEL surface, a ratiometric dye with a relatively low pKa is needed because the local pH is expected to be low. The halogenated fluorescein derivative Oregon Green 514 (OG), which has a pKa of ~ 4.8 was thus chosen, Fig. 3.3a. The protonation of OG results in a lower extinction coefficient in the absorption spectrum. To construct a ratiometric system, a second dye, 5,6-dicarboxyl-tetramethyl rhodamine (TMR), was chosen for its absorption band at ~560 nm. In order to pinpoint the location of these dyes (and thus measure the local pH) in an individual polyelectrolyte layer in the LBL assembly, it is also necessary to bind them covalently to the polymer. PAH has pendant amine groups that provide a reactive site for the covalent attachment of dyes functionalized with succinimidyl esters, forming stable amide bonds, Fig. 3.3a. To minimize the effects of dye attachment on the properties of the LBL assembly, a minimal loading of dye molecules (~1/200 PAH monomer units) was used. After each step of the LBL assembly process, the surface was rinsed with water in order to minimize retention of unbound dye. The dye labeled PAH (dye-PAH) has the characteristic absorption peaks of the two constituent dyes, Fig. 3.3b. The intensity ratio of the peaks at 560 and 510 nm was calibrated as a function of pH, Fig. 3.4g, showing a dramatic change near the pKa of OG, ~4, with the 560/510 ratio increases as decreasing pH.

A customized electrochemical cell with two chambers and two electrodes was built for the in-situ UV-Vis experiments. Nafion- and LBL modified- BPMs were clamped between the cathode and anode chambers, with the CEL side facing the cathode, Fig. 3.4a. Fig. 3.4b shows the six LBL modified BPM samples, S1-S6, where the dye-PAH/PAA probing bilayers gradually move away
from the Nafion CEL. For example, in the S1, two bilayers of dye-PAH/PAA were grown on the CEL surface of the BPM, followed by the remaining 8 PAH/PAA bilayers. In this case the attached dye molecules probe the environment in direct contact with the Nafion CEL. S4 sample has the structure of three bilayers of PAH/PAA on the Nafion CEL, followed by three dye-PAH/PAA bilayers capped with another four bilayers of PAH/PAA. The first three PAH/PAA bilayers act as a buffer zone between the Nafion CEL and the ratiometric probe layers. Increasing the buffer zone to ten PAH/PAA bilayers gave a sample in which the dye labeled-PAH probe a local environment that was farthest from the Nafion surface, S6. Together, these samples probe the local environment within the LBL film at varying distance from the strong acid CEL/weak acid polymer interface.

![Diagram](image)

Fig. 3.3. Attaching pH-responsive dyes to PAH and pH calibration. (a) Scheme for covalently attaching Oregon Green (OG) and tetramethylrhodamine (TMR) to PAH. (b) UV-Vis spectra of three dye-loaded PAH/PAA bilayers on a glass slide bathed in different pH solutions for calibration. The peak at 560 nm is due to TMR and the 480 and 510 nm peaks to OG. The spectra are normalized to the peak at 560 nm. The intensity ratio between the peaks at 560 nm to 510 nm (dash lines) is calibrated as a function of pH in Fig. 3.4g.
The spectroscopic interference from the BPM can be minimized by using a thinner AEL (~10 μm) with negligible background effect (see discussion on background subtraction in the Appendix B, Fig. B.5 and B.6). Qualitatively, the CEL surface of the Nafion BPM is more acidic as evidenced by the bubble formation upon contacting 0.1 M KHCO₃ solution, Fig. 3.4c. Quantification of the local pH can be done with the in-situ UV-Vis measurement, Fig. 3.4d and 3.4e for sample S1 and S4, while those of the remaining samples can be found in Fig. B.7 and B.8. In the S1 with the dye molecule being nearest to the Nafion BPM, the absorption at 560 nm is comparable to that of 510 nm, reporting a local pH of ~3.5 at open circuit voltage (OCV). For the remaining samples S2-S6 (Fig. 3.4e and Fig. B.7 and B.8), the peak intensity at 560 nm is much smaller. Interestingly, a steady decrease in the peak intensity ratio of 560/510 is observed from S1 to S6 (Fig. 3.4f), indicating the gradual pH increase from the Nafion CEL surface to the edge of the LBL film. When plotted as a function of the averaged distance from the CEL surface, the 560/510 ratio decreases most dramatically within the distance of four bilayers while changes little over the remaining six bilayers. This pictures a relatively sharp pH increase at CEL/LBL interface and mostly steady pH within the bulk of the LBL film.

Applying a reverse-bias current 4 mA (~3.03 mA/cm²) decreases 560/510 ratio for S1 but does not significantly change the values in other samples. This change in the peak ratio is reversible, Fig. B.9, and is unlikely to be caused by the electric field at the BPM Nafion/LBL interface since applying a bias to Nafion alone does not induce a similar change, Fig. B.10. It is thus plausible that the surface becomes more acidic when the BPM is subjected to a reverse bias, as more protons are introduced into the CEL than under open circuit conditions. Based on the calibration curve, under reverse bias pH values of ~2 to ~6 are measured for samples S1 to S6. The calculated pH value of Nafion is higher than expected, which may reflect the relatively low pH-sensitivity of the ratiometric dyes at very low pH, Fig. 3.4g. The observed trends are consistent with the results from spectral modeling, Fig. B.11.

Under reverse bias, protons generated at the AEL/CEL interface of the BPM migrate through the Nafion and weak acid LBL layers. The pH transition in the LBL layers happens within a region
of 10 bilayers, i.e. ~ 50 nanometers, in sharp contrast to the pH gradient found in the solution phase. Diffusion boundary layers with concentration gradients typically extend across 20-200 µm at an electrified solid/liquid interface, such as an electrode/electrolyte or membrane/electrolyte interface. The situation is more complicated by the use of nanostructures that exhibit high local current density and larger concentration gradients on the electrolyte side.

Fig. 3.4. Measurement of the local pH in the LBL film on the modified BPM. (a) Schematic of the UV-Vis measurement. (b) Schematic of the six samples (S1-S6) used for pH gradient measurements. Dye-PAH and PAH refer to the PAH polymer with and without dye attachment. Two or three bilayers of Dye-PAH/PAA are deposited as the probe layer. The location of the probe layer moves further away from the Nafion CEL in the LBL film with increasing sample number. (c) Photographs of the CEL surface of the Nafion BPM and LBL-modified BPM when bathed in 0.1 M KHCO₃ solution. The bubbles formed on the Nafion BPM indicate a lower surface pH. Scale bar represents 1 mm. UV-Vis spectra of sample (d) S1 and (e) S4 at open circuit voltage and 4 mA reverse current (current density ~3.03 mA/cm²). (f) Intensity ratio of the peaks at 560 and 510 nm as a function of the average number of bilayers from the CEL in the LBL BPM. The ratio changes more rapidly within the first few layers compared with the remaining layers. The error bars represent one standard deviation of two independent measurements. (g) Calibrated peak intensity ratio as a function of pH. The smaller ratio at higher pH reveals a gradual pH increase in the LBL film as one moves away from the CEL. The error bars represent one standard deviation of three independent measurements.

Three PAA/dye-PAH bilayers were used in all samples (except S1) because complete coverage of the CEL surface requires at least three to four bilayers, as discussed above. The dye-
PAH layers thus sense the average pH within a region spanning three LBL bilayers. As a result, the actual pH transition from the Nafion CEL to the outer edge of the 10 PAH/PAA bilayer assembly may in fact be sharper than that indicated by the data in Fig. 3.4f, particularly within the first few bilayers. Whether or not a similarly sharp ion gradient, as observed in the LBL film, exists in thick membrane electrolytes (commonly employed in fuel cells and electrolyzers) is an interesting question that could potentially be studied by the method developed in this work.

Under reverse bias conditions, the 10 LBL BPM has a significantly higher surface pH than the Nafion CEL, suggesting that the LBL film acts as a weak acid cation exchanger. The exact transport mechanism in the mixed polyanion/polycation PAH/PAA bilayers remains unknown and is a subject for further study. It is likely that PAH plays a relatively minor role in proton conduction because the local pH is several units below its pKa, so there are relatively few free amine groups available to accept protons from neighboring proton donors (-COOH or –NH₃⁺). On the other hand, PAA contains a high density of both proton donor and acceptor sites since the local pH is close to its pKa.

3.3.4 Electrochemical CO₂ reduction

The cross-membrane potential of the 10 LBL bilayer-modified BPM, was measured in 0.1 M KHCO₃ solution and is similar to that of the pristine Nafion BPM, Fig. 3.5a. Although the CEL of the modified BPM is terminated by a weaker acid cation exchange layer, the reference electrodes placed adjacent to the membrane surface are not able to detect the surface pH and sense only the pH of the electrolyte solution near the membrane. Both BPMs were able to sustain currents of 500 mA/cm² without reaching their limiting current. The onset potential of the HER at Pt is linearly dependent on the pH, and thus is often used as an indicator to probe the local pH. A vapor fed water electrolyser was constructed with Pt/C nanoparticle electrode as the cathode and anode and Ag/AgCl as a reference electrode. An activated Nafion CEM and quaternary ammonium-functionalized AEM were used as low and high pH reference standards. The Nafion BPM shows a
comparable onset potential to that of a Nafion CEM alone, Fig. 3.5b. The onset potential with the LBL-modified BPM was positive of that of the Nafion BPM, indicating a higher local pH. No attempt was made to calculate the exact pH based on the onset potential since the pH values of the standards, the Nafion CEM and the AEM, were unknown, but the higher local pH of the LBL-modified BPM is consistent with the ratiometric spectroscopic measurements described above.

![Graphs showing electrochemical properties of LBL-modified BPM and Nafion BPM](image)

Fig. 3.5. Electrochemical properties of the LBL-modified BPM and Nafion BPM. (a) Cross-membrane potential of the BPM with (LBL BPM) and without (Nafion LBL) LBL modification. Inset shows the four-electrode setup; the cross-membrane potential is recorded by the two reference electrodes placed directly against the faces of the BPM. Note that the results of the two samples are very similar. (b) Onset potential of the HER at a Pt catalyst with membranes of different compositions. An acidic Nafion CEM and a basic AEM were used as references. (c) CO faradaic efficiency as a function of cathode potential with the ionomer-free catalyst layer. (d) Hydrogen partial current density as a function of cathode potential. The LBL BPM here contains 10 PAH/PAA bilayers. The decreasing CO current density for Nafion BPM at higher potentials could be caused by flooding in the ionomer-free catalyst layer. The error bars represent one standard deviation of two independent measurements.

The electrolysis of CO₂ using the LBL-modified BPM was compared against a Nafion BPM in a zero-gap gas-fed electrolyser. In light of the dimensionality of the catalyst layer, experiments
were carried out both with and without added ionomers, which largely determine the local environment of the catalyst. Regarding ionic transport in the ionomer-free configurations, previous studies have pointed to the role of water and surface diffusion as feasible pathways. The BPM CEL side was placed next to a silver nanoparticle catalyst known to produce CO from CO$_2$. Fig. 3.5c shows that the CO FE with the LBL-modified BPM is higher than that of the Nafion BPM in the ionomer-free configuration and the CO current density remains similar at lower potentials, Fig. 3.5d. In comparison, the HER current density is substantially suppressed with the LBL-modified BPM, Fig. B.12. With ionomer added to the catalyst layer, a similar but smaller difference between the CO FE with the LBL-BPM and Nafion BPM exists, Fig. B.13. The observation that the CO partial current density is almost the same with the Nafion- and LBL-BPMs within the measured potential range is consistent with the pH-independence of the CO$_2$ reduction kinetics. In contrast, the reaction kinetics of the HER are strongly dependent on the local proton concentration as the reaction involves proton-coupled electron transfer as the rate determining step. The cell potentials of the Nafion- and LBL- BPMs were similar at a given overall current density in the configuration with ionomers, Fig. B.14. With the suppressed HER, the CO FE is improved but nevertheless lower than that obtained under alkaline conditions on a silver surface because the local pH at the LBL-modified BPM is still considered acidic. Adding LBL films that can buffer at higher pH may thus further improve the performance of the gas-fed electrolyser.

### 3.4 Conclusions

The low CO FE in a gas-fed CO$_2$ electrolyser containing a BPM was studied by visualising the cathode during the electrochemical reaction, and was found to be a consequence of the acidic local environment. PAH/PAA bilayers grown by LBL assembly on the BPM CEL surface increase the local pH and serve as a weak acid cation exchanger without increasing the overall resistance of the BPM. The local pH was quantified as a function of distance from the Nafion CEL by using a ratiometric pH indicator covalently attached to individual PAH layers. These measurements reveal
a sharp pH transition from ~2 to ~5 within the first few bilayers (~20 nm) and almost steady pH in the bulk of the LBL film (~30 nm). This is in contrast to the typical width of diffusion boundary layers at electrified solid/liquid interfaces that extends hundreds of µm. Understanding and controlling the pH distribution in a solid polymer electrolyte has important implications for a wide range of gas-fed electrochemical devices that include fuel cells and electrolysers, because electrochemical conversions occur at the triple phase boundary where the solid electrolyte provides the local environment for the reactant and catalyst. Incorporating a BPM with weak acid cation exchange layers into a gas-fed CO₂ electrolyser resulted in a suppressed HER activity and improved the Faradaic efficiency. The strategy employed here can be helpful to guide future electrolyser designs for achieving high current density and Faradaic efficiency in CO₂ reduction.

3.5 References


Chapter 4

High-voltage aqueous redox flow batteries based on catalyzed water dissociation and acid-base neutralization in bipolar membranes

Abstract

Aqueous redox flow batteries that employ organic molecules as redox couples hold great promise for mitigating the intermittency of renewable electricity through efficient, low-cost diurnal storage. However, low cell potentials and sluggish ion transport often limit the achievable power density. Here, we explore bipolar membrane (BPM)-enabled acid-base redox flow batteries in which the positive and negative electrodes operate in the alkaline and acidic electrolytes, respectively. This new configuration adds the potential arising from the pH difference across the membrane and enables an open circuit voltage of ~1.6 V. In contrast, the same redox molecules operating at a single pH generate ~0.9 V. Ion transport in the BPM is coupled to the water dissociation and acid-base neutralization reactions. Interestingly, experiments and numerical modeling show that both of these processes must be catalyzed in order for the battery to function efficiently. The acid-base concept provides a potentially powerful approach to increasing the energy storage capacity of aqueous redox flow batteries, and insights into the catalysis of the water dissociation and neutralization reactions in BPMs may be applicable to related electrochemical energy conversion devices.

4.1 Introduction

The intermittent nature of renewable energy sources such as solar and wind presents a barrier to their large-scale implementation, a problem that can potentially be addressed by an efficient and cost-effective means of electrical energy storage over periods of days. Electrochemistry provides a viable solution to the problem by storing charge that can be converted back to electrical power with high round-trip efficiency.\textsuperscript{1,2} Among electrochemical energy storage devices, aqueous redox flow batteries are promising because of the vast design space of redox molecules, the independence of energy and power density, the scalability of energy storage, and the manufacturability of cell hardware. To compete with alternative storage methods, however, improvements in energy and power density, cell lifetime, cost, and safety are still needed.\textsuperscript{3–5}

A higher battery potential increases the power density of redox flow batteries, which in turn reduces the stack cost.\textsuperscript{5} Increasing the cell potential has so far been achieved mainly by designing redox molecules with more extreme redox potentials,\textsuperscript{4,6–9} but the factors of reversibility, solubility, and raw materials availability must be considered for practical large-scale usage. The creation of a cross-membrane potential by means of pH gradient can add to the potential difference between the redox molecules, providing a simple tool for increasing the cell potential. This idea has been studied with water electrolysis at the anode and cathode, but the high overpotentials of the water oxidation and oxygen reduction reactions compromise the efficiency of energy storage.\textsuperscript{10–12} The use of a pH gradient to increase the voltage of a primary battery based on flowing redox molecules has been studied in microfluidic devices by generating a laminar flow of acidic and basic solutions.\textsuperscript{13,14} For this approach to scale to macroscopic dimensions, a membrane is needed to maintain the pH gradient while transporting ions that charge-compensate the anode and cathode reactions. Here we exploit the fact that bipolar membranes (BPM), composed of a cation exchange layer (CEL) and an anion exchange layer (AEL), can effectively manage the transport of proton and hydroxide ions while maintaining a stable pH gradient at high current densities.\textsuperscript{15–17} In contrast to conventional acidic or alkaline redox flow batteries that operate at a single pH, the BPM-enabled
acid-base redox flow battery places the positive and negative electrodes in high and low pH environments, respectively (Fig. 4.1a).

![Diagram of BPM-based acid-base redox flow battery](image)

Fig. 4.1. Schematic illustration of a BPM-based acid-base redox flow battery. (a) The charging process of the battery is shown, where ferrocyanide (Fe(CN)$_6^{4-}$) in aqueous KOH is reduced and SPV (sulfonatopropyl viologen, structure shown in Fig. 4.3a) in H$_2$SO$_4$ is oxidized at the positive and negative electrodes, respectively. The H$^+$ and OH$^-$ ions carry the charge in the bipolar membrane (BPM) that is composed of anion- and cation-exchange layers (AEL and CEL). The electrolytes are cycled through the cell using a peristaltic pump. (b) The transport of H$^+$ and OH$^-$ ions is coupled with the water dissociation and acid-base neutralization reactions during the charging and discharging processes, respectively. The AEL and CEL face the positive and negative electrodes, respectively. The BPM is subject to reverse bias when the flow battery is charging, and operates in forward bias during discharge.

The functioning of an acid-base redox flow battery relies on matching operating pH’s with the properties of the redox molecules, as well as effective ion management in the membrane electrolyte. A successful design must consider the stability of materials,$^{18,19}$ the pH-dependent reaction kinetics,$^{20-22}$ and the pH-dependent shifts in redox potentials.$^{15}$ The fast kinetics of the H$_2$/H$^+$ and O$_2$/OH$^-$ half reactions in acidic and basic media, respectively, have motivated the study of BPMs in H$_2$-O$_2$ fuel cells$^{20}$ and water electrolyzers,$^{15,23,24}$ where the thermodynamic potential of the overall reaction is unchanged because the membrane potential is matched by the Nernstian shift of the redox reactions. Previous efforts to use the membrane potential as an independent
element of energy storage have been compromised by the lack of reversible redox processes at the electrodes, resulting in a low system roundtrip efficiency.\textsuperscript{12,25}

To achieve high energy conversion efficiency, effective management of ion transport is also required as ions carry the current in the electrolyte. The transport of H\textsuperscript{+} and OH\textsuperscript{-} is coupled with the water dissociation and acid-base neutralization reactions at the AEL/CEL interface, which acts as a source or sink of ions in the charging and discharging processes, respectively (Fig. 4.1b). Water dissociation is a slow process, but it can be accelerated by an applied electric field, which creates an overpotential for the charging reaction, and by interfacial catalysis at the AEL/CEL junction.\textsuperscript{17,26} Acid-base neutralization in forward bias, on the other hand, is generally thought to be rapid and so has received less attention. A previous numerical simulation proposed a trap-assisted charge recombination mechanism for H\textsuperscript{+} and OH\textsuperscript{-} in acid-base fuel cells.\textsuperscript{21} More detailed experiments and simulations, which we present below, provide further insight into free energy losses associated with this key process.

The neutralization reaction of H\textsuperscript{+} and OH\textsuperscript{-} is rate-limited by their local concentrations in the region of the CEL/AEL interface. As a result, much of the potential generated across the BPM by the pH gradient can be lost when a forward bias is applied, unless the AEL/CEL interface is equipped with a suitable catalyst, such as graphene oxide (GO), to maintain the quasi-equilibrium of H\textsuperscript{+}, OH\textsuperscript{-}, and water. Understanding these effects enables us to successfully demonstrate a reversible BPM-based acid-base redox flow battery that achieves a ~1.6 V cell potential using the same redox molecules (ferrocyanide and a viologen derivative) which, operating at a single pH, create only a ~0.9 V overall potential.

4.2 Results and discussion

4.2.1 BPM under forward bias
The BPM plays an important role in the acid-base redox flow battery because it separates the positive and negative electrodes, prevents crossover of redox molecules, and conducts ions. To study the BPM in isolation, we monitored the cross-membrane potential by using a four-electrode setup (Fig. 4.2a), which eliminates the influence of the redox processes on the electrodes.\(^{17}\) 0.1 M KOH and 0.1 M HCl solutions were placed on the AEL and CEL sides of the BPM, respectively, creating a pH gradient with an open circuit potential of \(\sim 710\) mV (Fig. 4.2d). The BPM containing an interfacial GO catalyst layer had a smaller overpotential under both reverse and forward bias conditions. The difference in the overpotential reflects the acceleration of reaction rates by GO at the AEL/CEL interface since the potentials were corrected for ohmic resistance. Slower reaction kinetics in BPMs without catalyst were confirmed by electrochemical impedance spectroscopy (EIS) measurements (Fig. C.1). Compared to the inherently slow water dissociation reaction, it is surprising that the acid-base neutralization reaction, which is presumed to have very fast reaction kinetics, is also substantially affected by the presence of the catalyst (Fig. 4.2d).

To gain more insight into the effect of the catalyst, we constructed a one-dimensional numerical model with four segments representing the basic and acidic electrolytes separated by the AEL and CEL of a BPM (Fig. 4.2b). A potential difference was imposed on the two open boundaries that act as the reference electrodes, and the current density was collected based on the ionic fluxes. To study the influence of the catalyst on the rates of the dissociation \(k_d\) and neutralization \(k_n\) processes, we compared three models that differed in their expressions for \(k_d\) and \(k_n\). The experimental BPM without GO catalyst was represented by a constant \(k_d\) and \(k_n\) throughout all the domains, denoted Model 1 uncatalyzed \(k_d/uncatalyzed k_n\). For BPMs with an interfacial GO layer, a spacing of 20 nm at the AEL/CEL interface was assumed to be occupied by the catalyst. This approach further assumes that the presence of the catalyst increased the value of \(k_d\) by three orders of magnitude. In two other models, the neutralization kinetics were either unaffected or increased by the presence of the interfacial catalyst, corresponding to Model 2 catalyzed \(k_d/uncatalyzed k_n\), and Model 3, catalyzed \(k_d/catalyzed k_d\), respectively. It should be pointed out that Model 2 is non-physical (but still instructive, \textit{vide infra}), because a catalyst for water
dissociation must also catalyze the reverse reaction. Comparison of the computational and experimental results shows that even though catalyzing $k_d$ alone is sufficient to reproduce the overpotential difference under reverse bias (Model 2), the higher current densities obtained in the BPM with GO at a given forward bias are reproduced only when both $k_d$ and $k_n$ are catalyzed (Model 3) (Fig. 4.2c and 4.2d).

Fig. 4.2. The effects of interfacial catalysis in BPM. (a) The experimental four-electrode setup for measuring the potential drop across the BPM. Using two reference electrodes eliminates the influence of the electrochemical reactions at the electrodes. KOH and HCl are used as the electrolytes on the AEL and CEL sides, respectively, of the BPM. The dashed box represents the region of interest that was modeled in numerical simulations. (b) The experimental setup was simplified as a one-dimensional model that includes four segments and two open boundaries (dashed box). This region corresponds to the region in a. To explore the effect of catalysis on the potential-current density relation under reverse and forward bias conditions, we compared three models. Model 1 simulates the experimental BPM without a catalyst, imposing constant $k_d$ and $k_n$; Models 2 and 3 assume the presence of a catalyst layer at the AEL/CEL interface, which increases $k_d$ by three orders of magnitude; the neutralization rate constant $k_n$ is also increased by the catalyst in Model 3, but not in Model 2. (c) Cross membrane potential-current density curves from the three models, compared to the experimental results in shown in (d). Only model 3 with catalyzed $k_d$ and catalyzed $k_n$ can reproduce the trends observed in BPMs with and without catalyst layers (GO, graphene oxide) under both reverse and forward bias. The dashed lines indicate the open circuit condition. Error bars represent the standard deviation of three independent measurements. (g) Concentration profiles of H$^+$ and OH$^-$ near the AEL/CEL interface (Model 3). The neutralization reaction is rate-limited by the negligible amount of either H$^+$ or OH$^-$ in the AEL/CEL, resulting in a narrow reaction zone as shown in (f). (g) The integrated reaction rate of the dissociation, and (h), neutralization processes over the reaction zone. The neutralization rate increases to a maximum under a small reverse bias, even though the net reaction at that point is water dissociation. The dashed lines indicate the open circuit condition for Models 2 and 3.
We next sought to quantify the local concentrations of the species (OH\(^-\), H\(^+\), and H\(_2\)O) involved in the dissociation and neutralization processes in BPMs. The ion distribution profiles reveal high concentrations of OH\(^-\) and H\(^+\) inside the AEL and CEL, but negligible amounts of co-ions K\(^+\) and Cl\(^-\) as 100% permselectivity was assumed for the ion exchangers (Fig. C.2). Diffusion boundary layers at the membrane/aqueous electrolyte interface can also be seen under both reverse and forward polarizations. The thickness of the depletion layer at the AEL/CEL interface decreases as more ions are driven into the membrane under forward bias (Fig. C.2b). The depletion layer also causes most of the potential drop to be in the junction region (Fig. C.3). A key point is that the neutralization reaction requires the presence of both OH\(^-\) and H\(^+\) ions, most of which, however, are spatially confined by the immobilized charge in the bulk of the AEL and CEL (Fig. 4.2e). The overlap of these two species is limited to a narrow region at the AEL/CEL interface, where the concentration of the major charge carrier (OH\(^-\) for AEL and H\(^+\) for CEL) decreases rapidly in the direction of the other ion exchanger (CEL and AEL) (Fig. 4.2e). Significant reaction rates of dissociation and neutralization are found only in a region of ~ 2-3 nm thickness (the reaction zone) (Fig. 4.2f and C.4). The diffusional transport of OH\(^-\) and H\(^+\) into the CEL and AEL, respectively, is balanced by the electrostatic force at open circuit; further penetration, and thus higher reaction rate, would require the application of an increased forward bias (Fig. 4.2f).

To explore the effect of catalysis, we compared the integrated reaction rates of the dissociation and neutralization processes over the reaction zone for the three different models. The dissociation rate increases monotonically as the applied potential increases, which also results in an increase in the electric field (Fig. 4.2g and C.5). The neutralization rate decreases to a minimum around the open circuit potential (~300/500 mV for Models 2/3) and increases under reverse bias (Fig. 4.2h). Models 2 and 3 with catalyzed \(k_d\) exhibit larger dissociation rates over the whole potential range, as well as an accelerated neutralization rate even with an uncatalyzed \(k_n\) (model 2) under reverse bias. The net reaction in the reverse-biased BPM (800 mV, Fig. 4.2e) is water dissociation as evidenced by the changes in water concentration (Fig. C.6), but it produces the rate-limiting species OH\(^-\) and H\(^+\) in the CEL and AEL, respectively, which in turn intensifies the neutralization reaction.
The correlation between the two reactions also suggests the important role of water, which is sufficient when aqueous electrolytes are used, but might become a limiting factor in water-vapor fed devices such as H₂-O₂ fuel cells. Finally, increasing the catalytic acceleration to more than three orders of magnitude induces relatively smaller current changes in forward bias relative to that seen in reverse bias (Fig. C.7).

With the reaction zone for neutralization limited to the nanoscale region in which both reactants are present, mechanisms that effectively increase the local concentration elsewhere should increase the overall reaction rate. By assuming the presence of trap states in the bulk of the membrane, a trap-assisted recombination process was proposed that theoretically predicted a 4-5 orders of magnitude higher achievable current density than in the case without traps. The mechanism by which the GO catalyst in the experimental BPM increases the acid-base neutralization reaction remains unknown and requires further investigation, but the study of the opposite process (dissociation) has recently received significant attention and could potentially provide useful insight.

### 4.2.2 BPM based acid-base redox flow battery

Based on our understanding of the catalyzed acid-base neutralization process, we explored the incorporation of a BPM-based pH gradient into a conventional redox flow battery. Cell testing was conducted at room temperature by dissolving ferrocyanide in 2 M KOH as the positive electrode, and either the electroneutral viologen derivative SPV, or 2,7-difulfonate-9,10-anthroquinone (DSAQ) (Fig. 4.3a) in 1 M H₂SO₄ as the negative electrode (Fig. 4.1a). The electrolytes were separated by a BPM with the AEL/CEL facing the positive/negative sides, respectively. The polarization results were collected after applying a charging current of 30 mA/cm² to reach ~ 100% state of charge. Incorporating a GO catalyst into the BPM results in significantly improved cell performance for both the charging and discharging process (Fig. 4.3b) because of the enhanced dissociation and neutralization kinetics as discussed above (Fig. 4.2d).
To successfully harness the pH-derived cross-membrane potential in the acid-base redox flow battery, pH-independent redox couples are desired as the voltage gain due to the pH gradient could be offset by Nernstian shifts in the formal potentials of the molecules. To illustrate this concept, we compared two redox reactions that had distinct dependences on the pH at the negative electrode. The formal potential of the SPV redox couple is unaffected by pH (Fig. 4.3c) whereas that of DSAQ shifts positively as the pH changes from 14 to 0 (Fig. 4.3e). When coupled with ferrocyanide in base as the positive redox couple, SPV operating in acid results in an open circuit voltage of ~1.6 V, whereas a single alkaline condition gives only ~0.94 V using the same redox pair (Fig. 4.3d). The acid-base configuration therefore retains a large portion (~0.66 V) of the pH-derived cross-membrane potential (theoretically 0.83 V). In comparison, the cell with DSAQ shows only a ~0.35 V potential increase (Fig. 4.3f), with the remaining potential being lost due to the positive shift of the negative electrode in acid.

Fig. 4.3. Performance of the acid-base redox flow battery. (a) Structures of the redox couples used at the negative electrode. SPV: 1,1'-bis(3-sulfonatopropyl)-4,4'-bipyridinium, DSAQ: 2,7-diflufonate-9,10-anthroquinone. 0.1 M ferrocyanide in 2 M KOH was used as the positive electrolyte for all the cell performance tests. (b) Cell performance with and without GO as the catalyst in the BPM. Improved performance can be achieved using BPMs with GO due to the increased dissociation and neutralization rate constants. Electrolyte: 0.1 M DSAQ (1M H₂SO₄) in the negative electrolyte. (c) Cyclic voltammogram (CV) of 0.1 M SPV in 1 M H₂SO₄ (magenta) or in 1 M KOH (blue), and 0.5 M ferrocyanide in 1 M KOH (red); and CV of 0.1 M DSAQ in 1 M H₂SO₄ (magenta) or in 1 M KOH (blue), and 0.1 M ferrocyanide in 1 M KOH (red). The SPV redox couple is pH-independent whereas the formal potential of DSAQ shifts positively at lower pH. (d) and (f) Potential and power density versus current density curves at ~100% state of charge. With the common positive electrode, operating SPV in acid (acid-base with BPM) increases the cell potential by ~0.66 V compared to a cell operated under a single alkaline condition (alkaline with CEM). The same comparison with the DSAQ redox couple shows ~0.35 V increase in the cell potential.
The polarization test showed significant mass transport limitation at high current density during the discharging process. We thus carried out EIS measurements of the full cell in order to understand the impedance losses due to various processes. The EIS results indicated that impedance losses are associated with the series resistance (high frequency, \( \sim 10^5 \) Hz), the reaction kinetics inside the BPMs (intermediate frequency, \( \sim 10^3 \) Hz), and mass transport (low frequency, \( \sim 0.1 \) Hz) (Fig. C.8). When the concentration of redox molecules is low (0.05 M), the mass transport resistance increases under high forward bias, whereas changes in the dissociation and neutralization kinetics at the AEL/CEL interface are insignificant. On the other hand, more concentrated redox couples (0.3 M) lead to a slower neutralization process (Fig. C.9) because the negatively charged \( \text{Fe(CN)}_6^{4-}/\text{Fe(CN)}_6^{3-} \) species tends to compete with the charge carrier \( \text{OH}^- \) for sites in the AEL, limiting the amount of \( \text{OH}^- \) that is available for the neutralization reaction. A balance between the kinetic and transport resistance is achieved at intermediate concentrations (0.1 M and 0.15 M, Fig. C.10), resulting in the best discharging performance (Fig. 4.4a). Designing stable and positively charged redox couples for the positive side of the flow battery is thus a promising avenue for improving device performance.\(^{29-31}\) The cyclability of the acid-base redox flow battery depends on the chemical stability and the crossover rates of the redox couples, as well as the durability of the BPMs. Stability tests of BPMs under reverse bias (charging process) have been done,\(^ {17,26,32}\) but there are limited demonstrations of stable BPMs operating under forward bias. Nevertheless, preliminary charging-discharging tests suggest little performance degradation during the first ten cycles (Fig. 4.4b), even though more intensive cycling tests are still needed. Finally, the influence of the side reaction of water splitting is significant only at high cell potentials (> 2V, Fig. C.11), which is above the charging limits of our tests.
Fig. 4.4. Cell performance at different concentrations of ferrocyanide and cycling test. (a) Polarization and power density curves of cells operating at different concentrations of ferrocyanide in 2 M KOH; a negative electrolyte of 0.4 M DSAQ in 1M H₂SO₄ was used. The best cell performance was observed at intermediate concentrations (0.15 M). (b) Potential and current density versus time during the first ten charge-discharge cycles.

4.3 Conclusions

An acid-base redox flow battery was developed using a BPM that enables the positive and negative electrodes to operate under alkaline and acidic condition, respectively. The creation of a stable pH gradient allows the cross-membrane potential to be added to the formal potential differences of the redox molecules, resulting in a substantially increased cell potential relative to the same molecules at a single pH. The transport of H⁺ and OH⁻ is coupled to the water dissociation and acid-base neutralization process at the AEL/CEL interface in the BPM. Through a combined experimental and numerical simulation study, we found that the rate limiting factor in the acid-base neutralization reaction is the concentration of minority ions (H⁺ for AEL and OH⁻ for CEL), and equipping the interface with a catalyst significantly increases the reaction rate, resulting in higher discharging performance of the redox flow battery.

This study has demonstrated the principle by which a bipolar membrane-based redox flow battery can achieve higher voltage and thus higher energy storage capacity. This was shown at the proof-of-concept level by using off-the-shelf redox couples (ferro/105errocyanide and SPV) that are not indefinitely stable in the flow battery environment; for example, 105errocyanide is subject to slow decomposition in strong base, and SPV is air-sensitive in its reduced forms. Designing
stable redox molecules that are compatible with the acid-base environment and the electrostatic charges in the AEL/CEL is a remaining challenge, and such redox couples could also lead to higher power redox flow batteries. The long term stability of the flow battery also requires stable operation of BPMs under forward bias conditions and minimal species crossover, which depends on the size, charge, and pH of the electrolyte.\textsuperscript{33}

4.4 References


(8) Sevov, C. S.; Hickey, D. P.; Cook, M. E.; Robinson, S. G.; Barnett, S.; Minteer, S. D.; Sigman, M. S.; Sanford, M. S. Physical Organic Approach to Persistent, Cyclable, Low-


Chapter 5

Managing mass transport in alkaline fuel cells

Abstract

H₂-O₂ fuel cells provides an appealing solution to the problem of efficiently converting renewably generated hydrogen (e.g., from water electrolyzers) into electricity. In addition to the problem of leveling renewable electricity production with power demand, there is a critical need for fuel cell technology in the transportation sector, for example in long-haul trucking where long battery recharging times may preclude the use of electric vehicle technology. A technical challenge – especially for alkaline fuel cells that can utilize non-precious metal catalysts - is the limitation of their efficiency by the transport of different species in the catalyst layers. Our understanding of mass transport is hindered by a lack of detailed knowledge of the structures at both microscopic and system levels. Here, we present an unconventional architecture for the oxygen reduction reaction (ORR) electrode that offers better control over microscopic structure. This electrode architecture has been successfully demonstrated in gas-fed CO₂ electrolyzers, where current densities in excess of 1 A/cm² were achieved. The electrode is comprised of a sputtered catalyst film on a porous PTFE membrane, and its successful functioning in an alkaline fuel cell was found to depend critically on the ionomer loading. The combined use of electrochemical impedance spectroscopy (EIS) and numerical modeling helps to elucidate the essential role of ion and gas transport at low and high ionomer loadings, respectively. This electrode architecture provides a new way to construct the catalyst layers of fuel cells, and could be useful for understanding mass transport processes in various gas-fed electrochemical devices that employ membrane electrode assembly (MEA) configurations.
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5.1 Introduction

The net-zero carbon economy can be achieved by shifting to renewable energy sources such as solar and wind. The intermittency of these sources requires robust means to store the surplus energy in a stable form, which can be converted back to electricity during the peak demand.\textsuperscript{1,2} While the short-term storage problem can be addressed with efficient lithium ion-batteries, batteries are impractical for long-term (seasonal) storage or for long-haul transportation applications where cost and long charging times preclude their use. \text{H}_2-\text{O}_2 fuel cells hold great promise for both applications since they can convert chemically stored energy to electricity with high efficiency. Among the various kinds of fuel cells, alkaline polymer electrolyte fuel cells (APEFCs) enable the use of earth-abundant catalysts and could potentially rival their acidic counterpart, the proton exchange membrane fuel cells (PEMFCs) in efficiency, stability, and cost.\textsuperscript{3-5}

Many efforts have focused on designing fuel cell electrocatalysts with high activity and long durability, and on advancing our understanding of the interfacial charge transfer kinetics of hydrogen oxidation and oxygen reduction. On the other hand, the problem of species transport represents an important and complex problem at the system level that is not well understood. Rotating disk electrode (RDE) voltammetry is generally used for fast catalyst screening as it offers a relatively simple and precise control of convective flow for mass transport. The effect of mass transport can be accounted for using the well-known \textit{Koutecky-Levich} equation. The problem becomes more complicated when one switches to a fuel cell device where the catalysts coat the ion exchange membrane to form a membrane electrode assembly (MEA).\textsuperscript{6-8} Species transport in the catalyst layer is a multiscale phenomenon that involves the transport of gaseous reactants in the flow channels and the gas diffusion layers (GDL) with macroscopic pores (> 1 µm). The stacking of the catalyst, support, and ionomers generates narrower pores that collide with the gas molecules and slow down diffusion, while the microstructures in the catalyst support layer affect the transport at the local scale. Mass transport is also a multi-phase problem. The catalyst layer consists of a
random mixture of the solid catalyst and support particles, soft materials such as ionomers, condensed liquid water, and the gaseous reactants and water vapor.

The triple-phase boundary (TPB) theory assumes that the electrochemical reaction occurs mainly at regions where the catalyst/support, ionomer, and gas pores meet, providing the electronic, ionic, and gas transport pathways respectively. While the validity of the theory has been confirmed at a relatively large scale,\(^9,10\) the governing principles at the microscopic level remains unclear. For example, supports abundant in micropores (~4 nm) have been shown to enhance the activity because the catalyst nanoparticles deposited inside these pore are free of ionomer on their surface and thus their poisoning effect, leaving the ionic conduction pathway as an open question.\(^11\)

The supramolecular structure and behavior of ionomers also change dramatically in confinement, i.e., when the dimensions change from the micron to nanometer regime,\(^12\)–\(^14\) the latter being the typical thickness of the ionomer films in the catalyst layer.\(^15\)

Correlating microscopic transport theory with the macroscopic performance of fuel cells remains a challenge due to our lack of knowledge of the catalyst layer structure and its individual elements. Detailed characterization of the microstructure has been attempted by using techniques such as the nano-scale X-ray computed tomography (nano-CT)\(^16\) and cryo-STEM\(^17\), generating useful information only at certain scales. Novel designs of the catalyst layer that offer better control of the local structure would thus be beneficial. For example, it is possible to construct an ionomer-free architecture in which a nano structured thin film (NSTF) catalyst layer serves to conduct both the electrons and ions.\(^18\) Recently, Sargent et al. designed a catalyst/ionomer heterojunction to decouple the transport pathways for electrons, ions, and gas molecules in a CO\(_2\) electrolyzer, achieving \(\sim 1.2 \text{ A/cm}^2\) CO\(_2\) to ethylene current density.\(^19,20\)

Designing catalyst layers with more controllable architectures will greatly facilitate the study of molecule and ion transport processes and their impact on macroscopic performance. In this study, we monitored the transport of H\(_2\) gas using electrochemical impedance spectroscopy (EIS) of the alkaline hydrogen oxidation reaction (HOR) in an aqueous RDE experiment, where the gas diffusion could be well separated from the electrode charge transfer process. We then explored the
mass transport in an MEA configuration in which a thin Pt or Ag catalyst film was sputtered onto a porous polytetrafluoroethylene (PTFE) membrane, which was used as the oxygen reduction reaction (ORR) electrode for APEFCs. A much lower optimal ionomer loading was found for the Pt/PTFE architecture compared to the conventional catalyst layer. EIS measurements combined with numerical modeling revealed that the transport of oxygen gas was significantly reduced at higher ionomer coverage beyond a certain loading threshold. Quantitative resistance values obtained by fitting the EIS spectra to the proposed equivalent circuit explained the mass transport constraints at different ionomer loadings.

5.1 Results and discussion

5.2.1 The transport of $\text{H}_2$ gas in the aqueous RDE experiment

![Figure 5.1](image)

We began by carrying out EIS measurements on a Pt/C electrode in an RDE setup for the alkaline HOR process. The spectra exhibited two semicircles (Fig. D.1), with a lower frequency peak (~0.5 Hz) that depended on the rotation rate and a higher frequency one (~10 Hz) that
depended on the applied overpotential, (Fig. 5.1). The semicircle centered at ~ 0.5 Hz thus represents the transport of H₂ gas in the aqueous electrolyte, while the higher frequency arc is related to the electrode reaction as it is affected appreciably by the electrode potential. Similar H₂ transport behavior was observed in 0.1 M HClO₄, which was enhanced by increasing the rotation rate but not the applied potential (Fig. D.2). The effect is more obvious in the acidic electrolyte because of the disappearance of the reaction semicircle due to the much faster HOR reaction kinetics (Fig. D.3). Even though the transport in the RDE setup differs from those in the fuel cells, the ease of managing the mass transport offers an effective control system for comparison with the MEA configurations (vide infra).

5.2.2 Design of the catalyst layers

A typical two-electrode EIS spectrum of the conventional MEA configuration consists of two semicircles, possibly corresponding to the charge transfer and gas diffusion processes (Fig. D.4). Due to the complex structure of the catalyst layer, a precise interpretation of the EIS data remains a challenge. Following the design of Sargent, et al., we thus sought to create ORR electrodes by sputtering an Ag or Pt catalyst film onto a porous PTFE membrane. A nominally 400 nm thick metal layer was deposited as the catalyst layer (Fig. D.5). The anode HOR electrode was kept the same as in the conventional geometry by spraying a homogenized PtRu/C/ionomer ink on the AEM.

The sputtered Ag and Pt form continuous and dense films along the PTFE fibers, while retaining the original porous structures of the pristine substrate (Fig. 5.2a and 5.2b). Interestingly, without adding any ionomer, the Ag/PTFE electrode achieves ~ 1 A/cm² current density and ~ 170 mW/cm² peak power density (Fig. 5.2c), while the Pt/PTFE behaves very poorly under the same operating conditions, < 0.1 A/cm² and ~ 15 mW/cm² (Fig. 5.2d). The difference might be caused by the different surface properties of the Ag and Pt films, where the former can effectively acts as an ion conductor but the latter cannot. To test the hypothesis, we then sprayed a thin ionomer film onto the metal coated PTFE membranes. Adding the same amount of AEM ionomer (75 µL/cm²)
as in the conventional MEA to Pt/PTFE leads to a much improved fuel cell performance, 0.4 A/cm\(^2\) vs 0.08 A/cm\(^2\) (Fig. 5.3a). In contrast, the polarization and power curves of the Ag/PTFE with and without added ionomer show similar trends (Fig. D.6). This indicates the possible role of Ag as the surface ionic conductor, and suggests that the Pt/PTFE electrode requires the AEM ionomer in order to conduct ions. Replacing the AEM ionomer with the cation exchange ionomer Nafion results in poorer performance (Fig. D.7). This differs from the previous report using Nafion and Cu/PTFE for CO\(_2\) electrolysis,\(^{19}\) where the high current density may involve fast transport of the counter ions (HCO\(^3\), OH\(^-\)) in the Nafion film, which would show lower permselectivity in alkaline aqueous electrolytes.\(^{22}\)

![Image of catalyst layer with novel architectures.](image)

**Fig. 5.2.** Catalyst layer with novel architectures. Scanning electron microscope (SEM) images of the (a) Ag/PTFE and (b) Pt/PTFE. The polarization and power density curves of the APEFCs using the (c) Ag/PTFE and (d) Pt/PTFE as the ORR electrode. The anode: 0.4 mg\_metal/cm\(^2\) PtRu/C (60 wt%); AEM and ionomers: quaternary ammonia poly (N-methyl-piperidine-co-p-terphenyl) (QAPPT).\(^4\) The cell was heated at 80 °C, humidified H\(_2\) and O\(_2\) gas are fed with a flow rate 500 mL/min.
A dramatic impact of the AEM ionomer loading on the fuel cell performance was found for the Pt/PTFE electrode (Fig. 5.3a and 3b). Increasing the loading from 2 to 6 µL/cm² improves the limiting current density and peak power density from ~ 0.1 to > 0.8 A/cm², and < 50 to ~ 280 mW/cm², respectively. A further increase in loading above 6 µL/cm² leads to decreased performance (Fig. 5.3). The metallic loading in the 400 nm Pt/PTFE was measured to be ~ 1 mg/cm², which is about twice as high as in a conventional MEA cathode. Decreasing the thickness of the Pt film to 300 nm results in a lower cell performance (Fig. D.8). The requirement of high precious metal loading might be mitigated by sputtering a conductive support layer before depositing the thin catalytically active film.

![Fig. 5.3. The effects of ionomer loading on the fuel cell performance. (a) Polarization curves and (b) the power density curves. The testing conditions are the same as in Fig. 5.2, and can be found in the experimental section in the Appendix D.]

### 5.2.3 Mass transport in the PTFE-supported catalyst layer

We next explored mass transport in the catalyst/PTFE architecture by combining EIS measurements and numerical modeling. The model simulates a single Pt/ionomer coated PTFE fiber in the one-dimensional domain (Fig. 5.4a and 5.4b). It consists of a 400 nm porous electrode domain and a 10 µm electrolyte segment, the former accounting for the transport of electrons by the Pt film, ions by the ionomer, and gas by the gas-filled pores and PTFE fibers, while the latter
describes ionic transport within the electrolyte. We assumed an electrochemical-chemical-electrochemical (ECE) mechanism for the ORR process in the porous electrode (a detailed discussion is available in Appendix D). Two types of boundary conditions are compared, which fix the concentration of oxygen gas at the open boundary of the electrode (model 1) or the electrolyte (model 2). The first model represents the conditions in the novel architecture and the second resembles those in the RDE setup where the gas must diffuse through the electrolyte for the electrode reaction.

The experimental EIS spectra were taken at low overpotential (high cell voltage, 0.75 V) to minimize interference from the anodic HOR process, and thus can be considered as characteristic of the ORR electrode. The spectra consist of a semicircle and an inductive loop at high and low frequencies respectively (Fig. 5.4c). Similar inductive behavior has been observed in earlier reports. The presence of inductive loops has been proposed to be associated with intermediates in reactions involving two electrochemical steps, even though the physical origin remains elusive. The simulated EIS from model 1 reproduces the main features of the experimental spectra (Fig. 5.4f), while model 2 generates a spectrum reminiscent of those in the RDE setup (Fig. 5.4i and D.1).
To query the origin of the features in the EIS spectra and correlate them with the underlying processes, we simulated the spectra in the time domain, which enables tracing the phase shifts of multiple variables. The time domain approach mimics the experimental procedure in which the ac current response $i(t)$ to an ac voltage input $v(t)$ is collected at the electrode surface. The impedance was calculated by Fourier transforming the ac signals to the frequency domain. The validity of the time-domain model was confirmed by comparing with the frequency-domain model, which showed similar results in both the Nyquist and Bode plots for a system coupling an electrochemical reaction and a diffusional process (Fig. D.10). At low frequencies (~1 Hz) that correspond to the inductive loop region, the response $i(t)$ lags behind the input $v(t)$ (Fig. 5.4d) in the experiment, a feature reproduced by model 1 (Fig. 5.4g). At higher frequency, ~ 876 Hz in the experiment and ~ 10000 Hz in model 1, the opposite phase shift was observed (Fig D.11a and D.11b). As seen from the results in model 1, the capacitive current at higher frequency dominates...
and contributes to the capacitive arc in the Nyquist plots (Fig. D.11d). This contribution diminishes significantly and becomes smaller than the reaction current response at lower frequency, ~ 1 Hz (Fig. D.11c). In comparison, the current response \( i(t) \) in model 2 leads the voltage input \( v(t) \) at low frequency 10 Hz (Fig. 5.4j) even though the capacitive current is suppressed (Fig. D.11e).

The phase shifts of the system were determined by the reaction current response at low frequencies. We then monitored the phase shifts of the various parameters in the current expression, \( i = -F k_b c_{O2} \exp(-\alpha f \eta) \), including the oxygen concentration \( c_{O2} \) and overpotential \( \eta \), for the rate limiting step (a discussion of the full reaction mechanism is available in Appendix D):

\[
(\text{O}_2)_{ad} + \text{H}_2\text{O} + e^{-} \xrightarrow{k_b} \text{O}_2\text{H}_{ad} + \text{OH}^{-}
\]

The lagging phase of the overpotential \( \eta \) is the major contributor to the phase shift of the ac current in model 1 (Fig. 5.4h), as the oxygen concentration is set by the boundary conditions (Fig. 5.4b). For model 2, the phase of the current response is determined by the combined effect of the oxygen concentration \( c_{O2} \) and overpotential \( \eta \), where the former lags (Fig. 5.4k) and the latter leads (Fig. D.11f) the voltage input. Taken together, the phase analysis suggests that the inductive loop in model 1 was caused by the lagging response of the overpotential, while both the \( c_{O2} \) and \( \eta \) contribute to presence of the capacitive arc in model 2. The \( c_{O2} \) boundary condition in model 2 mimics the RDE experiment where diffusion through a bulk electrolyte is necessary, which is hypothesized to mask the inductive features observed in EIS spectra in earlier studies.\(^{23}\)

We then aimed at building an equivalent circuit to fit the EIS spectra. With the understanding that the inductive loop is closely related to the overpotential \( \eta \) that serves as the driving force for the electrochemical reaction, we added an inductor \( L_1 \) in parallel with a resistor \( R_1 \) in the Randles equivalent circuit (Fig. 5.4e). The parallel positioning of the inductor \( L_1 \) automatically sets the potential (and thus the driving force) for the reaction represented by the resistor \( R_1 \). The resistor \( R_3 \), constant phase element \( CPE_1 \), and Warburg \( W_1 \) correspond to the series resistance, a distributed interfacial capacitor, and the diffusion process respectively.\(^{26}\) The experimental and modeled EIS spectra at different potentials can be fitted to the proposed equivalent circuit well (Fig. D.12 and D.13), with a resulting \( \chi^2 \) between \( 10^{-4} \) and \( 10^{-5} \) (Table D.3 and D.4). Qualitatively, the
peak position of the higher frequency arc shifts to higher values while that of the lower frequency inductive loop remains unchanged as the overpotential increases (Fig. D.12), a trend that can be reproduced by model 2 (Fig. D.13). Resistance extracted by the fitting scheme showed decreased values for $R_s$, $R_1$, and $W_1$ at increased overpotentials for both the experimental and modeled EIS spectra (Fig. D.14).

Fig. 5.5. Experimental Nyquist plots with different ionomer loadings (a) 2 uL/cm$^2$, (b) 6 uL/cm$^2$, and (c) 75 uL/cm$^2$. Modeled spectra in model 1 with oxygen diffusion coefficients decreased by (d) 10-, (e) 100-, and (f) 1000-fold. $D_{O_2} = 7.9 \times 10^{-9}$ m$^2$/s. The Nyquist plots become more suppressed with increased ionomer loadings, which is similar to the trends by reducing the diffusion coefficients of oxygen in the modeling.

To study the effects of the ionomer loading on the mass transport, we compared the EIS spectra of the catalyst/PTFE fiber architecture with loadings at 2, 6, and 75 µL/cm$^2$. Overall, the spectra showed similar features of higher frequency semicircles and a lower frequency inductive loop in the Nyquist plots (Fig. 5.5a, 5.5b, and 5.5c). Interestingly, the semicircle becomes more suppressed at higher loading of ionomer. A similar trend can be reproduced in model 1 by decreasing the diffusion coefficients of oxygen $D_{O_2}$ in the porous electrode (Fig. 5.5d, 5.5e, and 5.5f). One striking similarity between the experimental and modeled EIS is the appearance of a
new semicircle at high frequencies with 75 µL/cm² ionomer (experiment, Fig. 5.5c) and decreased $D_{O_2}$ (model 1, $D_{O_2}/1000$, Fig. 5.5f). The comparison hints that a higher ionomer coverage may decrease the diffusion rate of the oxygen by blocking the pores within the catalyst layer in the catalyst/PTFE fiber geometry.

![Graph](image.png)

**Fig. 5.6.** Resistance values extracted from fitting the experimental EIS spectra to the equivalent circuit in Fig. 5.5e. (a) Comparison between 2 and 6 µL ionomers at cell voltage of 0.75 and 0.70 V. Smaller cell voltage corresponds to larger overpotential. (b) Resistance comparisons between 6 and 25 µL ionomers at DC current density of 0.208 and 0.333 A/cm². WR represents the diffusion resistance of the Warburg $W_R$ element at $\omega \to 0$. Galvanostatic mode was used in (b) while potentiostat mode in (a), but the equivalency of the two modes was confirmed in Fig. D.9.

We next quantified the resistance of the different processes by fitting the EIS spectra to the equivalent circuit. For ionomer loadings below 6 µL/cm², the resistance values of $W_R$, $R_s$, and $R_1$ decrease with increasing ionomer loading (Fig. 5.6a), suggesting that sufficient ionomer coverage is needed to facilitate ionic transport, lowering the series resistance and concentration polarization. For larger amounts of ionomers, we compared data for catalyst layers with 6 µL/cm² and 25 µL/cm² loadings at higher overpotentials, because the latter show significantly different polarization behavior in fuel cells only at high overpotentials (Fig. 5.2a) but similar features in the EIS spectra as the former (Fig. 5.5a and 5.5b). Higher transport resistances $W_R$ were observed in the 25 µL ionomer case, which is consistent with blocking effects of the ionomer film on oxygen diffusion beyond a certain loading threshold (Fig. 5.6b). On the other hand, the series and reaction resistance were similar between the 6 and 25 µL/cm² ionomer loadings. Resistance values
extracted from the modeled EIS with different oxygen diffusion coefficients agree well with the experimental trends, exhibiting lower $W_R$ and similar $R_s$ and $R_1$ with increasing $D_{O_2}$ (Fig. D.15).

Resistance values from the EIS fitting suggest different transport constraints for the low and high ends of the ionomer loadings. Sluggish ionic transport is expected with minimal amounts of ionomers, 0 and 2 µL/cm², which also increases the reaction resistance $R_1$ through the concentration polarization. Excessive ionomer, 25 and 75 µL/cm², mainly inhibits the diffusion of oxygen gas, possibly by obscuring the pores in the Pt/PTFE electrode. Model 1 was able to reproduce the effects of lower $D_{O_2}$, but was found to be insensitive to the transport of $OH^-$. This aspect of the model might be improved by accounting for the microscopic distributions of the ionomer and the catalyst film. The microscopic picture of the catalyst/ionomer interface could be different from the conventional MEA configuration because the optimal ionomer loading (6 µL) in the current architecture is ~ one order of magnitude lower than that in the conventional design. The proposed equivalent circuit allows for a better fitting to the modeled EIS than the experimental spectra, $\chi^2 \sim 10^{-5}$ vs $10^{-4}$ (Table D.2 vs D.4). One drawback of the circuit in fitting the experimental EIS is the sensitivity to the initial conditions due to the presence of two distributed elements, $W_R$ and $CPE_1$, in the circuit but only one major semicircle in the EIS spectra (except for at higher ionomer loading). This leads to two fitting results that differ slightly in the resistance values but show the same overall trends as discussed above (Table. D.4, D.5 vs D.6, D.7). The catalyst/PTFE fiber architecture offers easier control over the organization of the catalysts and ionomer, and thus the study of the effects of microstructure on mass transport and the fuel cell performance. This study will be further assisted by higher dimensional models that incorporate these structural features. The catalyst loading in the current design is high compared with that of conventional MEAs, but could be reduced by co-sputtering conductive substrates and thin catalyst films. One interesting finding is that the Ag/PTFE electrode reaches a high current density (~1 A/cm²) without added ionomer. The large activation overpotential (~0.38 V, Fig. 5.2a) at lower current densities can potentially be mitigated by employing alloyed catalysts with higher activities.27
5.3 Conclusions

In summary, we studied the mass transport in both the aqueous electrolyte environment and in an MEA geometry relevant to APEFCs. While the aqueous RDE setup allows for a relatively simple control of the mass transport, the study of mass transport in the MEA configuration is facilitated by designing a different architecture for the ORR electrode. This design employs a porous PTFE membrane sputtered with a thin Ag or Pt film as the catalyst. The ionomer loading was found to significantly affect the mass transport and the fuel cell performance for the Pt/PTFE electrode. Assisted by EIS and numerical modeling tools, the transport of ions and gases were proposed to limit the performance at lower and higher ionomer loadings. While the initial results of the catalyst/PTFE fiber architecture are encouraging, future efforts are still needed to improve the design such as reducing the catalyst loading and optimizing the substrate porosity. Compared with the conventional MEA configuration, the fiber architecture offers better control over the microstructure in the catalyst layer, which will be beneficial for studying the mass transport in a variety of gas-fed electrochemical devices.

5.4 References


Chapter 6

Conclusions and perspectives

A zero-carbon emission energy economy has been envisioned for many years, and as more countries are pledged to achieving that goal in the coming few decades, the likelihood of us being able to see its realization is getting higher. A major hurdle to 100 % renewable energy deployment is the intermittency of renewable sources such as wind, solar and even hydro, which requires efficient ways to store surplus energy. Electrochemistry has the potential to mitigate the problem by converting between electricity and chemicals, while photoelectrochemistry further eliminates the wiring process that allows for more flexibility in real-world applications.

A wide variety of electrochemical systems have been proposed, each with different characteristics in energy capacity and levels of maturity. While some of them have achieved faster advances and commercialization at small scales such as the PEM water electrolyzer and solid oxide CO2 cells, none have the capability to store terawatt hours of electricity at reasonable cost with the current state-of-the-art technology. To keep our choices open, the current thesis thus explored a wide range of devices: water and CO2 electrolyzers, redox flow batteries, and fuel cells.

A key idea developed by carrying out this thesis work is that basic knowledge is transferable among different devices, though there are requirements specific to particular ones. Two types of such knowledge relate to ion management and mass transport, corresponding to chapters 2, 3, 4 and 5, respectively. The use of BPMs provides an elegant solution to the ion transport problem of bulk electrolytes, and the acidic local environment facilitates the cathodic hydrogen production for the water electrolyzer but lowers the CO2 reduction efficiency in CO2 electrolysis cells. This difference originates from the different reaction mechanisms of the HER and CO2RR. Whereas the rate limiting step of the former involves a concerted proton electron transfer, it is the first electron transfer process for the latter. While the use of acidic and alkaline electrolytes improves the reaction
kinetics but leaves the thermodynamic potentials unchanged for water electrolysers and H2-O2 fuel cells, this is not the case for redox reactions without the participation of protons or hydroxide ions. This feature was employed in the acid-base redox flow battery, which adds the extra cross-membrane voltage to the overall battery potential.

Beyond being relevant to ion transport, the study of the equilibria between H2O, H+, and OH-, the key fundamental processes in the BPM, coincides with the resurgent interest in water structure during electrochemical reactions. From the thermodynamic point of view, the production of H2 in alkaline solutions is equivalent to the combined process of (a) the dissociation of water to H+ and OH-, and (b) the reduction of H+ to H2. This concept has recently been explored by correlating the water dissociation overpotential to that of the alkaline HER process. From a fundamental perspective, the water dissociation process was proposed to be initiated by local solvent fluctuation and assisted by the solvent electric field, a process reminiscent of Marcus theory for outer sphere charge transfer. Is it possible, then, to apply the same set of principles to the water dissociation process, i.e. by calculating the polarization of the solvent molecules induced by the separation of the proton and hydroxide ion and the associated free energy change? Unlike in the case of Marcus theory, there is now net change in the atomic configurations that would contribute to the free energy difference. Current theory also proposes a protonation-deprotonation mechanism for the water dissociation reaction (Appendix A), the validity of which has yet to be confirmed.

The understanding of water dissociation is closely tied to the opposite process, acid-base neutralization. The sluggish dissociation process was thought to be caused by the rapid recombination between the protons and hydroxide ions. Interestingly, in Chapter 4 we found that the addition of a graphene oxide (GO) catalyst in the BPM junction significantly accelerates the recombination process compared with uncatalyzed samples. We proposed at the phenomenological level that this is due to a narrow reaction zone where the overlap of proton and hydroxide ion concentrations occurs, indicating that the overall reaction rate is slow and possibly diffusion limited. Reminded by the fact that the hydrogen oxidation reaction (HOR) proceeds ~ 2 orders of magnitude slower in base and the oxygen reduction reaction (ORR) ~2 times slower in
acid, we further note a common feature in the two processes: there is acid-base recombination buried in the net reaction. For example, similar to the alkaline HER consideration above, the net reaction of the alkaline HOR is \(H_2 + 2OH^- - 2e^- \rightarrow 2H_2O\), which can be thought of consisting two steps (a) \(H_2 - 2e^- \rightarrow 2H^+\) and (b) \(2H^+ + 2OH^- \rightarrow 2H_2O\). The slower kinetics of the alkaline HOR could be explained if step (b) is slow and rate limiting. Indeed, several groups have proposed that the slower kinetics are caused by the more rigid structure of surface water in alkaline electrolytes, which might contribute to slowing down step (b). If the above picture proved to be true, the study of forward biased BPMs could be useful to guide the design of earth abundant HOR catalysts for alkaline fuel cells, a grand challenge that has hitherto not been solved.

So far, BPMs under reverse bias have received more attention than those operating in forward bias. It seems more challenging to operate the BPMs under forward bias as the process drives the ions to the BPM junction, where the rapid dissipation of charged ions is needed to maintain the depletion region. Future work should address ion crossover and the recombination reaction under forward biased conditions, which are relevant to the redox flow batteries and \(H_2-O_2\) fuel cells. The great promise of acid-base \(H_2-O_2\) fuel cells is the ability to operate the HOR and ORR in acid and base respectively, enabling the reduction of expensive metal loadings. However, the performance reported so far has been 1-2 orders of magnitude lower than the PEM or alkaline counterparts even at the same catalyst loadings. Characterizing BPMs under conditions relevant to fuel cell operation, i.e., with a water vapor feed, will be critical to fully evaluating their potential in fuel cells, as our current understanding of BPMs mainly comes from experiments in liquid aqueous electrolytes.

Mass transport is a complex problem for all gas-fed devices utilizing the membrane electrode assembly (MEA) configuration. The last chapter explores an alternative route to construct catalyst layers with more controlled microstructure. Mass transport is expected to be affected by the variations in the PTFE substrate, the catalyst, the thickness of the metal film, and the integration of the electrode with the AEM. The understanding of transport phenomena will be greatly assisted by higher dimensional numerical modeling incorporating these structural features. The 1D model in Chapter 5 represents our preliminary effort towards the goal. Operando characterization of the
catalyst layer in both the conventional and the PTFE fiber-based MEA will also provide valuable information for mass transport management.
Appendix A

Supporting information for chapter 2

A.1 Materials and methods

A.1.1 Materials

The commercial bipolar membranes used in this study were purchased from Fumatech FBM (Germany) with a thickness of around 150 μm; Nafion 117 dispersion (5%, in alcohol and water) was purchased from Sigma-Adrich; PPO (polyphenylene oxide), NMP (N-methyl-2-pyrrolidone), N,N-dimethylhexylamine, DMF (dimethylformate) and PDDA (polydiallyldimethylammonium chloride) were used as received from Sigma-Adrich; GO suspension (1 mg/mL, in water) was prepared following the method described by Kovtyukhova et al.\textsuperscript{1} Platinum wire (0.5 mm in diameter, 99.95%) was purchased from Alfa Aesar. Ag/AgCl (with 3 M NaCl filling solution) reference electrodes were purchased from BASI (MF-2052). All electrolytes were prepared using distilled and ion exchanged water (18.2 MΩ-cm) obtained from a Milli-Q Academic (model A10) water purifier.

A.1.2 BPM preparation

AEL Preparation\textsuperscript{2,3}

Brominated PPO with a DF (degree of functionalization) of 60 (2.5 g, 14.88 mmol) was dissolved in 30 mL of NMP. Then, N,N-dimethylhexylamine (0.52 g, 4.02 mmol) was added slowly. The mixture was stirred at room temperature for 48 h. N,N,N',N'-tetramethyl-1,6-hexamethylenediamine (0.51 g, 2.95 mmol) was added to the resulting mixture. Subsequently, the solution was cast onto
a levelled glass plate, and dried at 82 °C under ambient pressure for 24 h followed by vacuum
drying for 24 h at 80 °C to give a ~100 μm thick, transparent, tough film. The resulting membrane
was X27Y33 (33% diamine crosslinked) in the bromide form, where 27 represents total mol % of
Br groups being reacted with N, N-dimethylhexamine and 33 represents total mol % of Br groups
being reacted with N,N,N',N'-tetramethyl-1,6-hexamediamine.

**BPM Preparation**

Customized bipolar membranes were prepared with solvent-exchanged Nafion solution, GO
and a cross-linked AEL (anion exchange layer). Exchanging alcohol and water in the as-received
Nafion solution with DMF (dimethylformate) followed the procedure described in the literature. Briefly, 20 mL of Nafion solution dissolved in a short chain alcohol mixture was heated under vacuum in a water bath set at 50 °C, until the volume of the remaining solution was about 10% of the starting solution. Then 20 mL of DMF was added to the solution. The mixture was placed under vacuum at 80 °C. This process was repeated five times to ensure complete solvent exchange. The final 20 mL of solution was 5 % Nafion in DMF, denoted as DMF-Nafion. A bipolar membrane was fabricated by mounting a 3 cm× 3 cm AEL onto a glass substrate with double-sided tape. The edges of the exposed side of the AEL were covered with Kapton tape to mask a 2 cm × 2 cm area. The AEL was then modified with GO solution by layer-by-layer (LBL) assembly. A certain amount of GO solution (about 5 mL) was cast to cover the exposed AEL surface and left to stand for 20 minutes. After washing thoroughly with nanopure water, 5 mL of PDDA solution (\( M_w = 1.2 \times 10^5 \), 20 wt% in water), acting as polycation, was deposited onto the GO modified AEL. More layers of GO solution were cast if more than one layer of GO was desired. For BPM without catalyst (0GO BPM), less than 5 μL of GO solution was added to lower the resistance and to provide a better comparison with the BPMs with catalyst. The small amount of GO allows us to safely ignore the GO catalytic effect. After GO deposition, 400 μL of DMF-Nafion solution was cast onto the GO-modified AEL and the assembly was heated to 120 -130 °C on a hot plate for one hour to achieve higher cation
conductivity in the Nafion CEL. The bipolar membrane was then placed in a convection oven at 60 °C overnight before it was finally stored in 0.5 M KNO₃ solution before testing.

A.1.3 Membrane characterization

The cross-section of the customized bipolar membranes was characterized using field emission scanning electron microscopy (FESEM, FET NanoSEM 630, accelerating voltage 10 kV).

A.1.4 Electrochemical characterization

The direct current (DC) current density-voltage curve, J-E curve, was carried out in a four-compartment electrochemical cell, as shown in Fig. A.1. The BPM was subjected to a given current in the center of the cell, while two auxiliary membranes, one AEM and one CEM, were placed on each side of the test membrane to minimize the influence of the electrochemical reaction products at the working and counter electrodes. Two Pt wires, serving as working and counter electrodes, were used to apply current in the two outside chambers, while two Ag/AgCl reference electrodes were fixed in the two middle chambers using Haber-Luggin capillaries. The CEL of the studied BPM was in contact with 0.5 M HCl solution, and the AEL side was in contact with 0.5 M NaOH solution. Electrolyte solution was flowed through the cathode and anode chambers using a peristatic pump.

Prior to the J-E curve measurements, the BPMs were conditioned in pure water overnight. Galvanostatic steps were applied for 5 minutes at each current density to allow the membrane to achieve steady state. The potential drop across the BPM was then recorded as the potential difference between the two reference electrodes. Reported results were averaged from three repeats.

Electrochemical impedance spectroscopy (EIS) measurements of the BPMs were conducted with the same setup. However, 0.5 M KNO₃ was used as the electrolyte in both the cathode and anode compartments. During the measurements, the flow of electrolyte was paused by stopping
the peristatic pump in order to achieve a better signal-to-noise ratio. Before incrementing to the next current density, the pump was used to refresh the electrolytes, which ensured the same starting conditions for all measurements. Moreover, the system was subjected to the targeted DC current for 10 minutes to reach an equilibrium state prior to applying the AC input signal.

EIS experiments were conducted using an Autolab (PGSTAT128N), in galvanostatic mode with a frequency response analyzer (Metrohm, Netherland), in the frequency range of alternating current from 5 mHz to 100 kHz distributed uniformly on the logarithmic scale. The amplitude of the AC input signal was adjusted accordingly at a given DC current to ensure both a good signal-to-noise ratio and the absence of distortion in the signal as confirmed by symmetric Lissajous plots. EIS data were fitted by a complex nonlinear least-squares algorithm using the Zview 3.0 software package.

A.1.5 Equivalent circuit (EC)
The EC consists of a series connection of a resistor $R_b$ which represents the resistance from the membrane and electrolyte bulk, Gerischer impedance $G_E1$ and a block of a resistor $R_w$ and a constant phase element (CPE) $CPE1$ connected in parallel (Fig. A.2).

The Gerischer impedance $G_E1$ couples the diffusion process to a chemical reaction that reacts as a sink or source to the studied species.\(^5,6\)

$$\frac{\partial \delta c_{H^+}}{\partial t} = D_{H^+} \frac{\partial^2 \delta c_{H^+}}{\partial x^2} + k_e \delta c_{H^+} \quad \text{(A.1)}$$

where $D_{H^+}$ and $\delta c_{H^+}$ are the diffusion coefficient and change in $H^+$ concentration, and $k_e$ is the effective water dissociation rate constant. Under semi-infinite boundary conditions, the solution to equation A.1 follows:

$$Z = \frac{R}{\sqrt{2}} \times \left( \frac{1}{\sqrt{a} + \frac{1}{a}} \right) - j \left( \frac{1}{\sqrt{a} - \frac{1}{a}} \right) \quad \text{(A.2)}$$

$$R = \frac{R_{gas} T}{\pi^2 \delta c_{H^+} \sqrt{D_{H^+} k_e}} \quad \text{(A.3)}$$

$$a = \left( \frac{\omega}{k_e} \right)^2 + 1 \quad \text{(A.4)}$$

where $\omega$ is the applied frequency and $R_{gas}$, $T$, and $F$ are the gas constant, temperature and Faraday constant, respectively. Considering that the protonation-deprotonation mechanism is catalyzed by a base, as was proposed by Simon:\(^7\)
\[ A + H_2O \xrightarrow{k_2 \over k_-2} AOH^- + H^+ \] (A.5)

We assumed that the EIS AC input signal produces a transient change in H\(^+\) concentration, \(\delta c_{H^+}\). Then, by applying a chemical equilibrium analysis,

\[
\begin{align*}
A & + H_2O \xrightarrow{k_2 \over k_-} AOH^- + H^+ \\
\text{Initial:} & & C_A & & C_w & & C_{AOH^-} & & C_{H^+} \\
\text{Change:} & & -\delta c_{H^+} & & -\delta c_{H^+} & & \delta c_{H^+} & & \delta c_{H^+} \\
\text{Final:} & & C_A - \delta c_{H^+} & & C_w - \delta c_{H^+} & & C_{AOH^-} + \delta c_{H^+} & & C_{H^+} + \delta c_{H^+}
\end{align*}
\]

The reaction rate can then be expressed as:

\[
R_{c_{H^+}} = k_2(C_A - \delta c_{H^+})(C_w - \delta c_{H^+}) - k_-(C_{AOH^-} + \delta c_{H^+})(C_{H^+} + \delta c_{H^+}) \\
= (k_2C_w + k_-2(C_{AOH^-} + C_{H^+}))\delta c_{H^+} = k_e \delta c_{H^+}
\] (A.6)

In writing the last two equations, we eliminated the infinitely small terms and assumed that the water concentration is not affected appreciably.

Equation A.6 supports the idea that the second term on the right side of equation A.1 is the net product of water dissociation. Below the formal potential, -0.83V at room temperature, the water dissociation reaction will not produce net products. However, as pointed out by Hurwitz and Dibiani,\(^5\) the acid or base catalyst in the reaction layer is able to hold H\(^+\) and OH\(^-\) up to a frequency range as high as 1 MHz, so all the changes in \(c_{H^+}\) within the reaction layer are virtual changes. As a result, the dissociation reaction constant at the formal potential is also virtual in the sense that it does not produce any real concentration changes. As such, the rate constant \(k_d\) can be viewed as characterizing the forward reaction rate constant of water dissociation, \(k_e\). The parameter that we extract from the Gerischer element \(GE1\) is thus the forward rate constant \(k_d\).

The current across the reaction layer is composed of two sources: electrical double layer (EDL) charging current and water dissociation current. The former was represented by a constant phase element (CPE) due to the heterogeneity at the AEL/CEL interface. The latter was modelled by a resistor \(R_w\) that gives the resistance of the water dissociation reaction at various biases. The equivalent capacitance is estimated from the CPE using the relation:
\[ C = R_w^{(1-n)/n} Q^{1/n} \]  
\[ Z_{CPE} = \frac{1}{Q(j\omega)^n} \]  

where \( Q \) and \( n \) are the pseudo-capacitance and CPE order, respectively, as extracted from the CPE element.
Fig. A.3. Experimental (black squares) and modelled (green lines) Nyquist plots of BPM with 4 layers of GO, 4GO BPM at different reverse bias potentials. The equivalent circuit is described in Fig. A.2.
Fig. A.4. Experimental (black squares) and modelled (green lines) Nyquist plots of BPM with no GO, 0GO BPM at different reverse bias potentials. The red lines are modeled spectra with a fixed depletion layer thickness. Specifically, the depletion layer thickness at various potentials are averaged for the 0GO BPM. We then repeated the EIS modeling at the fixed (average) depletion thickness while other parameters were allowed to float freely. This fitting scheme (red lines) shows that the chi squared values are in the range of 0.03-0.6, which is much larger than that of the fitting at individually optimized depletion layer thicknesses (green lines).
Fig. A.5. Experimental (black squares) and modelled (green lines) Nyquist plots 3D BPM at different reverse bias potentials.
A.1.6 Determination of the depletion layer thickness

To calculate the depletion layer thickness, the experimental EIS spectra were first fitted to the equivalent circuit in Fig. A.2, as was done in Fig. A.3, A.4 and A.5 for 4GO/0GO and 3D BPMs. The extracted parameters were those related to $R_b$ representing the bulk resistance, the Gerischer element GE1 representing the reaction-coupled diffusion process (equations A.1-A.4), $R_w$ the water dissociation resistance, and a CPE representing the electric double layer.

In the fitting software package, the Gerischer element has two parameters: GET and GEP, corresponding to $R$ (Ω, equation A.3) and $k_e$ ($=k_d s^{-1}$). The CPE element has two parameters: CPET and CPEP, corresponding to Q and n in Equation A.8. The parameter n is a unitless number, and as the overall units of Z are Ω. The Q parameter has units of Ω^{-1}.s^n. The capacitance is thus calculated according to equation A.7, from which the depletion layer thickness $d$ can be obtained by using equation 2.2 in the main text.

As a critical analysis, one may recall that the equation used to calculate the depletion layer thickness is derived for two parallel plates of area A separated by a distance $d$. Strictly speaking, the depletion region considered here, as depicted in Fig. 2.4, is not a conventional plate capacitor because the depletion region has a finite thickness. However, the equivalent circuit we used to model the process is a constant phase element CPE, which is meant to simulate processes in which a large heterogeneity exists. As shown in Fig. A.9 below, there is indeed a large decay of the net charge density from the middle to the edge of the depletion region, indicating a non-uniform distribution of charge in the “capacitor”. More importantly, as a general rule, a CPE resembles an ideal capacitor when the n parameter (CPEP) approaches 1. This is indeed the case by comparing the n parameters for the 3D BPM, ~ 0.9 (Table A.4), to that of the 0GO BPM, ~ 0.6-0.7 (Table A.3). The former has a much thinner depletion region (Fig. A.5), and one may imagine that the thin depletion region in the 3D BPM makes it structurally resemble the planar capacitor, and thus have close to unit n parameters.
Table A.1. Parameters extracted from EIS and calculated values of capacitance and depletion layer thickness for 4GO BPM

<table>
<thead>
<tr>
<th>Reverse current (mA/cm²)</th>
<th>Cross membrane potential (V)</th>
<th>Rp (Ω)</th>
<th>GET (×10⁴, Ω⁻¹)</th>
<th>GEP (kd, s⁻¹)</th>
<th>Rw (Ω)</th>
<th>CPET (×10⁵)</th>
<th>CPEP</th>
<th>Capacitance (×10⁶, F)</th>
<th>Depletion layer thickness (nm)</th>
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<tbody>
<tr>
<td>0.3</td>
<td>0.64 (0.012)²</td>
<td>15.67</td>
<td>37.71 (7.29)</td>
<td>1.03 (0.08)</td>
<td>16.68 (6.36)</td>
<td>5.41 (5.38)</td>
<td>0.75 (0.16)</td>
<td>2.81 (0.50)</td>
<td>25.70 (4.16)</td>
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<tr>
<td>0.4</td>
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<td>13.72</td>
<td>67.36 (3.17)</td>
<td>1.30 (0.02)</td>
<td>17.22 (0.71)</td>
<td>10.46 (3.73)</td>
<td>0.61 (0.04)</td>
<td>1.60 (0.04)</td>
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<td>0.5</td>
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<td>14.78</td>
<td>101.35 (5.39)</td>
<td>1.32 (0.14)</td>
<td>16.28 (1.69)</td>
<td>5.18 (4.02)</td>
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<td>35.86 (12.62)</td>
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<td>0.6</td>
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<td>139.56 (18.11)</td>
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<td>16.70 (2.03)</td>
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<td>204.02 (18.25)</td>
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<td>15.70 (2.04)</td>
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<td>774.94 (24.76)</td>
<td>2.00 (0.11)</td>
<td>9.23 (0.15)</td>
<td>0.73 (0.07)</td>
<td>0.91 (0.02)</td>
<td>2.87 (0.43)</td>
<td>24.99 (3.75)</td>
</tr>
<tr>
<td>4.0</td>
<td>0.89 (0.54)</td>
<td>13.50</td>
<td>1473.43 (148.13)</td>
<td>1.92 (0.24)</td>
<td>10.80 (0.64)</td>
<td>2.55 (0.53)</td>
<td>0.77 (0.03)</td>
<td>2.07 (0.27)</td>
<td>34.69 (4.92)</td>
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<td>9.98 (0.92)</td>
<td>2.45 (1.28)</td>
<td>0.79 (0.08)</td>
<td>2.32 (0.50)</td>
<td>31.33 (5.99)</td>
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<td>7.90 (0.58)</td>
<td>1.90 (0.70)</td>
<td>0.81 (0.04)</td>
<td>2.17 (0.31)</td>
<td>33.19 (5.06)</td>
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<tr>
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<td>1473.43 (148.13)</td>
<td>1.92 (0.24)</td>
<td>10.80 (0.64)</td>
<td>2.55 (0.53)</td>
<td>0.77 (0.03)</td>
<td>2.07 (0.27)</td>
<td>34.69 (4.92)</td>
</tr>
<tr>
<td>30</td>
<td>1.30 (0.006)</td>
<td>8.29</td>
<td>6.59 (0.02)</td>
<td>1.45 (0.01)</td>
<td>0.76 (0.01)</td>
<td>0.74 (0.08)</td>
<td>96.21 (10.19)</td>
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<td></td>
</tr>
</tbody>
</table>

a. The unit of CPET is Ω⁻¹·s⁻¹; CPEP.

b. Capacitance is calculated according to equation A.7.

c. Depletion layer thickness is calculated based on equation 2.2 in the main text.

d. Values in the bracket indicate the standard deviation in a set of three repeated measurements. Standard deviations of < 1 % of the average values are not labeled in the table.

e. Extracting accurate values of kd at reverse potential > 1.1 V were not successful because the lower frequency semicircles in the EIS spectra become small and noisy at those biases (Fig. A.3 and A.4)

143
Table A.2. Parameters extracted from EIS and calculated values of capacitance and depletion layer thickness for 1GO BPM

<table>
<thead>
<tr>
<th>Reverse current (mA/cm²)</th>
<th>Cross membrane potential (V)</th>
<th>Rb (Ω)</th>
<th>GET (X10⁶, Ω⁻¹)</th>
<th>GEP (kd, s⁻¹)</th>
<th>Rw (Ω)</th>
<th>CPET (x10⁵)</th>
<th>CPEP Capacitance (x10⁶, F)</th>
<th>Depletion layer thickness (nm)</th>
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<tbody>
<tr>
<td>0.25</td>
<td>0.64 (0.05)</td>
<td>22.57 (1.06)</td>
<td>26.19 (13.88)</td>
<td>0.75 (0.06)</td>
<td>36.03 (9.35)</td>
<td>1.28 (0.58)</td>
<td>0.79 (0.07)</td>
<td>1.54 (0.21)</td>
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<tr>
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<td>0.81 (0.01)</td>
<td>35.92 (7.06)</td>
<td>1.37 (0.47)</td>
<td>0.77 (0.04)</td>
<td>1.28 (0.07)</td>
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<td>70.49 (12.02)</td>
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<td>35.25 (3.17)</td>
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<td>0.71 (0.07)</td>
<td>1.04 (0.22)</td>
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<td>19.33 (2.05)</td>
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<td>0.97 (0.28)</td>
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<tr>
<td>0.70</td>
<td>0.76 (0.01)</td>
<td>21.62 (1.70)</td>
<td>168.03 (19.66)</td>
<td>0.96 (0.05)</td>
<td>30.28 (3.84)</td>
<td>1.36 (0.60)</td>
<td>0.76 (0.05)</td>
<td>1.04 (0.23)</td>
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<td>20.38 (0.39)</td>
<td>264.20 (13.80)</td>
<td>1.16 (0.12)</td>
<td>27.99 (0.95)</td>
<td>1.59 (0.20)</td>
<td>0.74 (0.02)</td>
<td>0.99 (0.18)</td>
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<tr>
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<td>642.24 (14.89)</td>
<td>1.54 (0.02)</td>
<td>21.99 (0.96)</td>
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<td>0.79 (0.02)</td>
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<td>1126.23 (54.44)</td>
<td>2.11 (0.13)</td>
<td>19.70 (0.17)</td>
<td>0.98 (0.03)</td>
<td>0.79 (0.01)</td>
<td>1.01 (0.11)</td>
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<tr>
<td>4.0</td>
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<td>19.36 (0.24)</td>
<td>1452.97 (126.96)</td>
<td>3.56 (0.69)</td>
<td>16.24 (0.33)</td>
<td>0.76 (0.07)</td>
<td>0.83 (0.01)</td>
<td>1.18 (0.01)</td>
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<td>10</td>
<td>1.11 (0.01)</td>
<td>15.30 (0.21)</td>
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<td></td>
<td>11.50 (0.31)</td>
<td>0.65 (0.09)</td>
<td>0.83 (0.02)</td>
<td>0.96 (0.04)</td>
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<td>1.29 (0.07)</td>
<td>11.54 (0.07)</td>
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<td>0.43 (0.02)</td>
<td>0.83 (0.06)</td>
<td>0.66 (0.02)</td>
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<tr>
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<td>8.69 (0.06)</td>
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<td></td>
<td>9.19 (0.09)</td>
<td>0.21 (0.01)</td>
<td>0.84 (0.02)</td>
<td>0.27 (0.08)</td>
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Table A.3. Parameters extracted from EIS and calculated values of capacitance and depletion layer thickness for 0GO BPM

<table>
<thead>
<tr>
<th>Neve</th>
<th>Cross membrane potential (V)</th>
<th>Rb (Ω)</th>
<th>GET (X10^4, Ω⁻¹)</th>
<th>GEP (kd, s⁻¹)</th>
<th>Rw (Ω)</th>
<th>CPET (x10^6)</th>
<th>CPEP</th>
<th>Capacitance (x10^6, F)</th>
<th>Depletion layer thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.63 (0.02)</td>
<td>40.54</td>
<td>6.95 (1.8)</td>
<td>0.58 (0.10)</td>
<td>437.23 (20.10)</td>
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<td>0.55 (0.01)</td>
<td>0.80 (0.12)</td>
<td>90.41 (13.24)</td>
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<tr>
<td>0.12</td>
<td>0.72 (0.01)</td>
<td>52.16</td>
<td>22.80 (16.9)</td>
<td>0.62 (0.04)</td>
<td>345.10 (7.34)</td>
<td>1.00 (0.04)</td>
<td>0.65</td>
<td>0.47 (0.01)</td>
<td>149.38 (2.97)</td>
</tr>
<tr>
<td>0.15</td>
<td>0.73 (0.01)</td>
<td>52.44</td>
<td>29.07 (19.2)</td>
<td>0.71 (0.01)</td>
<td>311.53 (3.03)</td>
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<td>0.66 (0.01)</td>
<td>0.44</td>
<td>160.06 (1.50)</td>
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<tr>
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<td>0.77</td>
<td>55.12</td>
<td>47.12 (16.5)</td>
<td>0.67 (0.07)</td>
<td>286.07 (8.01)</td>
<td>2.74 (3.54)</td>
<td>0.69 (0.01)</td>
<td>4.10 (6.33)</td>
<td>117.37 (96.25)</td>
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<td>180.49 (0.74)</td>
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<td>83.18 (4.02)</td>
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<td>187.42 (2.20)</td>
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<td>210.77 (1.78)</td>
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<td>0.37</td>
<td>192.80 (0.27)</td>
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<td>0.87</td>
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<tr>
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<td>161.40 (0.79)</td>
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<td>0.75</td>
<td>0.34 (0.01)</td>
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<tr>
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<td>0.96</td>
<td>48.52</td>
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<td>141.80 (0.44)</td>
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<td>0.74 (0.01)</td>
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<td>227.35 (2.32)</td>
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<td>125.15 (0.49)</td>
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<td>0.75</td>
<td>0.30</td>
<td>233.94 (2.55)</td>
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<td>0.33 (0.03)</td>
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<td>0.33 (0.03)</td>
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<td>0.24 (0.01)</td>
<td>59.97 (0.24)</td>
<td>0.24 (0.01)</td>
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<td>0.17</td>
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<td>46.02</td>
<td>0.16</td>
<td>46.02</td>
<td>0.16</td>
<td>0.78</td>
<td>0.80</td>
<td>690.41</td>
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Table A.4. Parameters extracted from EIS and calculated values of capacitance and depletion layer thickness for 3D BPM

<table>
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<tr>
<th>Reverse current (mA/cm²)</th>
<th>Cross membrane potential (V)</th>
<th>Rb (Ω)</th>
<th>GET (X10⁴, Ω⁻¹)</th>
<th>GEP (kd, s⁻¹)</th>
<th>Rw (Ω)</th>
<th>CPET (x10⁵)</th>
<th>CPEP</th>
<th>Capacitance (x10⁶, F)</th>
<th>Depletion layer thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
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<td>(0.31)</td>
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<td>0.01</td>
<td>3.25(0.36)</td>
<td>2.01(0.88)</td>
<td>0.98(0.05)</td>
</tr>
<tr>
<td>0.6</td>
<td>0.72</td>
<td>17.14</td>
<td>(0.55)</td>
<td>400.16</td>
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<td>3.44(0.36)</td>
<td>1.05(0.19)</td>
<td>0.99(0.02)</td>
</tr>
<tr>
<td>0.8</td>
<td>0.75</td>
<td>16.92</td>
<td>(0.99)</td>
<td>581.73</td>
<td>0.09</td>
<td></td>
<td>3.49(0.65)</td>
<td>4.91(6.86)</td>
<td>0.98(0.07)</td>
</tr>
<tr>
<td>1.5</td>
<td>0.80</td>
<td>15.27</td>
<td>(1.69)</td>
<td>1441.57</td>
<td>0.09</td>
<td></td>
<td>3.65(1.92)</td>
<td>3.34(2.28)</td>
<td>0.87(0.18)</td>
</tr>
<tr>
<td>3.0</td>
<td>0.85</td>
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<td>(1.99)</td>
<td>3643.60</td>
<td>0.13</td>
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<td>3.31(0.79)</td>
<td>2.72(1.53)</td>
<td>0.86(0.10)</td>
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<tr>
<td>4.2</td>
<td>0.88</td>
<td>14.03</td>
<td>(0.26)</td>
<td>5536.40</td>
<td>0.14</td>
<td></td>
<td>2.79(0.44)</td>
<td>2.78(1.95)</td>
<td>0.88(0.08)</td>
</tr>
<tr>
<td>5.5</td>
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<td>2.78(0.58)</td>
<td>1.72(0.28)</td>
<td>0.90(0.06)</td>
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<td>7.0</td>
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<td>12.29</td>
<td>(0.66)</td>
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<td>2.91(0.62)</td>
<td>2.68(0.82)</td>
<td>0.85(0.05)</td>
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</table>
A.2 Numerical model of the BPM

A.2.1 Model formulation

The potential distribution and ionic transport can be described by coupling Poisson’s equation and the Nernst-Planck equation.

\[ \nabla (-D_i \nabla C_i - z_i u_i F_c \nabla V) = R_i \quad \text{(A.9)} \]

\[ \nabla (\varepsilon \varepsilon_0 E) = \rho_v \quad \text{(A.10)} \]

Where, \( E \) is the electric field, \( \varepsilon \) and \( \varepsilon_0 \) are the relative dielectric constant and the vacuum permittivity with a value of \( 8.854 \times 10^{-12} \) F/m, respectively. The value of \( \varepsilon \) is taken as 80 for water. \( \rho_v \) is the net space charge density, which arises because of the concentration difference between cations and anions. \( D_i, u_i, C_i, z_i \) are the diffusion coefficient, mobility, concentration and charge of species \( i \), respectively. \( V \) is the potential, the gradient of which is electric field. In equation A.9, \( R_i \), is the generation term describing contributions to concentration from the chemical reaction. In the BPM system, \( H^+ \) and \( OH^- \) are generated by the water dissociation reaction under reverse bias conditions, while the amount of supporting electrolyte is assumed to be conserved. The generation term for \( H^+ \) and \( OH^- \) is written as:

\[ R_i = k_d C_{H_2O} - k_b C_H^+ C_{OH^-} \quad \text{(A.11)} \]

where \( k_d \) is the dissociation rate constant and \( k_b \) the backward reaction rate constant, or the recombination rate constant. In writing the first term on the right side, we included a \( C_{H_2O} \) constant in \( k_d \). Incorporating the catalyst is tantamount to increasing \( k_d \) by two orders of magnitudes in our model, i.e., \( 2 \times 10^{-3} \) 1/s . These equations were programmed and solved with COMSOL v 5.1, using a finite element methodology. Time dependent studies of at least 30 seconds were allowed to reach steady states.
A.2.2 Electric field and catalytic effect

As is discussed in the main body of the paper, electric field-enhanced water dissociation is taken into account by setting the forward reaction rate constant as a function of the electric field across the BPM junction, based on Onsager’s weak electrolyte theorem:\(^8\)

\[
k_d = k_d(0) \times \frac{J_1\left(4\left(-\frac{E}{2}\right)^{0.5}\right)}{2\left(-\frac{E}{2}\right)^{0.5}}
\]  

where \(k_d(0)\) is the dissociation rate constant without electric field, \(E\) is the electric field, \(T\) is the temperature, and \(J_1\) is the Bessel function of the first type.

The mechanism of how the catalyst affects water dissociation has been discussed by Tuckerman et al.\(^9,10\) One of the most popular views accepts the protonation-deprotonation reaction, equation A.5. A detailed version of a comprehensive model would explicitly consider the concentration of active catalytic sites and the catalytic reaction network.\(^11\) Yet, the model proposed in the present study is able to capture the basic catalytic effect by increasing the effective forward reaction rate constant, as demonstrated in equation A.6. The detailed mechanism of catalyzed water dissociation is then implied in the effective rate constant \(k_e\). In principle, our model can be modified to describe a different water dissociation mechanism as long as the generation term \(R_i\) is able to be correlated with the proposed mechanism, such as through a detailed chemical equilibrium analysis.

A.2.3 Boundary and initial conditions

The model is a 1-D model composed of a 20 \(\mu m\) AEL and 20 \(\mu m\) CEL with 200 \(\mu m\) of electrolyte solution on both sides. The two layers of electrolyte are an important component of the model as experimentally there will always be some amount of solution between the tips of the reference electrodes (Fig. A.1), no matter how close they are placed to the membrane surface. The
concentration of the supporting electrolyte KNO$_3$ is fixed to be 0.1 mol/m$^3$ at the two boundaries, while the concentration of H$^+$/OH$^-$ is fixed as 10$^{-4}$ mol/m$^3$, which is the concentration of these species in pure water. The low concentration chosen to ease the simulation cost may limit the H$^+$/OH$^-$ flux at large reverse bias, as is discussed in the main text. The right boundary of the diffusion layer is set as ground and the targeted potential is imposed on the left boundary where the current density is collected based on the total flux of all the charged species. The initial values of relevant parameters in the simulation are listed in Table A.5. The diffusion coefficients of H$^+$ and OH$^-$ and dielectric constant are set to the smaller values than those in normal aqueous system.$^{12-13}$ However, they simplify the interpretation of the results and can better describe the BPM system.$^{13}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{H^+} / D_{OH^-}$</td>
<td>2e-10 m$^2$/s</td>
<td>Diffusion coefficients of H$^+$ and OH$^-$</td>
</tr>
<tr>
<td>$D_{K^+} / D_{NO_3^-}$</td>
<td>1e-10 m$^2$/s</td>
<td>Diffusion coefficients of K$^+$ and NO$_3^-$</td>
</tr>
<tr>
<td>$c_{H_2O}$</td>
<td>56 M</td>
<td>Concentration of water</td>
</tr>
<tr>
<td>$c_{K^+} / c_{NO_3^-}$</td>
<td>0.1 mM (In membrane) 0.5 mM (In electrolyte)</td>
<td>Concentration of supporting electrolyte</td>
</tr>
<tr>
<td>$c_{H^+} / c_{OH^-}$</td>
<td>1e-4 mM</td>
<td>Concentration of H$^+$ and OH$^-$</td>
</tr>
<tr>
<td>$k_d(0)$</td>
<td>2e-5 1/s</td>
<td>Forward reaction constant without electric field</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>10</td>
<td>Relative dielectric constant</td>
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</table>
A.3 Supplementary results

Fig. A.6. Concentration profiles of the ionic species obtained from simulation at all reverse biases, for the BPM with catalyst. (a) $\text{H}^+$ (solid lines) and $\text{OH}^-$ (dashed lines); (b) $\text{K}^+$ (solid lines) and $\text{NO}_3^-$ (dashed lines). The arrows indicate the profile evolution as the potential changes.
Fig. A.7. Simulated results of BPMs without catalyst. (a) J-E curves with (hollow) and without (solid) catalyst; (b) potential distribution of a BPM without catalyst; (c) Water dissociation products H⁺ and OH⁻ concentration distribution in the BPM; (d) Electrolyte KNO₃ ion distribution. Insets in (b) (c) and (d) are enlarged versions of the AEL/CEL junction region.
Fig. A.8. Simulated result of a BPM without catalyst under forward bias conditions. (a) J-E curve under forward and reverse bias conditions; (b) potential distribution under forward bias; (c) Water dissociation products H\(^+\) and OH\(^-\) concentration distributions in the BPM; (d) Electrolyte KNO\(_3\) ion distribution. Note the absence of a depletion region under forward bias conditions. Insets in (b) (c) and (d) are enlarged version of the AEL/CEL junction region.
Fig. A.9. Determination of the depletion region thickness from simulation. The distance from the point where charge density drops to half of the maximum in the AEL to its counterpart point in CEL is taken as the depletion region thickness. The magenta and orange boxes represent the depletion region on the AEL and CEL sides, respectively. The depletion thickness in this case is the distance between the left side of the magenta box and the right side of the orange box. The two curves are for BPMs with and without catalyst at a reverse bias of 2 V, and the boxes representing the depletion layer are for BPM with catalyst.
Fig. A.10. Comparison of the EIS spectra of the 1GO BPM taken in pH neutral (a-d) and asymmetric conditions (e). (a-d): with the pH neutral electrolyte 0.5 M KNO$_3$, the gradual appearance of the intermediate semicircle as the reverse bias current increases is observed. (b) and (d) show an enlarged version of the intermediate semicircle in the square of (a)(c). From zero bias to 0.8 mA/cm$^2$ and above, the intermediate semicircle becomes more obvious, which confirms the gradual formation of the depletion region and the intensification of the water autodissociation reaction under the electric field. (e) Spectra taken under asymmetric conditions exhibit the intermediate semicircle even at open circuit, because of the intrinsic electric field across the AEL/CEL interface. The intrinsic electric field arises because of the acid-base neutralization reaction at the AEL/CEL interface, which leaves the fixed membrane charge near the interface unbalanced, i.e. the formation of a depletion region. As such, even though the asymmetric condition is more relevant to standard operating conditions for BPMs, it doesn’t provide information on the depletion layer thickness and water dissociation kinetics below the open circuit voltage (ideally 0.834 V, assuming 1M fixed charge density in the AEL and CEL). Thus, the asymmetric pH spectra do not inform us about the trend in the water dissociation reaction during the early stages of formation of the depletion region.
A.4 References


Appendix B

Supporting information for chapter 3

B.1 Materials and methods

B.1.1 Materials

Nafion bipolar membranes were fabricated using a Nafion 117 dispersion (5 wt% in alcohol and water mixture) purchased from the Fuel Cell Store. Carbon gas diffusion layers (GDL) were purchased from the Fuel Cell Store (Toray 120). Polyphenylene oxide (PPO), N-methyl-2-pyrrolidone (NMP), N,N-dimethylhexylamine, dimethylformate (DMF), NNNN-tetramethyl-hexanediamine, poly(diallyldimethylammonium chloride) (PDDA), nickel foam, silver nanoparticles (NP) (trace metal basis, > 99%) poly(acrylic acid) (PAA) and poly (alkylamine hydrochloride) (PAH) were used as received from Sigma-Aldrich. A graphite oxide (GO) suspension in water (1 mg/ml in water) was prepared according to the method of Kovtyukhova et al.\textsuperscript{1} Oregon Green 514 (OG), Eosin-5-isothiocyanate and 5(6)-carboxyl-tetramethylrhodamine N-succinimidyl ester (TMR) were purchased from Molecular Probes. Platinum wires (0.5 mm diameter, 99.95%) and Pt/C (50 wt%) were obtained from Alfa Aesar. Ag/AgCl with 3M NaCl filling solution reference electrodes were purchased from BASI. Electrolytes were prepared by dissolving the salts in nanopure water (18.2 MΩ-cm) using a Milli-Q Academic water purifier.

B.1.2 Materials characterizations
Scanning electron microscopy was carried out using a field-emission scanning electron microscope (FESEM, Zeiss, accelerating voltage 4 kV). Transmission electron microscope images were taken with an FEI Talos microscope at 200 kV.

B.2 Supplementary results

Fig. B.1. Characterization of the Ag catalyst on a GDL. (a) SEM image of the Ag NP/C mixture deposited on the carbon paper GDL. (b) TEM image of the Ag nanoparticles.

Fig. B.2. (a) Overall current density of the CO₂ electrolyser used for the visualization experiment. (b) The CO Faradaic efficiency of a control experiment with the same configuration, except that there is no hole in the center of the carbon paper.
Fig. B.3. Visualisation of the cathode side of the BPM-based CO$_2$ electrolyser. Different parts of the cathode are indicated in the optical micrograph. The upper left shows a conducting copper foil that connects the carbon paper GDL to the external circuit; the hole made in the center of the GDL allows direct access of the light beam to the CEL side of the BPM. Figures shown in the main text are zoomed-in views of the CEL region.
Fig. B. 4. TEM images of the LBL-BPM. (a) HAADF image. EDS mapping of F (b) Br (c) and their overlap map (d). The F element signal is from the Nafion polymer and Br comes mainly from the eosin-labeled PAH. A thin layer of Br (~50 nm) can be seen on the Nafion surface.
Background subtraction for the UV-Vis experiments

The in-situ spectroelectrochemical cell used in the main text contains two glass slides, two segments of transparent liquid electrolyte, each about 1 cm in length, and the dye labelled LBL-BPM. The spectroscopic backgrounds from the glass slides and liquid electrolyte are steady and could be easily subtracted. The LBL-BPM was composed of a LBL film with dye-PAH, an AEL, a transparent Nafion CEL, and a molecularly thin GO interfacial layer. The first component is absorbing in the spectroscopic region of interest, while the latter two are transparent, leaving the AEL as the largest factor affecting the background measurement.

The AEL used in this study, PPO functionalized with quaternary ammonium groups, has a pale yellow color that changes slightly at higher pH, which can be induced by applying a reverse bias to the BPM. Fig. B.5a shows UV-Vis spectra of the Nafion BPM without dye-PAH at the open circuit potential and with 4 mA reverse bias current, which is representative of all the samples tested. Upon applying a reverse bias, two differences are noted: the absorbance increases at a constant level between 450 nm to 800 nm, and an absorbance shoulder at around 420 nm becomes apparent.

![UV-Vis spectra of the Nafion BPM without dye-PAH](image)

Fig. B.5. (a) UV-Vis spectra of the Nafion BPM without dye-PAH under open circuit voltage (OCV) and 4 mA reverse current conditions. (b) The difference between the spectra at 4 mA and OCV shown in (b).
The absorbance difference between 450 nm and 800 nm does not change the analysis of the ratiometric indicator method employed in the main text, as we are looking at the relative absorbance ratio in the two bands, and moving the background up or down vertically does not affect this value. The emerging shoulder at 420 nm does not interfere with the data analysis because the absorption bands for OG and TMR are at 480 nm, 510 nm, and 560 nm.

The difference in the UV-Vis background spectra of under 4 mA and open circuit conditions is shown in Fig. B.5b. The baseline between 450 nm and 600 nm is flat (< 0.001) on the scale of the signal of the samples (~0.01), while the absorption bands end above 450 nm, below which the largest background difference can be observed.

![Graphs showing UV-Vis spectra under different conditions](image)

Fig. B.6. (a) Original UV-Vis spectra of the sample S1, under OCV and 4 mA, before baseline correction, with OCV of the Nafion BPM as background. (b) The same experiment was done with 4 mA reverse current applied to the Nafion BPM as background. (c)(d) UV-Vis spectra after baseline correction. The 560/510 ratios are 0.957 (OCV) and 1.24 (4 mA) in (c), 0.968 (OCV) and 1.20 (4 mA) in (d).
To illustrate that there is a negligible background effect, we compared UV-Vis spectra of sample S1 with two different backgrounds, under OCV and 4 mA, Fig. B.6a and B.6b. Regardless of the background employed, the conclusion that the peak at 510 nm decreases while that at 560 nm remains almost the same still holds. Finally, the variation (~0.01 scale) of peak ratios after the baseline correction due to the different backgrounds (Fig. B.6c and B.6d) are smaller than the standard deviation (~0.1 scale) seen in Fig 3.4f. It is thus reasonable to use the OCV background for samples under OCV and the 4 mA background under reverse bias, followed by baseline correction. This process is repeated for each sample where the same batch of BPM was used for taking backgrounds and LBL modification.

Fig. B.7. UV-Vis spectra of sample (a) S2 and (b) S3, under OCV and 4 mA reverse current.
Fig. B.8. UV-Vis spectra of sample (a) S5 and (b) S6 under OCV and 4 mA reverse current.

Fig. B.9. UV-Vis spectra of the S1 at OCV (black), followed by 4 mA reverse current (red) for 10 minutes, followed by OCV again (blue). The almost overlapped absorbance at 510 nm and 560 nm in the OCV after applying 4 mA reverse current confirms the reversibility of the test.
Fig. B.10. UV-Vis spectra of LBL modified Nafion, under OCV and 4 mA current. Two bilayers of dye-PAH/PAA are deposited onto the Nafion. Compared to the S1 sample, Fig. 3.4d, the negligible difference between the OCV and 4 mA indicates the increased 560/510 ratio in the S1 sample under 4 mA is likely the result of decreased pH under reverse bias, which is absent in the Nafion membrane.
Fig. B.11. UV-Vis results using spectral modeling. The three prominent absorption peaks are fitted as Gaussian functions. The spectra are then obtained by overlapping the simulated peaks. (a) Simulated spectra as a function of pH. (b) Calibration of intensity ratio. (b) Simulated intensity ratios of the S1-S6 samples. The values and the overall trends are consistent with those without modeling, as reported in the main text.

Fig. B.12. H₂ partial current density as a function of cathode potential (a) with ionomer-free catalyst layer and (b) with Nafion ionomer. The suppressed H₂ current density can be seen in both cases.
Fig. B.13. Comparison of (a) the CO FE and (b) CO partial current density, between the Nafion BPM and LBL BPM as a function of cathode potential, in the Nafion ionomer-containing configuration. Compared to Fig. 3.5c and 3.5d, the same trend that LBL BPM increases the CO FE but retains similar CO current density can be observed.

Fig. B.14. Overall current density vs cell potential curve for the Nafion- and LBL- BPMs in the configuration with ionomer.
B.3 Reference

Appendix C

Supporting information for chapter 4

C.1 Materials and methods

C.1.1 Materials

Chemicals were purchased from Sigma Aldrich and used as received unless otherwise stated. Anion exchange membrane Fumasep FAS-30 and cation exchange membrane Nafion 211 were purchased from the FuelCellStore. Sulfonated poly(ethyl ethyl ketone) (SPEEK) was prepared according to a previous report.\(^1\) Graphene oxide (GO) was prepared based on the method of Kovtyukhova \textit{et al.}\(^2\) Platinum wires (0.5 mm diameter, 99.95\%) were obtained from Alfa Aesar. Ag/AgCl with 3M NaCl filling solution reference electrodes were obtained from BASI.

2,7-difufonate-9,10-anthroquinone was purchased from AK Scientific Inc and was ion exchanged twice with 0.1M HCl before drying at 70°C. 1,1'-bis(3-sulfonatopropyl)-4,4'-bipyridinium was prepared from 4,4'-bipyridine and propane sulfone (TCI Chemicals), according to literature methods.\(^3\) Carbon paper Sigracet GDL 39 AA was purchased from Ion Power and pretreated according to published procedures.\(^4\) The peristaltic pump used to cycle the electrolyte was purchased from MasterFlex.

C.1.2 BPM fabrication

BPMs were prepared according to the procedure described previously with slight modifications.\(^5\) The Fumasep anion exchange layer (AEL) (3.5 cm by 3.5 cm) was bathed in 1 M KOH at 70°C for 30 min before being thoroughly rinsed with water. The edges of the AEL were
taped onto clean glass slides, exposing an area of ~ 3 cm by 3 cm for the AEL. 5 mL of GO suspension (3 mg/ml) was dropped onto the AEL surface and left to stand for 20 mins. After washing away the GO solution, the GO/AEL was dried using an air gun. 0.5 mL SPEEEK solution (~5 wt% in DMF solvent) was mixed with 0.5 mL DMF and air sprayed onto the exposed surface of the GO/AEL on a hot plate at 120°C. The SPEEEK/GO/AEL BPM was peeled off the glass substrate and transferred to a hot press, operated at 115°C and 2000 psi for 1 h. The obtained BPM (dry thickness ~60 um) was stored in air before testing.

C.1.3 Electrochemical measurements

The potential across the BPM was measured by using a four-electrode setup as reported previously. The BPM was placed between two center chambers with an extra cation exchange layer (CEL) and AEL between the outer chambers to minimize the influence of electrochemical products. Two Ag/AgCl references electrode were fixed in the two central chambers and placed near the membrane surfaces using Haber-Luggin capillaries. Two platinum wires were employed as counter and working electrodes. 0.1 M HCl and 0.1 M KOH were cycled through the chambers facing the CEL and AEL sides, respectively. The current was supplied through a DC power supply (Agilent E3612) and the potential difference between the two reference electrodes was monitored by using a potentiostat (EZStat Pro Potentiostat-Galvanostat, NuVant systems). Positive current in this work denotes forward bias of the BPM.

Cyclic voltammetry (CV) of the redox molecules was carried out in aqueous electrolytes. Concentrations of either 0.1 M or 0.5 M were used for CV measurements, in which a glassy carbon electrode (5 mm in diameter), platinum wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. The CV tests were done using PGSTAT302N (Metrohm, Autolab), with a 100 mV/s scan rate.

C.1.4 Flow battery testing
In a typical experiment, the positive electrolyte was 0.1 M ferrocyanide in 2 M KOH (6.5 mL) and the negative electrolyte was either 0.1 M DSAQ or 0.4 M SPV in 1 M H$_2$SO$_4$ (6.5 mL) for redox flow batteries incorporating BPMs. For tests that involved alkaline conditions on both sides of the cell, 0.1 M redox molecules were used in 2 M KOH electrolytes. All the measurements started in the fully discharged states of the redox couples and were done at ambient temperature (ca. 23°C).

Two metallic back plates and two graphitic carbon bipolar plates with serpentine flow fields were used on both the positive and negative sides. A piece of membrane (BPM or CEL) was sandwiched with PTFE gaskets on both faces to leave a window of 1 cm x 1 cm area. The window spaces were filled with two pieces of carbon paper (1 cm x 1 cm) as electrodes. The electrolytes were cycled through the flow fields using a peristaltic pump at ~20 mL/min. The whole setup was placed inside a glove bag with high purity argon purging before and during the experiment. The polarization curves were obtained by galvanostatic charging at 30 mA/cm$^2$ of the battery to approximately 100% state of charge (SOC), followed by CV scan at 100 mV/s between 2 V and 0.2 V. The galvanostatic charge and discharge tests were performed at 30 mA/cm$^2$, with upper and lower potential limits at 1.6 V and 0.4 V.

In the acid-base redox flow batteries incorporating BPMs, the CEL side of the BPM faced the acidic electrolyte (DSAQ or SPV in H$_2$SO$_4$) and the AEL side faced the alkaline electrolyte (ferrocyanide in KOH). For the control experiments under alkaline conditions, a piece of Nafion CEM was used to separate the two electrode compartments with 2 M KOH in both sides. To study the effect of water splitting in the acid-base redox flow battery, 2 M KOH and 1 M H$_2$SO$_4$ without the redox active molecules were separated by a BPM. CV (100 mV/s) and constant potential (at 1.8 V and 2 V) tests were carried out.

For studying the dependence of battery performance on the ferrocyanide concentration, concentrations of 0.05, 0.10, 0.15 and 0.35 M were prepared in 2 M KOH as the positive electrolyte, while on the negative side 0.4 M DSAQ in 2 M H$_2$SO$_4$ was used consistently. At the lowest concentration (0.05 M), a lower charging current density 10 mA/cm$^2$ was used. Electrochemical
impedance spectroscopy (EIS) was used to measure the impedance losses at different concentrations, but with larger electrolyte volumes (20 mL) to ensure a steady electrolyte composition during the experiment. The EIS tests were carried out at approximately 100% SOC between the positive and negative electrodes and thus include impedance losses from the solution and the membrane, the water dissociation/acid-base association reactions, and the redox processes occurring at the two electrodes. The AC modulation was 5% of the applied DC current, with frequency ranging between $10^5$ to 0.1 Hz, distributed evenly on a logarithmic scale.

C.2 Numerical modeling of forward biased BPM

The numerical model was modified from previous models\textsuperscript{5,6} to include the kinetics of the acid-base neutralization reaction. The ionic transport and electric potential distribution are described using Nernst-Planck-Poisson equations:

$$\frac{\partial c_i}{\partial t} = \nabla \left( D_i \nabla c_i + z_i \frac{d_i}{RT} F c_i \nabla V \right) + R_i$$ (C.1)

$$\varepsilon \varepsilon_0 \frac{d^2 V}{dx^2} = -F \left( \sum z_i c_i + z_m Q_m \right)$$ (C.2)

where $a$, $D$, and $z$ are the concentration, diffusion coefficient, and charge of the mobile species $i$, and $z_m$ and $Q_m$ are the charge number and fixed charge density of the AEL and CEL. $F$, $\varepsilon$, $\varepsilon_0$, and $V$ are Faraday’s constant, the dielectric constant, permittivity, and electric potential. $R_i$ is the reaction term due to the water dissociation and acid-base neutralization reaction. The diffusion coefficients in the AEL/CEL domains were taken to be $1/10$ of the corresponding values in the aqueous electrolyte in order to account for tortuosity.\textsuperscript{6} 100% permselectivity of the AEL/CEL was assumed, excluding the contribution of $K^+$ and $Cl^-$ as charge carriers inside the membranes. The dielectric constant has been found to be an essential parameter in determining the electric field. Values of 30 and 80 were used for the AEL/CEL membranes and the electrolyte, respectively.

The transport considers five species including $H^+$, $OH^-$, $K^+$, $Cl^-$ and $H_2O$. The transport of $H_2O$ is usually not considered to be a limiting factor if the BPM is in contact with an aqueous electrolyte.\textsuperscript{7}
However, the role of water is less well understood for BPMs in H\textsubscript{2}-O\textsubscript{2} fuel cells where water is mainly supplied from the vapor phase. The variation of H\textsubscript{2}O concentration as a function of electric potential also gives insight into the interplay between the dissociation and acid-base neutralization processes under different operating conditions. H\textsubscript{2}O was treated as a neutral molecule with a self-diffusion coefficient.

The reaction term on the right-hand side of equation C.1 is mainly contributed by the water dissociation and acid-base neutralization reactions, and can be written as:

\begin{align*}
R_{H^+} &= R_{OH^-} = k_{d(\text{eff})}c_{H_2O} - k_{n(\text{eff})}c_{H^+}c_{OH^-} \quad \text{(C.3)} \\
R_{H_2O} &= -R_{H^+} \quad \text{(C.4)} \\
R_{K^+} &= R_{Cl^-} = 0 \quad \text{(C.5)}
\end{align*}

\(k_{d(\text{eff})}\) and \(k_{n(\text{eff})}\) are the effective dissociation and neutralization rate constants. It has been known that the reaction kinetics could be affected by the junction electric field and the interfacial catalysts.

The electric field increases the dissociation rate constant \(k_d\) but does not affect the recombination rate constant \(k_n\), according to the Onsager's theory of weak electrolyte:

\[
f(b) = \frac{k_d(E)}{k_d(0)} = 1 + b + b^2 + \frac{b^3}{18} + \frac{b^4}{180} + \frac{b^5}{2700} + \frac{b^6}{356700}
\]

\[
b = 0.09636 \frac{E}{\varepsilon T^2}
\]

where \(E\) is the electric field. The effect of certain groups of the catalyst on \(k_d\) is usually explained by the protonation-deprotonation cycle:

\[
B + H_2O \xrightarrow{k_1} BH^+ + OH^- \quad \text{(C.8)}
\]

\[
BH^+ + H_2O \xrightarrow{k_2} B + H_3O^+ \quad \text{(C.9)}
\]

Assuming chemical equilibriums, the catalytic activity can be expressed as a function of the total density, \(pK_a\), and local pH of the active sites. This method has been incorporated into a comprehensive numerical model that successfully reproduced the behaviors of BPMs with CELs of different \(pK_a\). Alternatively, the catalytic effect can be represented at a phenomenological level where the dissociation constant \(k_d\) for the domains with deposited catalysts are increased while
those of the remaining domains are left unchanged. The latter method was used because even though the first approach is capable of accounting for the catalytic activity of the bulk AEL/CEL, their contribution is expected to diminish as the pKₐ's of the AEL/CEL become more extreme, as is the case for BPMs used in this study. Also, it remains to be seen if the protonation-deprotonation mechanism applies to the catalyst (graphene oxide, GO) employed in this work.

The influence of the catalyst on the neutralization rate constant kₙ is less well understood and has generally been assumed to be unimportant in previous reports. As discussed in the main text, three models that differ in the expressions for the kₐ and kₙ were compared. In the first model (uncatalyzed kₐ and uncatalyzed kₙ), both kₐ and kₙ are constant throughout the entire system, corresponding to the experimental BPM sample without an interfacial catalyst. The second model (catalyzed kₐ and uncatalyzed kₙ) assumes an experimental BPM with catalyst GO that occupies a 20 nm space at the AEL/CEL interface (10 nm within each layer). In this model, kₐ is increased by three orders of magnitude within the 20 nm region but takes the same value as in the free solution outside this region due to the absence of catalyst. The kₙ is set to a constant value in the entire domain as in the first model, consistent with the conventional method in literature. We note a fundamental problem with this model, as any catalyst for a reversible reaction should accelerate the rate of the reverse reaction by the same factor as the forward reaction. The third model (catalyzed kₐ and catalyzed kₙ) considers that the catalyst can affect both the dissociation and neutralization processes. This model has the same parameterization of kₐ as the second model, but the kₙ is also increased by the same factor within the 20 nm catalyzed zone. The comparison between the results of these three models and the experimental polarization measurements helps to elucidate the role of the catalyst in BPMs. Simulations with different orders of magnitude improvement in kₐ and kₙ were also carried out, Fig. C.7. The catalytic effect is schematically shown in Fig. 2b for the three models:

Model 1 uncatalyzed kₐ and uncatalyzed kₙ:

\[
\begin{align*}
    k_{d(\text{cat})} &= 1, \text{ all } x \quad (\text{C.10a}) \\
    k_{n(\text{cat})} &= 1, \text{ all } x \quad (\text{C.10b})
\end{align*}
\]
Model 2 catalyzed \( k_d \) and uncatalyzed \( k_n \):

\[
k_{d(cat)}(x) = \begin{cases} 
10^3, & -10 \text{ nm} < x < 10 \text{ nm} \\
1, & \text{x elsewhere}
\end{cases} \quad (C.11a)
\]

\[
k_{n(cat)} = 1, \text{all} \ x \quad (C.11b)
\]

Model 3 catalyzed \( k_d \) and catalyzed \( k_n \):

\[
k_{d(cat)}(x) = \begin{cases} 
10^3, & -10 \text{ nm} < x < 10 \text{ nm} \\
1, & \text{x elsewhere}
\end{cases} \quad (C.12a)
\]

\[
k_{d(cat)}(x) = \begin{cases} 
10^3, & -10 \text{ nm} < x < 10 \text{ nm} \\
1, & \text{x elsewhere}
\end{cases} \quad (C.12b)
\]

The effective rate constant includes the contribution from both electric field and catalysis:

\[
k_{d(\text{eff})} = k_d(0)f(b)k_{d(cat)} \quad (C.13)
\]

\[
k_{n(\text{eff})} = k_n(0)k_{n(cat)} \quad (C.14)
\]

This approach of describing the catalytic effect assumes that the presence of the GO catalyst does not change the physical separation between the AEL and CEL (abrupt junction model), but catalytically increases the reaction rates. The effect can be viewed as an averaged result of an abrupt junction and a catalyzed neutral layer,\(^6\) which is reasonable given the patchy distribution of the GO catalyst at the AEL/CEL junction by the layer-by-layer assembly method used in the experimental part of this study (only one GO layer was deposited). Additionally, the thickness of the reaction zone, Fig. 4.2f and Fig. C.4, is on the scale of a few nanometers, which is close to the value of the catalyzed neutral region in a model that correctly reproduces the polarization curve of a commercial BPM.\(^6\)

The one-dimensional model mimics the experimental four-electrode setup (Fig. 4.2a and 4.2b), consisting of four segments that represent the two electrolyte diffusion layers (200 µm each) and the AEL/CEL (20 µm each). The two open boundaries refer to the tips of the two reference electrodes whose electric potentials are fixed, while the total current density is calculated according to the ionic fluxes of the various species:

\[
i = F \sum z_i j_i = F(j_{k^+} + j_{H^+} - j_{Cl^-} - j_{OH^-}) \quad (C.15)
\]
The continuities in the concentrations and electric potential were maintained at the inert boundaries between the left electrolyte/AEL, the AEL/CEL, and the CEL/right electrolyte. The concentrations and electric potentials at the left and right boundaries were set at fixed values. Maximum mesh sizes of 1 µm, 0.5 nm, and 0.1 nm were set for the four segments, left electrolyte/AEL and CEL/right electrolyte inner boundaries, and AEL/CEL interface, respectively. The above equations were solved using the COMSOL Multiphysics 5.1 package, with a time-dependent study. Steady states were achieved when the current density changed insignificantly with time. The parameters and initial conditions for a typical simulation are listed in Table C.1, and carried out in this manner unless stated otherwise.

The overall water dissociation, acid-base neutralization rates, and the water areal concentration change were calculated by integrating the rates over the whole reaction zone:

\[
\text{Int } R_{\text{dissociation}} = \int_{\text{reaction zone}} k_{d}(\text{eff})c_{H_{2}O}(x) \, dx
\]  
\[
\text{Int } R_{\text{neutralization}} = \int_{\text{reaction zone}} k_{n}(\text{eff})c_{H^{+}}(x)c_{OH^{-}}(x) \, dx
\]  
\[
\text{Integrated water} = \int_{\text{reaction zone}} (c_{H_{2}O}(x) - c_{H_{2}O}(0)) \, dx
\]

where the reaction zone refers to the region near the AEL/CEL interface with nonzero integrand values.
Table C.1. Parameters for the simulation and initial conditions.

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<tr>
<th>Parameter</th>
<th>Value</th>
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<td>Temperature, $T$</td>
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</tr>
<tr>
<td>$D_{H^+}$, $D_{OH^-}$</td>
<td>$2 \times 10^{-9} , m^2/s$</td>
</tr>
<tr>
<td>$D_{H_2O}$</td>
<td>$9.6 \times 10^{-9} , m^2/s$</td>
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<tr>
<td>$D_{OH^-}$</td>
<td>$2.5 \times 10^{-8} , m^2/s$</td>
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<tr>
<td>$Q_m$</td>
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<td>$\varepsilon$</td>
<td>$80$ (electrolyte), $30$ (AEL/CEL)</td>
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<td>$K_{eq(0)}$</td>
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<td>$k_{d(0)}$</td>
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<th>AEL</th>
<th>CEL</th>
<th>right electrolyte</th>
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<td>$c_{OH^-}$ (mol/l)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$c_{H_2O}$ (mol/l)</td>
<td>56</td>
<td>56</td>
<td>56</td>
<td>56</td>
</tr>
</tbody>
</table>

* $V_{app}$ is the applied electric potential
C.3 Supplementary results

Fig. C.1. EIS tests of the BPMs with and without GO catalysts. (a) Nyquist plots of the BPM with GO catalyst. (b) Nyquist plots of the BPM without GO, the inset shows enlarged view of the results at 2 and 10 mA/cm². The samples with GO catalyst show smaller resistance semicircles, indicating faster reaction kinetics. The difference between the two samples is much larger in reverse bias (negative current density) than in forward bias.

Fig. C.2. Concentration distributions of ionic species in Model 3. (a) Concentration profiles of OH⁻ and H⁺ as a function of position at open circuit (500 mV), and under forward (200 mV) and reverse bias (800 mV). (b) Enlarged view at the AEL/CEL interface, where the depletion layer containing minimal amounts of both ions can be seen. The thickness of the depletion layer decreases at lower potentials. (c) Distribution of K⁺ and Cl⁻ ions that are excluded from the BPM because perfect permselectivity was assumed.
Fig. C.3. Electric potential distribution in Model 3. A large portion of the potential drop occurs across the AEL/CEL interface.

Fig. C.4. The distribution of dissociation reaction rates in Model 3. A significant dissociation rate is seen only within a narrow region of ~3 nm, i.e. the reaction zone.
Fig. C.5. Effect of electric field as a function of potential in Model 3. (a) The strength of the electric field in different models. (b) The effect of the electric field on the dissociation process; the expression for $f(b)$ is shown in equation C.6.

Fig. C.6. Changes in water concentration. (a) The distribution of water concentration in Model 3. There is a net increase/decrease in water concentration under forward/reverse bias conditions. Most of the change happens within the BPM. (b) The net water concentration change as a function of potential. The overall shape of the curve resembles those in Fig. 4.2c. The integrated water concentration refers to the integrated net water concentration changes over the reaction region (~25 um to ~25 um).
Fig. C.7. Effect of the catalytic power on the potential-current density relation with Model 3. Increasing the catalytic effect in Model 3 from 0 to $10^2$ induces a much larger increase for the forward bias current than in the reverse bias current. However, reverse bias current is enhanced more when the catalytic factor is increased from $10^3$ to $10^{3.5}$.

Fig. C.8. EIS tests of the BPM-based acid-base redox flow battery with 0.05 M ferrocyanide in 2 M KOH at the positive electrode. (a) Nyquist plots and (b) Bode plots at different current densities. Three components of the impedance can be identified: the ohmic resistance (~$10^5$ Hz), the reaction kinetics of the dissociation and neutralization processes (~$10^3$ Hz), and the transport resistance (~0.1 Hz). The resistance ascribed to transport increases under forward bias (40 mA/cm$^2$), while the semicircle associated with the reaction process does not change significantly.
Fig. C.9. EIS tests of the BPM-based acid-base redox flow battery with 0.3 M ferrocyanide in 2 M KOH at the positive electrode. (a) Nyquist plots and (b) Bode plots at different current densities. Large increases in the kinetic processes can be observed due to the migration of the anions $\text{Fe(CN)}_6^{4-}/\text{Fe(CN)}_6^{3-}$ into the AEL in competition with OH$. The latter is involved in the acid-base neutralization process.

Fig. C.10. EIS tests of the BPM-based acid-base redox flow battery with 0.1 M ferrocyanide in 2 M KOH at the positive electrode. (a) Nyquist plots and (b) Bode plots at different current densities. A balance between the transport and kinetic processes is achieved with an intermediate concentration of ferrocyanide, which results in the best cell performance as shown in Fig. 4.4a.
Fig. C.11. Influence of water splitting. (a) Cyclic voltammogram of the acid-base configuration with 2 M KOH and 1 M H$_2$SO$_4$ at the positive and negative electrodes, respectively. (b) Current density versus time at a given cell potential. The low current density (~3 mA/cm$^2$) at 1.8 V suggests negligible influence of the water splitting reaction on the acid-base redox flow battery, as the highest potential during charging was set to 1.6 V.

C.4 References


Appendix D

Supporting information for chapter 5

D.1 Materials and methods

D.1.1 Materials

Pt/C and PtRu/C nanoparticles (60 wt%, on HAS Ketjenblack), Nafion dispersion (D521, 5 wt%), and carbon paper with microporous layer were purchased from the FuelCell Store. PTFE membrane filters (aspire laminated, hydrophobic, polypropylene backer, 0.1 micron) were purchased from Sterlitech. Anion exchange membranes (AEM) and ionomers (aQATTP, Cl⁻ as counter ion) were the same as in previous literature.¹ Fuel cell hardware and the fuel cell test stand (850e, multi-range) were purchased from Scribner. Pt wire (0.5 mm diameter) and Ag/AgCl reference electrode (filled with 3 M KCl) were purchased from Alfa Aesar and BASI, respectively. All other chemicals were received from Sigma-Aldrich without purification.

D.2 Sample preparation and testing

D.2.1 Rotating disc electrode (RDE) experiment

For the aqueous hydrogen oxidation reaction (HOR) in the RDE configuration, Pt/C powders (60 wt%, 0.25 mg) were dispersed in 0.5 mL deionized (DI) water (18.2 MΩ) using a bath sonicator (Branson 5510) for one hour. Ice-water mixture was used and refreshed during the sonicating process. 20 μL of the sonicated catalyst ink was pipetted onto a glassy carbon electrode disk (5 mm in diameter, Pine Instruments). The electrode was polished with alumina (50 nm) and raised...
with water. After dried in air, the electrode was connected to a rotating rod and was bath in 0.1 M KOH (99.98% purity) or 0.1 M HClO₄ solution saturated with H₂ gas (ultra-high purity, Air gas). The electrochemical measurement was done in a PTFE cell to prevent possible contamination from silicate dissolution. A Pt wire was used as the counter electrode and Ag/AgCl the reference electrode. Polarization curves were recorded with a scan rate of 5 mV/s and the potential was reported with respect to the reversible hydrogen electrode (RHE) by correcting for pH shifts. A rotating rate of 400 rpm was used for the polarization tests.

Electrochemical impedance spectroscopy (EIS) was carried out using Autolab (128N or 301 N, Metrohm) after the polarization experiment. Different direct current (DC) voltages was imposed by an AC voltage perturbation of 10 mV amplitude. The linearity and signal-to-noise was monitored through the Lissajous plots. 50 frequencies distributed evenly on the logarithm scale between 10⁴ to 0.05 Hz was used for typical EIS experiments.

D.2.2 Fuel cell tests

For fuel cell tests with the conventional membrane electrode assembly (MEA) configuration, procedures from previous literature were followed.¹ Pt/C and PtRu/C powder (60 wt%, 6 mg) and 75 uL AEM ionomer (2 wt% in DMSO) were added to 1.5 mL 1-propanol. The mixture was sonicated in a bath sonicator for an hour to obtain the uniform catalyst ink. The prepared ink was sprayed onto a piece of AEM (QATTP 35 um, 3 cm by 3cm), which was held flat by a heated vacuum table at ~ 60 °C. The active area (2 cm by 2 cm) was set by a window cut in the PTFE mask. The spraying process was accomplished by a spraying gun (Master Airbrush, G233) attached to a modified 3D printer (Creality, Ender) that fixes the gun ~ 2 cm above the membrane and controls the motion in the X-Y dimensions. Pt/C and PtRu/C was sprayed on the two sides of the AEM and served as the cathode and anode electrode, respectively. The metal loading was determined to be ~ 0.4 mg/cm². The catalyst coated membrane was activated in 1 M KOH solution in a 70 °C oven overnight to replace the Cl⁻ with OH⁻.
For fuel cells with the novel architectures discussed in the main text, only one side of the AEM was deposited with the PtRu/C as the anode electrode. The cathode was fabricated by sputtering Ag or Pt films onto the PTFE substrate at ~ 0.1 nm/s sputter rate with a sputtering tool. Approximately 400 nm nominal thickness was used for Pt and Ag samples. The Pt/PTFE samples were further modified by spraying AEM or Nafion ionomers. A target amount of ionomer (for example, 75 uL 2 wt% AEM ionomer, or 30 uL 5 wt% Nafion) was dispersed in 0.5 mL 1-propanol. The mixture was sprayed on the Pt films with a window mask that gave an active sample area of ~ 2 cm by 1.2 cm.

The catalyst coated AEMs (on one or both sides), after activation, was pressed between two pieces of carbon papers placed between two bipolar plates, which was screwed together using a torque wrench (6.0 N*m). For the novel configuration, the cathode was replaced with the prepared Pt/PTFE electrode. As the PTFE substrate is electronically insulating, two pieces of Cu foil were placed on the top and bottom edge of the Pt film to connect the catalyst to the carbon plate (Fig. D.5).

Humidified \( \text{H}_2 \) and \( \text{O}_2 \) gas were fed into the fuel cells at 0.5 L/min flow rate with a backpressure of 0.2 MPa. The temperature of the water humidifier and the fuel cell were set to 80 °C. Gavanostatic polarization was carried out to obtain the polarization curves. EIS spectra at large current densities were taken using the frequency response analyzer (FRA) built within the fuel cell test stand. Frequency range was set to between 0.1 Hz to 5000 Hz. The amplitude of the AC current was taken to be 5 % of the applied DC current. For smaller current densities, the EIS spectra was obtained with Autolab in the potentiostat mode. The equivalency of the galvanostat and potentiostat mode in the EIS measurements was confirmed (Fig. D.8).

**D.3 Numerical modeling**

**D.3.1 Model description**
The novel geometry in the Pt/PTFE cathode has a relatively simple structure that could be captured by a one-dimensional (1D) model (Fig. 5.4 b). The electrochemical oxygen reduction reaction (ORR) can happen in the Pt/PTFE architecture because the sputtered Pt forms a continuous conductive film and the ionomer provides pathways for the ionic transport. The oxygen diffusion is ensured by the pore space and the PTFE fibers that have high affinity to oxygen gas. The ionomer coated Pt/PTFE fiber was thus modeled by a porous electrode of 400 nm, which can conduct electrons, ions, and oxygen gas simultaneously. Adjacent to the porous electrode is the AEM that conducts hydroxide. In the 1D model, however, we also allow the AEM to conduct the counter ion (K⁺), because total exclusion of counter ions in the electrolyte domain will cause large electric field fluctuation at the electrode surface and thus makes the modeling prone to diverge. Unlike in the case of aqueous electrolyte, a mature theory describing the electrode/polymer electrolyte interface has not been established.

The diffusion of ions and oxygen gas in the porous electrode is described by the Nernst-Plank equation without the convective term:

\[ J_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi_f \]  

where \( D_i, c_i, z_i, u_i \) stand for the diffusion coefficient, concentration, charge, and mobility of species \( i \). Nernst-Einstein relation was employed to relate the mobility and diffusion coefficient. \( \phi_f \) is the potential of the electrolyte. No correction was done for the diffusion coefficients due to the tortuous environment in the porous electrode, as this will only change the specific value but not the overall trend of the results.

More complicated transport phenomena exist in the conventional MEA configuration, and could also be present in the current novel geometry. For example, the oxygen gas in pores < 100 nm experiences the Knudsen diffusion due to the frequent collision with the pore walls. This effect may not be as obvious in the Pt/PTFE cathode, as the pore size is generally large. However, similar effect at local level could exist due to the rough surface of the catalyst film. The diffusion of oxygen gas through the ionomers covering the catalyst/support agglomerates has been recognized as the major obstacle to achieve low metal loading. For the novel cathode electrode studied here, this
effect becomes apparent only with high ionomer coverage, as described in the main text, which is accounted for by decreasing the effective diffusion coefficient of oxygen gas in the porous electrode. This approach reproduces the depressed feature in the EIS spectra fairly well.

The electrode reaction was assumed to proceed in an ECE sequence, following previous literature. This mechanism considers a fast \( O_2 \) adsorption process (a), followed by the first electron transfer process that is also the rate limiting step (b), followed by a rapid chemical (c) and another electron transfer step (d).

\[
\begin{align*}
O_2 & \leftrightarrow (O_2)_{ad} \quad \text{(a)} \\
(O_2)_{ad} + H_2O + e^{-} & \rightarrow O_2H_{ad} + OH^- \quad \text{(b)} \\
O_2H_{ad} + H_2O & \xrightleftharpoons[k_{cb}]{k_{cf}} 3OH_{ad} \quad \text{(c)} \\
OH_{ad} + e^{-} & \xrightarrow[k_{df}]{k_{db}} OH^- \quad \text{(d)}
\end{align*}
\]

The kinetics of the reactions are based on Butler-Volmer equations:

\[
\begin{align*}
\eta &= \phi_s - \phi_l - E_{eq} \quad \text{(D.2)} \\
E_{eq} &= -\frac{RT}{F} \ln \left( \frac{c_{OH^-}}{c_{O_2}} \right) \quad \text{(D.3)} \\
v_b &= k_bc_{O_2}\exp(-\alpha_f\eta) \quad \text{(D.4)} \\
v_c &= k_cf c_{2H_{ad}} - k_{cb} c_{OH_{ad}}^3 \quad \text{(D.5)} \\
v_d &= k_{df} c_{OH_{ad}} \exp(-\alpha_f\eta) - k_{db} c_{OH^-} \exp((1 - \alpha)\eta) \quad \text{(D.6)} \\
i_f &= -F(v_b + v_d) \quad \text{(D.7)}
\end{align*}
\]

where \( \phi_s, E_{eq} \) stand for the electrode potential and the overall equilibrium potential. \( k_i \) is the rate constant, and \( f = F/(RT) \). Two surface adsorbed species are assumed to be present, and their time dependent evolutions are:

\[
\begin{align*}
\frac{\partial c_{O_2H_{ad}}}{\partial t} &= v_b - v_c \quad \text{(D.8)} \\
\frac{\partial c_{OH_{ad}}}{\partial t} &= 3v_c - v_d \quad \text{(D.9)}
\end{align*}
\]
D.3.2 Boundary conditions

The model consists of a 400 nm porous electrode, and a 10 um electrolyte region. The electrode potential at the left boundary of the porous electrode is set to a target value, and the electrolyte potential at the right boundary of the electrolyte to 0 (i.e. the reference electrode), where the concentration of ions are also fixed to 0.1 M. We considered two types of constraint for the oxygen gas. In the first model, the oxygen concentration is fixed at the left boundary of the porous electrode, corresponding to the novel architecture that has gas being fed in mainly through the back of the Pt/PTFE. The second model set the oxygen concentration at the right edge of the electrolyte, a scenario similar to the RDE experiments, where the gas has to diffuse through the electrolyte. The two models successfully reproduce the overall features of the experimental EIS spectra both with the novel architecture and the RDE setup (Fig. 5.4).

D.3.3 Time-domain EIS modeling

The EIS spectra are obtained by solving the equations in the frequency domains. To gain more insights into the origin of the unique features in the EIS spectra, we modeled the EIS spectra in the time domain, which allows us to trace the phase shifts of the relevant variables. A steady state simulation was first carried out. The model then simulates an experimental EIS measurement, where a single sine voltage \( \nu \) was imposed on the steady DC voltage \( V \), and the resulted time-varying current was collected at the point of interest (\( x=0 \)). Subtracting from the overall current the stationary DC current \( I \) generates a single sine current \( i \) which has the same frequency as the input voltage \( \nu \) as long as the perturbation is small enough (Fig. 5.4). At least two periods of time duration with 50 points in each period was employed. The time domain signals were Fourier transformed into the frequency domain using Matlab R2018a.

We compared the EIS spectra from the frequency- and time-domain simulations for a simple system that couples a redox reaction with a diffusion process. The two methods generate very
similar spectra (Fig. D.9). Even though the time-domain model provides a more straightforward method, we did notice it to be less robust than the frequency-domain approach. For more complicated systems, the time-domain simulations failed to converge at certain frequencies.

The modeling was carried out using COMSOL 5.6 using the MUMPS solver. Relative tolerance of $10^{-4}$ was used for stationary and frequency simulations. A 0.01 nm mesh size was used between all the boundaries.

Table D.1. Parameters for the numerical model

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
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<tr>
<td>$D_k$</td>
<td>2e-10 m$^2$/s</td>
</tr>
<tr>
<td>$D_{OH^{-}}$</td>
<td>6e-10 m$^2$/s</td>
</tr>
<tr>
<td>$D_{O_2}$</td>
<td>7.9e-12 m$^2$/s (electrolyte), 7.9e-10 m$^2$/s (electrode)</td>
</tr>
<tr>
<td>$k_b$</td>
<td>4.5e-4 m/s</td>
</tr>
<tr>
<td>$k_{ef}$</td>
<td>1e-3 mol/(m$^2$s)</td>
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<tr>
<td>$k_{cf}$</td>
<td>1e-3 mol/(m$^2$s)</td>
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<tr>
<td>$k_{df}$</td>
<td>1e-3 m/s</td>
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<tr>
<td>$k_{df}$</td>
<td>1e-4 mol/(m$^2$s)</td>
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<tr>
<td>$c_0$ (concentration of O$_2$)</td>
<td>50 mmol</td>
</tr>
</tbody>
</table>
D.4 Supplementary results

Fig. D.1. Nyquist plots the Pt/C electrode in RDE setup during the alkaline HOR process at different potentials.

Fig. D.2. EIS measurements of the Pt/C RDE electrode during the acidic HOR process. (a) Bode plots at different rotating rate, at 0.01 V (vs RHE). (b) Bode plots at different applied potentials (vs RHE). The shifting of the peak position with the rotating rate but not potential indicates that it relates to the diffusion process, which is similar to the alkaline HOR (Fig. 5.1).
Fig. D.3. Polarization curves of the Pt/C RDE electrode in the (a) alkaline and (b) acidic HOR process. Much faster reaction kinetics were observed in the acidic electrolyte.

Fig. D.4. (a) Polarization and power density curve of the APEFCs with the conventional MEA configurations for both the cathode and anode. (b) Nyquist plot of the cell at 0.1 A/cm² applied current density. Testing conditions are the same as those in Fig. 5.2 and 5.3.
Fig. D.5. Photographs of the Pt/PTFE cathode to be assembled into the APEFC. Two pieces of copper foil cover the top and bottom edge of the Pt/PTFE to connect the catalyst film and the carbon plate. Ionomers were deposited only to the active area (the purple box).

Fig. D.6. Polarization and power density curves of the Ag/PTFE with and without AEM ionomers. The ionomer loading is 75 uL/cm². In contrast to the Pt/PTFE electrode (Fig. 5.3), no significant difference was observed.
Fig. D.7. Polarization and power density curves of the Pt/PTFE without ionomer and with Nafion ionomer. Incorporating the Nafion ionomer leads to decreased performance.

Fig. D.8. Polarization and power density curves of the Pt/PTFE electrode with different thickness of the Pt electrode.
Fig. D.9. (a) Nyquist and (b) Bode plots of the experimental EIS measurements with potentiostat and galvanostat modes. No significant difference was noted, suggesting the equivalency of the two modes. 25 uL ionomer were used.

Fig. D.1. Comparison of the modeled EIS spectra between the time- (red triangle) and frequency- (black line) domain for a simple system coupling an electrochemical reaction and a diffusion process. The similar Nyquist (a) and bode plots (b) indicate the two methods are equivalent.
Fig. D.2. The time variation of input voltage and overall current response for (a) the experiment at 876 Hz (Fig. 5.4c) and (b) the model 1 at 10000 Hz (Fig. 5.4f). Current leads voltage in both cases. The time variation of the input voltage and the capacitive current response for the model 1 at (c) 1 Hz and (d) 10000 Hz. Much smaller capacitive current was seen at the lower frequency. (e) Capacitive current and (f) overpotential as a function of time in model 2 at 10 Hz.
Fig. D.3. (a) Nyquist plots of the experimental EIS at cell potentials 0.81, 0.76, and 0.70 V. Smaller cell potential means larger reaction overpotential. (b) The negative of the imaginary impedance as a function of frequency. The peak position of the higher frequency arc shifts to larger values and the lower frequency inductive loop remains unaffected.

Fig. D.4. (a) Nyquist plots of the modeled EIS at -0.20 and -0.25 V. More negative potential means larger reaction overpotential and the thermodynamic equilibrium potential is set to 0 V. (b) The negative of the imaginary impedance as a function of frequency. The peak position shift is consistent with the experiments shown in Fig. D.12.
Fig. D.5. Extracted resistance values by fitting the (a) experimental and (b) modeled (model 1) EIS at different overpotentials. Applying a larger overpotential leads to decreased values.

Fig. D.6. Extracted resistance values from fitting the simulated EIS spectra in model 1 with different diffusion coefficients for the oxygen gas. Decreasing the $D_{O2}$ mainly affects the transport resistance $WR$. 
Table D.2. Fitted data of modeled EIS spectra, with different diffusion coefficient, \( D_{O2} \)

<table>
<thead>
<tr>
<th></th>
<th>( D_{O2}/10 )</th>
<th>( D_{O2}/100 )</th>
<th>( D_{O2}/1000 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_s )</td>
<td>1.54e-5</td>
<td>1.89e-5</td>
<td>2.07e-5</td>
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<tr>
<td>( R_1 )</td>
<td>1.31e-5</td>
<td>6.37e-6</td>
<td>5.58e-6</td>
</tr>
<tr>
<td>( L_1 )</td>
<td>2.19e-6</td>
<td>9.43e-7</td>
<td>8.34e-7</td>
</tr>
<tr>
<td>( W-R )</td>
<td>8.43e-6</td>
<td>1.85e-5</td>
<td>4.86e-5</td>
</tr>
<tr>
<td>( W-T )</td>
<td>0.4754</td>
<td>0.0011</td>
<td>0.0032</td>
</tr>
<tr>
<td>( W-P )</td>
<td>0.5038</td>
<td>0.2691</td>
<td>0.3674</td>
</tr>
<tr>
<td>CPE-T</td>
<td>12.24</td>
<td>9.956</td>
<td>4.804</td>
</tr>
<tr>
<td>CPE-P</td>
<td>0.9951</td>
<td>1.008</td>
<td>1.075</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>2.52e-5</td>
<td>4.72e-5</td>
<td>5.20e-5</td>
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</tbody>
</table>

a. Unit for \( R_s, R_1, W-R \) is \( \Omega \cdot m^2 \), CPE \( m^2 \cdot \Omega^{-1} \cdot s^{-\alpha} \), W-T sec, \( L_1 \Omega \cdot \text{sec/m}^2 \).

Table D.3. Fitted data of modeled EIS spectra, under different biases

<table>
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<tr>
<th></th>
<th>-2.0 V</th>
<th>-2.5 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_s )</td>
<td>1.54e-5</td>
<td>1.17e-5</td>
</tr>
<tr>
<td>( R_1 )</td>
<td>1.31e-5</td>
<td>7.61e-6</td>
</tr>
<tr>
<td>( L_1 )</td>
<td>2.23e-6</td>
<td>9.97e-7</td>
</tr>
<tr>
<td>( W-R )</td>
<td>8.43e-6</td>
<td>3.10e-6</td>
</tr>
<tr>
<td>( W-T )</td>
<td>0.4863</td>
<td>0.1701</td>
</tr>
<tr>
<td>( W-P )</td>
<td>0.5060</td>
<td>0.4341</td>
</tr>
<tr>
<td>CPE-T</td>
<td>12.48</td>
<td>11.08</td>
</tr>
<tr>
<td>CPE-P</td>
<td>0.9929</td>
<td>1.006</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>4.40e-5</td>
<td>8.80e-5</td>
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</tbody>
</table>
Table D.4. Fitted data of experimental EIS spectra, with 2 uL of ionomer (fitting scheme one)

<table>
<thead>
<tr>
<th></th>
<th>0.81 V</th>
<th>0.76 V</th>
<th>0.70 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs*</td>
<td>1.606</td>
<td>1.027</td>
<td>0.8172</td>
</tr>
<tr>
<td>R1</td>
<td>1.241</td>
<td>0.8730</td>
<td>0.6661</td>
</tr>
<tr>
<td>L1</td>
<td>0.1235</td>
<td>0.1017</td>
<td>0.1030</td>
</tr>
<tr>
<td>W-R</td>
<td>6.227</td>
<td>4.268</td>
<td>3.618</td>
</tr>
<tr>
<td>W-T</td>
<td>5.90e-4</td>
<td>4.27e-4</td>
<td>5.67e-4</td>
</tr>
<tr>
<td>W-P</td>
<td>0.4410</td>
<td>0.4201</td>
<td>0.3686</td>
</tr>
<tr>
<td>CPE-T</td>
<td>3.06e-4</td>
<td>2.25e-4</td>
<td>1.56e-4</td>
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<tr>
<td>CPE-P</td>
<td>0.7951</td>
<td>0.8247</td>
<td>0.8501</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>9.03e-4</td>
<td>4.01e-4</td>
<td>4.49e-4</td>
</tr>
</tbody>
</table>

*Unit for Rs, R1, W-R is \( \Omega \), \( \Omega \cdot \text{s} \cdot \text{CPE} \), \( \Omega \cdot \text{sec} \). W-T, L1 \( \Omega \cdot \text{sec} \).*

Table D.5. Fitted data of experimental EIS spectra, with 6 uL of ionomer (fitting scheme one)

<table>
<thead>
<tr>
<th></th>
<th>0.74 V</th>
<th>0.70 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>0.6344</td>
<td>0.2311</td>
</tr>
<tr>
<td>R1</td>
<td>0.1836</td>
<td>0.1711</td>
</tr>
<tr>
<td>L1</td>
<td>0.0199</td>
<td>0.0115</td>
</tr>
<tr>
<td>W-R</td>
<td>1.008</td>
<td>0.7818</td>
</tr>
<tr>
<td>W-T</td>
<td>4.70e-4</td>
<td>2.35e-4</td>
</tr>
<tr>
<td>W-P</td>
<td>0.4016</td>
<td>0.3992</td>
</tr>
<tr>
<td>CPE-T</td>
<td>6.48e-5</td>
<td>3.34e-4</td>
</tr>
<tr>
<td>CPE-P</td>
<td>0.9411</td>
<td>0.7912</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>1.26e-3</td>
<td>1.24e-3</td>
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Table D.6. Fitted data of experimental EIS spectra, with 2 uL of ionomer (fitting scheme two)

<table>
<thead>
<tr>
<th></th>
<th>0.81 V</th>
<th>0.76 V</th>
<th>0.70 V</th>
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<tbody>
<tr>
<td>Rs</td>
<td>1.587</td>
<td>1.037</td>
<td>0.8086</td>
</tr>
<tr>
<td>R1</td>
<td>1.353</td>
<td>0.8792</td>
<td>0.6855</td>
</tr>
<tr>
<td>L1</td>
<td>0.1253</td>
<td>0.0713</td>
<td>0.0867</td>
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<tr>
<td>W-R</td>
<td>3.665</td>
<td>4.360</td>
<td>6.137</td>
</tr>
<tr>
<td>W-T</td>
<td>2.09e-9</td>
<td>1.05e-8</td>
<td>1.1e-8</td>
</tr>
<tr>
<td>W-P</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>CPE-T</td>
<td>5.55e-4</td>
<td>4.51e-4</td>
<td>4.46e-4</td>
</tr>
<tr>
<td>CPE-P</td>
<td>0.7502</td>
<td>0.7787</td>
<td>0.7854</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>7.00e-4</td>
<td>8.42e-4</td>
<td>1.42e-3</td>
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Table D.7. Fitted data of experimental EIS spectra, with 6 uL of ionomer (fitting scheme two)

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<th>0.74 V</th>
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<tr>
<td>Rs</td>
<td>0.6600</td>
<td>0.2390</td>
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<tr>
<td>R1</td>
<td>0.1845</td>
<td>0.1840</td>
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<tr>
<td>L1</td>
<td>0.0103</td>
<td>0.0072</td>
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<tr>
<td>W-R</td>
<td>1.106</td>
<td>0.7963</td>
</tr>
<tr>
<td>W-T</td>
<td>2.19e-9</td>
<td>2.62e-10</td>
</tr>
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<td>W-P</td>
<td>0.5</td>
<td>0.5</td>
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<tr>
<td>CPE-T</td>
<td>0.0014</td>
<td>0.0019</td>
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<td>CPE-P</td>
<td>0.7215</td>
<td>0.6795</td>
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<td>( \chi^2 )</td>
<td>0.0017</td>
<td>0.0027</td>
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</table>
Table D.8. Fitted data of experimental EIS spectra, with 6 uL of ionomer (fitting scheme one)

<table>
<thead>
<tr>
<th></th>
<th>0.208 A/cm²</th>
<th>0.333 A/cm²</th>
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</thead>
<tbody>
<tr>
<td>Rs</td>
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<td>0.1998</td>
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<tr>
<td>R1</td>
<td>0.0711</td>
<td>0.0750</td>
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<tr>
<td>L1</td>
<td>0.0032</td>
<td>0.0041</td>
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<tr>
<td>W-R</td>
<td>0.3335</td>
<td>0.3218</td>
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<tr>
<td>W-T</td>
<td>4.32e-4</td>
<td>4.16e-4</td>
</tr>
<tr>
<td>W-P</td>
<td>0.4365</td>
<td>0.4444</td>
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<tr>
<td>CPE-T</td>
<td>3.49e-6</td>
<td>5.58e-6</td>
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<td>CPE-P</td>
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<td>χ²</td>
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<td>9.10e-4</td>
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Table D.9. Fitted data of experimental EIS spectra, with 25 uL of ionomer (fitting scheme one)

<table>
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<td>Rs</td>
<td>0.2383</td>
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<tr>
<td>R1</td>
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<tr>
<td>L1</td>
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<td>0.0065</td>
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<tr>
<td>W-R</td>
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<td>W-T</td>
<td>6.75e-4</td>
<td>1.01e-3</td>
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<tr>
<td>W-P</td>
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<td>0.3836</td>
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<td>CPE-T</td>
<td>5.03e-6</td>
<td>8.64e-6</td>
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<td>CPE-P</td>
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<td>1.27</td>
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<td>χ²</td>
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</table>

Table D.10. Fitted data of experimental EIS spectra, with 6 uL of ionomer (fitting scheme two)

<table>
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<th>0.333 A/cm²</th>
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</thead>
<tbody>
<tr>
<td>Rs</td>
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<tr>
<td>R1</td>
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<td>L1</td>
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<td>0.0031</td>
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<td>W-R</td>
<td>0.3790</td>
<td>0.3574</td>
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<td>W-T</td>
<td>4.47e-9</td>
<td>4.75e-10</td>
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<td>W-P</td>
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<tr>
<td>CPE-T</td>
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<td>0.0015</td>
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<td>CPE-P</td>
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<tr>
<td>χ²</td>
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<td>1.99e-3</td>
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Table D.11. Fitted data of experimental EIS spectra, with 25 uL of ionomer (fitting scheme two)

<table>
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<tr>
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</thead>
<tbody>
<tr>
<td>Rs</td>
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<tr>
<td>R1</td>
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<td>L1</td>
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<td>0.0034</td>
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<td>W-R</td>
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<td>W-P</td>
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<td>CPE-T</td>
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<td>0.0037</td>
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<td>9.03e-4</td>
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D.5 References

