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Electrodes for Solid Oxide Electrolysis (SOE) and Natural-Gas Assisted Steam Electrolysis (NGASE)

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Electrodes for Solid Oxide Electrolysis (SOE) and Natural-Gas Assisted Steam Electrolysis (NGASE)

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Electrolysis requires $V > V_{\text{Nernst}}$

SOE are more efficient
- low cathode losses
- lower Nernst Potential ($\Delta S$)

No external power required.
Produces pure $\text{H}_2$.
High efficiency possible.
Membrane can be mixed conducting

CTP Hydrogen Corp:
www.ctphydrogen.com
NGASE Works!

60% H₂O, 4% H₂, Co/ceria | YSZ(50 μm) | Pd/ceria, CH₄

Spontaneous Reaction

Conversion 10%
Conversion 50%
Conversion 80%
Conversion <3%

Current density (A/cm²)
Potential (V)

1023K
Research Issues:

1) We need electrodes capable of utilizing methane. 
   Ni electrodes ubiquitous but form carbon fibers; we need alternatives.

   (M. L. Toebes, et al., Catalysis Today, 2002)

2) We need to understand the effect of polarity on electrodes. 
   The common air electrode, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, changes with polarization.
   a) LSM is activated by cathodic (fuel cell) polarization.
   b) LSM is deactivated by anodic (SOE) polarization.
Electrode and Cell Fabrication:

**Tape casting/lamination with pore formers**

**Impregnate active components using**
1. Aqueous salt solutions
2. Perovskite nanoparticles
3. Molten salts
4. Electrodeposition
Advantages:

1. Separate firing temperatures for YSZ and active phase.
   - Avoids solid-state reactions between LSF & YSZ.
   - Can use low-melting solids (CuO).

2. Composite is non-random structure.

   a) Electrical conductivity of LSM-YSZ
   700°C in air, composites calcined at 1523 K.

   b) CTE of LSCo-YSZ

<table>
<thead>
<tr>
<th>LSCo Weight Fraction in YSZ</th>
<th>0%</th>
<th>35%</th>
<th>45%</th>
<th>55%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE (10⁻⁶/K), 300 to 1073 K</td>
<td>10.3</td>
<td>11.7</td>
<td>12.6</td>
<td>12.6</td>
</tr>
</tbody>
</table>

CTE of LSCo is 23x10⁻⁶/K
Cu-based anodes are stable in hydrocarbons but not suitable for CH$_4$ utilization

- Low catalytic activity (ceria is the catalyst)
- Limited to use at lower temperatures; sintering causes loss of electrode conductivity.
Solution 1: Electroplate Cu onto Co cermets

Idea: “Coat” thermally stable Co with chemically stable Cu:

Cu and Co do not form alloys
Key is to deposit evenly throughout the pores; Co plating is much easier than Cu

But Cu segregates to Co surface

![Graph showing XPS of 250-nm Co film on Cu with heating]
Co plated Cu stable in CH₄ at 800°C for 3 h

Dramatic increase in thermal stability with Cu-Co

R_Ω as a function of time at 900°C

Dramatic increase in thermal stability with Cu-Co
Solution 2: Ceramic anodes

Problem: Oxides have either poor conductivity at low P(O_2) or poor catalytic activity

Concept: Separate the two required functions

Anode current collector: Porous ceramic, optimized for conductivity

Anode functional layer: Optimized for catalytic performance
Thin to avoid need for high conductivity

Key point:
If $\delta = 10 \ \mu$m and $R_{\text{ohmic}}$ must be $< 0.1 \ \Omega \cdot \text{cm}^2$, $\sigma$ need only be 0.01 S/cm!
Current collector: 
La$_{0.3}$Sr$_{0.7}$TiO$_3$
Functional layer: 
1wt%Pd-40wt% ceria in YSZ

![SEM image of porous material](image)

20 µm

YSZ electrolyte
Porous YSZ-active region

La$_{0.3}$Sr$_{0.7}$TiO$_3$ current collector
Catalysis is crucial!

700°C H₂ (3% H₂O)

Need combination of ceria and metal

40 wt% CeO₂
Pd 1 wt%
Ni 1 wt%
Cu 5 wt%
A remaining issue:
Conductivity of ceria layer is not stable at low $P(O_2)$:

Ceria film in porous YSZ
Wet $H_2$ at 973 K (1.1 V) Methanol (1.25 V)

Need to develop other ways to make functional layer conductive:
1) Use composites of YSZ with doped SrTiO$_3$
2) Dope the YSZ with Ce, Ti, or Nb.
How does polarity affect electrodes?

Characterization:

Impedance spectroscopy allows separation of electrode and electrolyte losses:

- Losses (electr)
- Losses (fuel cell)

Nernst

Impedance spectroscopy allows separation of electrode and electrolyte losses:

- Losses (electr)
- Losses (fuel cell)

Slope of V-i curve

Electrolyte losses
Polarization activation with LSM-YSZ

700°C, H₂/3%H₂O, OCV after applying current

Note: These changes are reversible. τ ~ 120 minutes.
What we believe is happening:

1) Dense LSM covers YSZ Gaps in LSM film caused by reduction
2) Performance limited by Gas can get to YSZ interface.
   oxygen diffusion.

Process driven by surface interactions between LSM & YSZ
LSM Particles on YSZ (100): Effect of calcination temperature


850°C  1050°C  1150°C
Movement of particles is reversible:

1) LSM is stable in 10%H₂O-90% H₂ at 700°C.
2) Reducing LSM-YSZ electrode “activate” it.
Consequences for electrolysis (anode environment is oxidizing):

285 mA/cm²; 700°C; 85%H₂-15%H₂O| air

LSM-YSZ anode

LSF-YSZ anode
Publications Citing DOE Support (2006 -)

Support Layers can be added for strength:

Dense YSZ

Porous YSZ

Dense YSZ

Porous YSZ

Laminated cell

Final Product

FFC, Inc.