

Electrodeposition of Cu into a Highly Porous Ni/YSZ Cermet

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Abstract

The electrochemical deposition of Cu into 0.12 cm and 60 μm thick, highly porous (65 vol. %) Ni/YSZ (yttria-stabilized zirconia) cermets was investigated. An electrochemical cell in which the electrolyte solution was allowed to flow through the porous Ni/YSZ substrate was used in order to eliminate mass transfer limitations and determine conditions for which the potential drop in the electrolyte solution was minimized. Conditions were established which allowed for uniform Cu deposition throughout the porous substrate. The use of electrodeposition to make a Cu-coated Ni-YSZ cermet anode for a solid oxide fuel cell (SOFC) was also demonstrated.

Introduction

The development of high-performance electrodes for solid-oxide fuel cells requires the optimization of anode porosity, microstructure, and composition.¹ While a variety of approaches have been used to synthesize porous anodes and cathodes,²⁻⁷ deposition of materials into a porous matrix of the electrolyte material which is pre-sintered onto the dense electrolyte layer⁸⁻¹⁴ has several advantages over the more common co-sintering method. These include lower processing temperatures for the active components and less stringent requirements for matching the CTE with that of the electrolyte. We have previously demonstrated this approach for the synthesis of Cu/CeO₂/YSZ (yttria-stabilized zirconia) anodes for SOFCs which use YSZ as the electrolyte in which both the Cu and CeO₂ were added using impregnation of aqueous solutions containing dissolved salts of Cu or Ce.^{8, 10, 11} A similar approach has also been demonstrated for Sr-doped LaMnO₃/YSZ and Sr-doped LaCoO₃/YSZ cathodes.^{9, 12, 13}

Although wet impregnation into a porous electrode matrix has proven to be a versatile method for electrode synthesis, it gives limited control over the microstructure of the deposited components. Electrochemical deposition is another method that can in theory be used for the addition of active components to a conducting porous electrode structure. This approach has the potential to allow for more control over the morphology of the deposits and may be particularly useful for the production of layered microstructures. Electrochemical deposition of uniform layers throughout a highly porous substrate is challenging and several criteria need to be met in order to obtain uniform deposition throughout the pores. First, diffusional limitations must be minimized in order to insure that the surface reaction is rate limiting throughout the

length of each pore. Second as shown schematically in Figure 1, the potential drop in the bulk of the electrolyte solution must also be minimal in order to obtain a constant reaction rate throughout the length of a pore.

While there are several reports in the literature of the electrodeposition into porous cellular electrodes that have uniform pore structures,¹⁵⁻¹⁸ we are unaware of any previous studies of electrochemical deposition into random porous materials where the pore size is on the order of several microns. Here we report our initial studies of the electrochemical deposition of Cu into a porous Ni/YSZ cermet anode and the identification of conditions which allow for the deposition of uniform Cu layers.

Experimental

Porous Ni/YSZ cermet substrates approximately 1.2cm in diameter and 0.12cm in thickness were used in the Cu electrodeposition experiments. These substrates were produced by sintering die-pressed discs containing NiO (Alfa Aesar) and YSZ (8mol% yttria, Tosoh) powders with graphite used as a pore former in air at 1673 K for 4 hours followed by annealing in H₂ at 1073 K for 6 hours to reduce the NiO to Ni. The substrates used in this study contained 65 wt. % Ni, 35 wt. % YSZ, and had porosity of ~65 vol. % as determined using the Archimedes method.

Deposition experiments were conducted using electrochemical cells containing aqueous solutions of CuSO₄ and H₂SO₄. As will be discussed below, the concentrations of CuSO₄ and H₂SO₄ were varied in order to adjust the conductivity of the solution and to control mass transfer limitations. Cu was used as counter and reference electrodes and the porous Ni/YSZ substrate was used as the working electrode. The configuration of the

two electrochemical cells used in this study are shown in Figure 2 and consisted of a standard two electrode cell (cell A) and a cell in which the electrolyte solution was allowed to flow through the porous substrate (cell B). The latter cell is described in more detail in the results section below. For both cells the electroplating solution in the beaker was well mixed using a magnetic stir bar.

Results and Discussion

Initial Cu deposition experiments were conducted using the two-electrode cell configuration shown in Figure 2A with 0.5 M concentrations of both CuSO_4 and H_2SO_4 and an applied DC current of 50 mA for 2 hours. Following deposition, the distribution of Cu throughout the porous Ni/YSZ cermet was evaluated using cross-sectional scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDAX) (JEOL 6400). As shown in Figure 3, Cu deposition was inhomogeneous with the bulk of the Cu being deposited near the two exposed surfaces of the Ni/YSZ cermet. Varying the CuSO_4 concentration from 0.02 to 1.5 M, the H_2SO_4 concentration from 0.5 M to 1 M, and decreasing the applied current to 10 mA were studied as means to render the surface reaction the rate limiting step and achieve more uniform Cu deposition throughout the porous Ni/YSZ cermet. This proved unsuccessful and Cu deposition occurred primarily on the outer surfaces of the Ni/YSZ cermet for all deposition conditions that were studied.

For the relatively thick porous Ni/YSZ substrates used in this study, it is likely that the inhomogeneous Cu deposition was due in large part to mass transfer limitations; although a high potential drop in the electrolyte solution can not be ruled out as a contributing factor. In order to eliminate mass transfer limitations and evaluate how the

potential drop in the solution affects deposition in the porous substrate, a novel flow through electrochemical cell was employed. A schematic diagram of this cell is shown in Figure 2B. The porous Ni/YSZ cermet disk was attached to a glass tube which was placed vertically in the electrolyte solution as shown in the figure. The glass tube was filled with the electrolyte solution which flowed through the Ni/YSZ cermet at a flow rate of several ml/min during Cu deposition. This flow through geometry minimized diffusional limitations in the electrolyte solution by using convective transport to supply Cu ions to the surface of the pores in the electrode. In addition to the working electrodes, the cell was equipped with two reference electrodes, one placed on the inside of the tube to which the Ni/YSZ cermet was attached and one placed external to the tube in the electrolyte bath. The difference in the potentials of the two reference electrodes, $\Delta\varepsilon_{\text{ref}}$, during Cu deposition provides a measure of the uniformity of the potential in the electrolyte solution throughout the porous Ni/YSZ cermet.

As noted in the introduction, the potential drop in the electrolyte solution in the porous substrate needs to be minimized in order to obtain uniform Cu deposition along the length of each pore. For the flow through cell, this will occur when there is a negligible voltage difference between the two reference electrodes, i.e. $\Delta\varepsilon_{\text{ref}} \approx 0$. In order to determine conditions which approach this limit, deposition experiments were performed as a function of the composition of the electrolyte solution and applied potential. $\Delta\varepsilon_{\text{ref}}$ as a function of both CuSO_4 concentration and the applied potential at a constant H_2SO_4 concentration of 0.5 M is displayed in Figure 4A. These data show that $\Delta\varepsilon_{\text{ref}}$ increases with both applied potential and CuSO_4 concentration. While the former was anticipated, the latter is somewhat surprising since one would expect the

conductivity of the electrolyte solution to increase with increasing ionic strength. This result is consistent, however, with the previous studies of Kamelin et al.¹⁷⁻¹⁹ in which it was found that the electrical conductivity of H₂SO₄/CuSO₄ electrolyte solutions decreases with increasing CuSO₄ concentration at constant H₂SO₄ concentration. Kamelin et al. attributed this to the influence of the CuSO₄ on hydrosulfate ion dissociation and to a lesser extent to an increase in solution viscosity with increasing CuSO₄ content.

Figure 4B shows how $\Delta\varepsilon_{\text{ref}}$ varies as a function of H₂SO₄ concentration and the applied potential at a constant CuSO₄ concentration of 0.02 M. In this case the expected result was obtained and $\Delta\varepsilon_{\text{ref}}$ increases with increasing applied potential and decreases with increasing H₂SO₄ concentration. During collection of the data in Figure 4 it was observed that for conditions for which $\Delta\varepsilon_{\text{ref}}$ was greater than ~0.03 V a thick Cu film was deposited on the surface of the cermet exposed to the beaker containing the electrolyte solution suggesting inhomogeneous Cu deposition. Analysis of the cermets following each experiment confirmed this and showed that the majority of the Cu was deposited near the exposed surface. Thus, the data in Figure 4 help to identify conditions for which potential gradients in the electrolyte solution can be minimized and indicate that a low CuSO₄ concentration and a high H₂SO₄ concentration will be required in order to obtain uniform Cu deposition in the porous Ni/YSZ cermets.

Since the results presented in Figure 4 indicate that an electrolyte solution containing 0.02 M CuSO₄ and 0.5 M H₂SO₄ should have a minimal potential drop in the electrolyte solution and allow for homogeneous Cu deposition in a porous Ni/YSZ cermet these conditions were chosen for additional study. A deposition experiment was performed in the flow through cell using this electrolyte composition and an applied

current of 50 mA at $\sim 0.35\text{V}$ for 4 hours. XRD analysis following Cu deposition showed only the presence of Cu and Ni with no indication of oxide formation. The Cu distribution in the Ni/YSZ cermet as determined by EDAX is presented Figure 3. Note that within the uncertainty of the measurement there is a uniform Cu concentration throughout the thickness of the Ni/YSZ cermet.

Due to the local nature of the probe, the EDAX experiments provide only a qualitative measure of the uniformity of the deposited Cu layer in the porous electrode. In order to provide additional insight into how well the Cu layer covered the Ni, experiments were performed in which the Cu-coated Ni/YSZ cermets were exposed to methane at 1073 K for 3 hours. Ni is an excellent catalyst for the formation of carbon filaments when exposed to dry hydrocarbons at high temperatures.²⁰⁻²² This is demonstrated in Figures 5A and B which show a Ni/YSZ cermet before and after methane exposure. Note that after the methane treatment the Ni/YSZ cermet is completely covered by a thick layer of carbon. In contrast to Ni, Cu does not catalyze carbon formation from dry hydrocarbons.²⁰ Thus, if the electrodeposited Cu layer completely covers all of the exposed Ni surfaces in the Ni/YSZ cermet, the cermet should be inert to carbon deposition when exposed to methane at 1073 K. This test was performed using Ni/YSZ cermet that was coated with Cu using the flow through cell at a current of 50 mA at $\sim 0.35\text{V}$ for 4 hours with an electrolyte solution containing in 0.02 M CuSO_4 and 0.5 M H_2SO_4 . The resulting Cu/Ni/YSZ cermet which contained equal amounts of Cu and Ni by weight was exposed to methane at 1073 K for 3 hours. Figures 5C and D show the Cu-coated Ni/YSZ cermet before and after methane exposure, respectively. Note that methane treatment caused little change in the appearance of the

Cu-coated Ni/YSZ cermet and there was no evidence for carbon deposition. In a previous study of Cu/Ni-alloy/YSZ cermet anodes produced by aqueous impregnation,²⁰ carbon deposition upon exposure to CH₄ at 1073 K was observed when the alloy contained as little as 10 % Ni. Thus, the lack of carbon deposition on the sample in 5D suggests that intermixing of the Cu and Ni layers did not occur to an appreciable extent and that the deposited Cu layer completely covered the exposed Ni surfaces.

The results of this study demonstrate that with judicious choice of the electrolyte composition and deposition rate, the flow through method eliminates mass transfer limitations and allows for the uniform electrodeposition of a metal layer throughout a highly porous substrate. This approach however is not particularly well suited for the manufacture of SOFCs where a Cu/Ni/YSZ electrode would need to be connected to a thin, dense YSZ electrolyte layer. Another approach to minimizing mass transfer limitations during electrodeposition into a porous electrode that would be more suitable to cell manufacturing is to use a very thin electrode layer. We tested this approach in an electrolyte supported SOFC. The cell consisted of a dense, sintered disk of YSZ which was 1.2 cm in diameter and 300 μm in thickness. A 60 μm thick, porous Ni/YSZ anode matrix (65 wt% Ni, 35% porous) was then applied by screen printing a slurry containing NiO and YSZ powders, and graphite pore formers, followed by sintering at 1673 K in air. A Sr-doped LaMnO₃ (LSM) cathode was then applied to the exposed surface of the electrolyte disk using an LSM ink and then sintered in air at 1523 K. The cell was then reduced in H₂ at 973 K for 2 hours. These conditions were sufficient to reduce the NiO to Ni without reducing the LSM. Cu was then deposited electrochemically in the porous Ni/YSZ anode layer using a 0.02 M CuSO₄/0.5 M H₂SO₄ electrolyte solution with 0.2

mA of applied current. After deposition the Ni to Cu ratio in the anode was approximately 4 to 1. The LSM cathode was covered with wax to seal it off from the acidic electrolyte solution during Cu deposition. Following Cu deposition the wax layer was removed. A cell was also made in which Cu was not deposited into the anode.

Figure 6 shows the voltage and power densities as a function of current density for the cell with the Ni/YSZ anode while operating on humidified H₂ at 1073 K. Due to the thick electrolyte layer, the cell performance is modest with a maximum power density of 160 mW/cm². As expected, when the anode in this cell was exposed to methane for several hours at 1073 K, the performance diminished and large amounts of carbon were deposited on the anode.

The performance curves for the cell in which Cu was deposited in the Ni/YSZ anode are also shown in Figure 6. This cell had a maximum current density of 100 mA/cm² when operating on humidified H₂ at 1073 K. The lower performance of this cell compared to the one with the Ni/YSZ anode is consistent with the fact that Cu is a much poorer H₂ oxidation catalyst than Ni. This result indicates that the Ni in three-phase boundary region near the anode-electrolyte interface is substantially covered with Cu and furthermore shows that Cu was deposited throughout the porous anode. A VI curve while operating this cell with CH₄ as the fuel at 1073 K is displayed in Figure 7. While the cell performance is poor due to low the low catalytic activity of Cu for methane oxidation, the cell exhibited stable performance for 24 hours with no evidence for carbon deposition on the anode. This result further demonstrates the uniform deposition of Cu throughout the anode and that all of the Ni was covered with Cu.

It is useful to compare the results obtained here to our previous study of Cu/Ni/YSZ cermets in which both Cu and Ni were added via impregnation of a solution containing both $\text{Cu}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ followed by reduction in hydrogen.²⁰ The co-impregnation method resulted in Ni-Cu alloy deposits rather than the layered microstructure produced here. For the alloys it was found that the Ni to Cu ratio needed to be less than 1 to 4 in order to suppress the activity for carbon formation from methane. The fact that for the electrochemically Cu-coated anode used in this study much less Cu was needed in order to suppress the carbon forming reactions indicates that the layered microstructure was relatively stable and that the Cu did not diffuse into the Ni during cell operation.

In addition to establishing conditions for which Cu can be electrodeposited uniformly throughout a porous metal cermet, this study provides a new approach to the synthesis of Cu-based anodes for use in SOFCs. As we have shown previously Cu/CeO₂/YSZ composite anodes in which both the Cu and ceria components were added via wet impregnation of aqueous salt solutions are active for the direct oxidation of hydrocarbons at 973 K and highly resistant to deactivation due to carbon deposition.¹⁰ The results of this study show that the carbon deposition activity of conventional Ni/YSZ cermet anodes can be passivated using a thin electrodeposited layer of Cu. With the addition of an oxidation catalyst, such anodes would also be active for the direct oxidation of hydrocarbons. This approach may have some advantages over impregnated Cu/CeO₂/YSZ anodes, especially when operating at high temperatures. While Cu/CeO₂/YSZ anodes are stable at 973 K, sintering of the Cu layer tends to occur at temperatures above 1073 K and this can cause a decrease in performance. Layered

systems such as Cu/Ni may help to stabilize the Cu from sintering while at the same time eliminating the activity for the deleterious carbon forming reactions.

Cu deposition onto Ni/YSZ cermet anodes has also been proposed as a method to optimize their catalytic activity for the steam reforming of methanol to produce H₂ and CO. Ni is an excellent methane reforming catalyst and Ni/YSZ cermet anodes are used in internal reforming SOFCs in which this reaction takes place on the anode. In addition to the need to use a high steam to carbon ratio in order to avoid carbon deposition, the fact that the steam reforming reaction is endothermic and this can cause large temperature gradients in the SOFC especially near gas inlet is another drawback of this approach. These temperature gradients can decrease cell efficiency and cause internal stresses that can lead to cell fracture. Boder and Dittmeyer have proposed adding Cu to Ni/YSZ cermet anodes to decrease their catalytic activity for methane reforming with the goal of obtaining a more uniform reaction rate throughout the thickness of the anode and the length of the cell.²³ They used wet impregnation of aqueous solutions of Cu(NO₃)₂ to deposit Cu on the Ni/YSZ anode. The results of this study suggest that electrodeposition could also be used for the addition of Cu. Electrodeposition may have advantages since by varying the electrolyte solution composition and applied potential one may be able to control the depth to which Cu is deposited into the anode and thereby maintain a high concentration of exposed Ni near the anode-electrolyte interface where it is need to catalyze the electrochemical reactions.

Conclusions

In this study the electrodeposition of Cu throughout a highly porous Ni/YSZ cermet was demonstrated. Obtaining uniform Cu deposition required both minimization of mass transfer limitations within the pores and a highly conducting electrolyte solution. A flow through electrochemical cell and thin substrates were used as means to minimize mass transfer limitations. For aqueous $\text{CuSO}_4/\text{H}_2\text{SO}_4$ electrolyte solutions it was shown that low concentrations of CuSO_4 were required in order to achieve high conductivity. Ni/YSZ cermets that were electroplated with Cu were stable when exposed to methane at 1073 K and were inactive for the formation of carbonaceous deposits.

Acknowledgements

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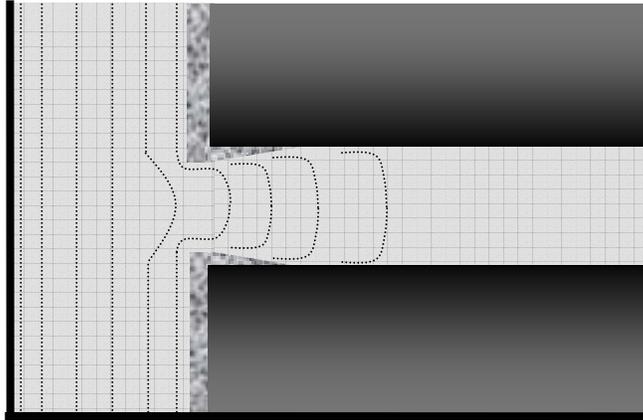
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Figure Captions

1. Schematic diagram of potential distribution in electrolyte solutions with high and low resistance. The dotted lines are lines of constant potential.
2. Schematic diagrams of the (A) two electrode and (B) flow through electrochemical cells used in this study.
3. Distribution of Cu in a porous Ni/YSZ cermet deposited using (○) the two electrode electrochemical cell and (●) flow through electrochemical cell.
4. $\Delta\varepsilon_{\text{ref}}$ as a function of applied potential and (A) CuSO_4 concentration at a constant H_2SO_4 concentration of 0.5 M and (B) H_2SO_4 concentration at a constant CuSO_4 concentration of 0.02 M.
5. Pictures of a Ni/YSZ cermet (A) before and (B) after exposure to CH_4 at 1073 K for 3 hours (the latter sample is contained in a ceramic boat), and of a Cu-coated Ni/YSZ cermet (C) before and (D) after exposure to CH_4 at 1073 K for 3 hours.
6. Voltage and power density versus current for an SOFC with (▲) Ni/YSZ cermet anode and (●) Cu-coated Ni/YSZ cermet anode operating with H_2 fuel at 1073K.
7. Voltage and power density versus current for an SOFC with Cu-coated Ni/YSZ cermet anode operating with CH_4 fuel at 1073K.

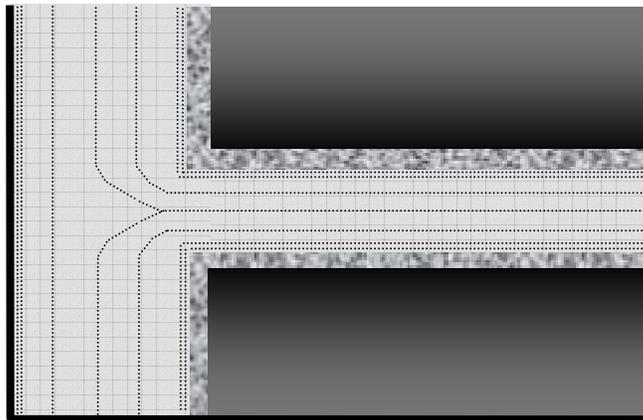
figure 1

High Solution Resistance



Distance from Cu electrode

Low Solution Resistance



Distance from Cu electrode

figure 2.

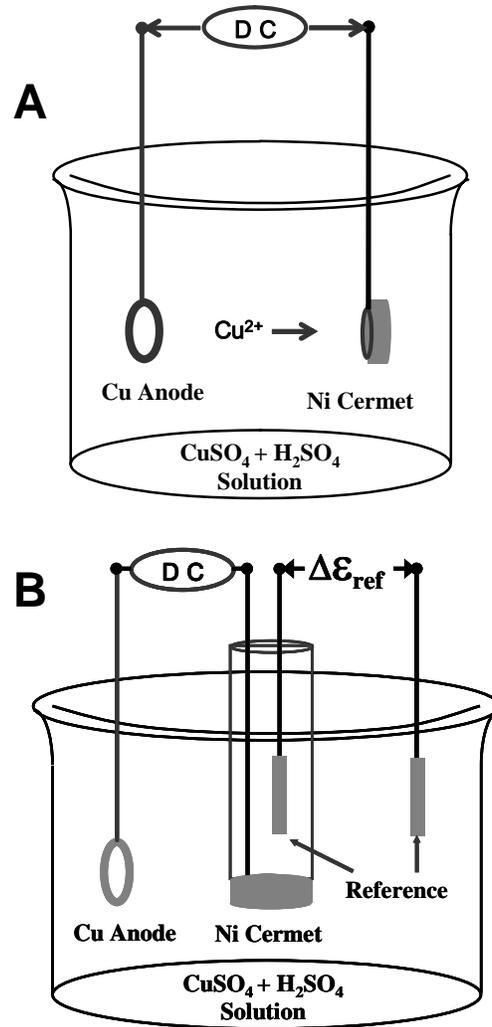


figure 3

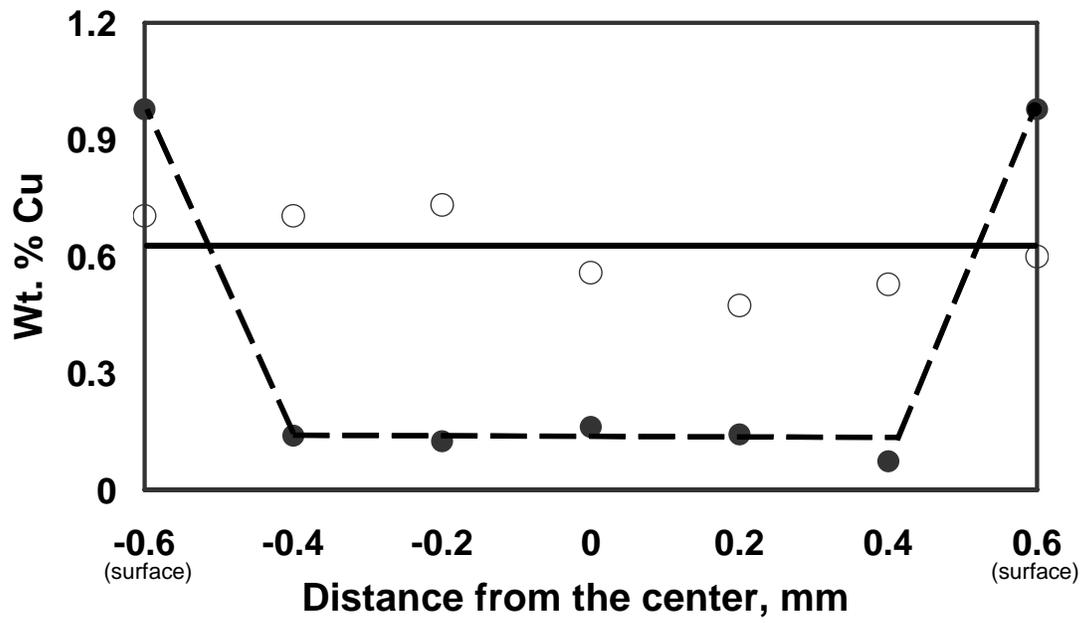


figure 4

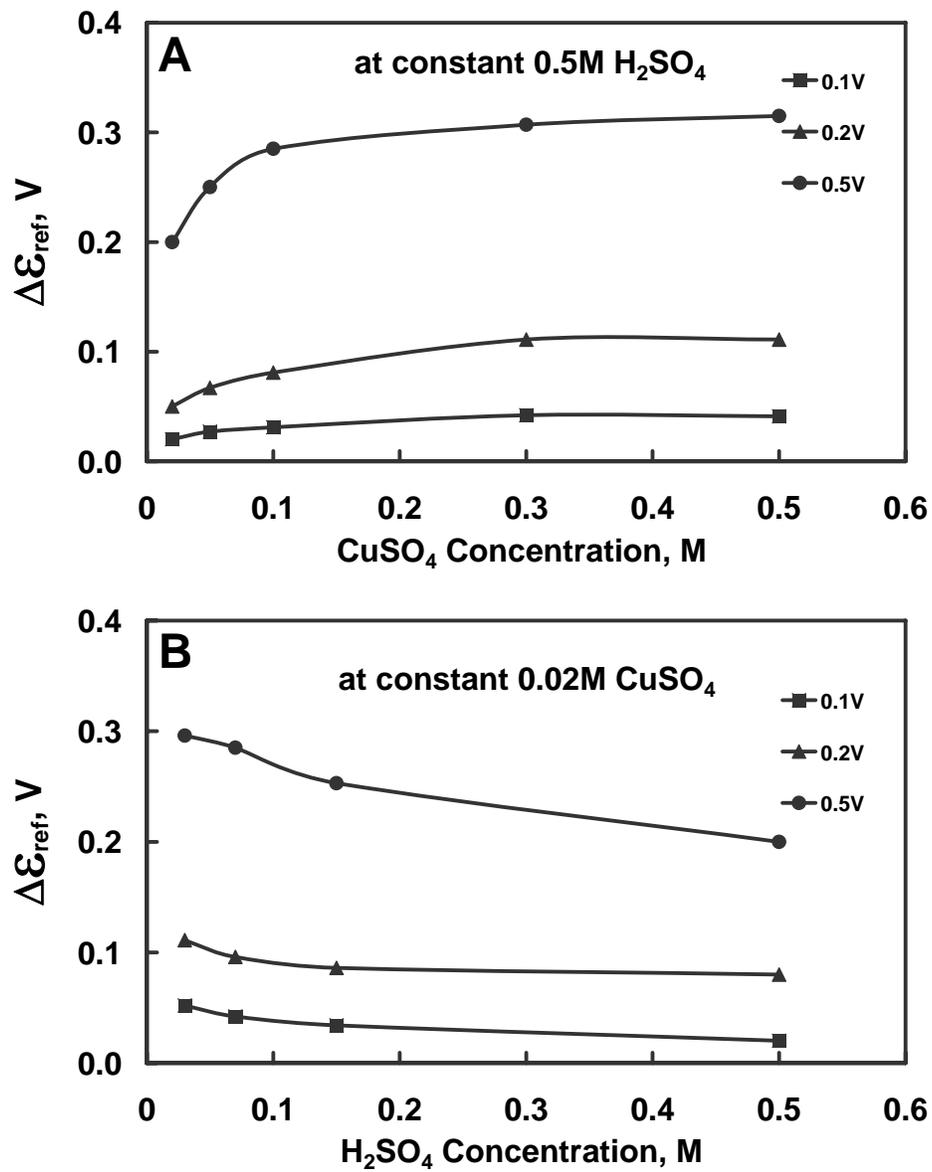


figure 5

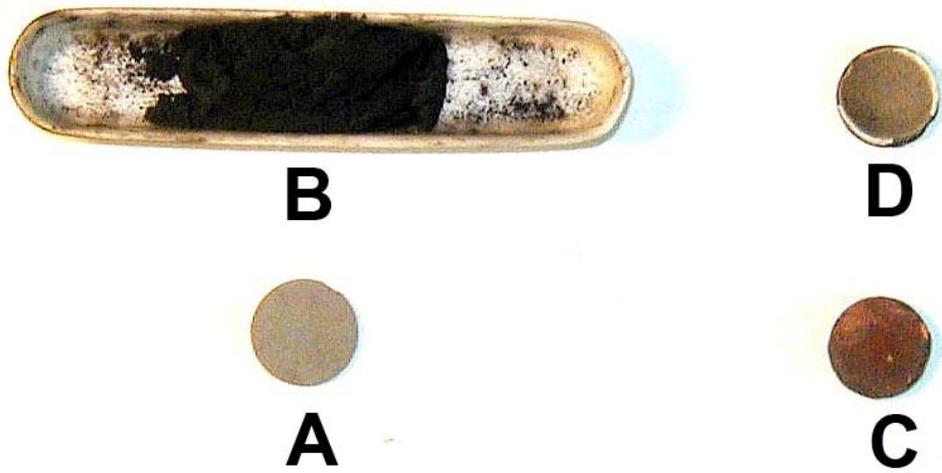


figure 6

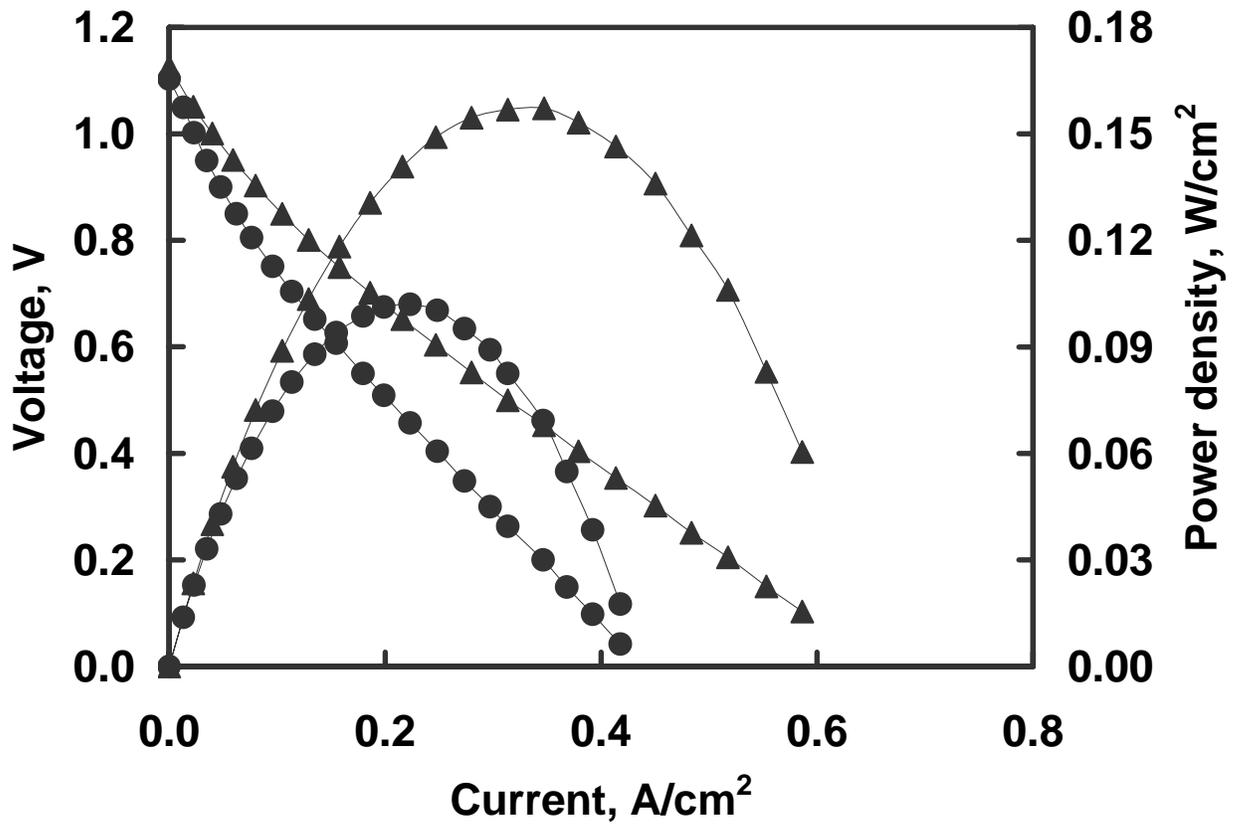


figure 7

