



Short communication

Preparation of Cu–Ni/YSZ solid oxide fuel cell anodes using microwave irradiation

Shamiul Islam, Josephine M. Hill*

Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr. NW, Calgary, Alberta, T2N 1N4, Canada

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ABSTRACT

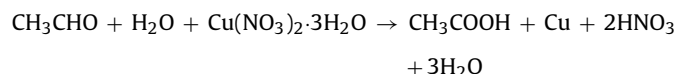
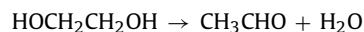
A microwave irradiation process is used to deposit Cu nanoparticles on the Ni/YSZ anode of an electrolyte-supported solid oxide fuel cell (SOFC). The reaction time in the microwave is only 15 s for the deposition of 6 wt% Cu (with respect to Ni) from a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$). The morphology of the deposited Cu particles is spherical and the average size of the particles is less than 100 nm. The electrochemical performance of the microwave Cu-coated Ni/YSZ anodes is tested in dry H_2 and dry CH_4 at 1073 K, and the anodes are characterized with scanning electron microscopy, electrochemical impedance spectroscopy, and temperature-programmed oxidation. The results indicate that preparation of the anodes by the microwave technique produces similar performance trend as those reported for Cu–Ni/YSZ/ CeO_2 anodes prepared by impregnation. Specifically, less carbon is formed on the Cu–Ni/YSZ than on conventional Ni/YSZ anodes when exposed to dry methane and the carbon that does form is more reactive.

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1. Introduction

Solid oxide fuel cells (SOFC) are high temperature (773–1273 K) electrochemical devices that directly convert the chemical energy of a fuel into electricity. Direct utilization of dry hydrocarbon fuels at the anode of SOFC can help to reduce the operational cost and the complexity of a system [1,2]. The conventional SOFC Ni/YSZ anodes catalyze the formation of coke in the presence of hydrocarbon fuels and this coke can severely damage the anode structure. Thus, metals such as Cu, which does not catalyze the C–C bond formation, have been added to the Ni in the anode to reduce or prevent carbon formation when operating with hydrocarbon fuels [3–5]. The most common way of incorporating Cu in the anode is to impregnate copper nitrate $\text{Cu}(\text{NO}_3)_2$ solution in the anode followed by a calcination step to decompose $\text{Cu}(\text{NO}_3)_2$ to CuO, which is finally reduced to Cu in situ in H_2 during cell testing. Multiple impregnation and subsequent calcination steps are often required to obtain a sufficient Cu loading, which makes impregnation a very time consuming process [4,6]. Also the distribution of deposited particles obtained by impregnation is not always homogeneous. Electrodeposition has also been used to deposit Cu in the anode of electrolyte and anode-supported SOFC. This technique requires a significant time (hours) for the deposition of Cu in an anode-supported SOFC [7]. The time required for deposition of Cu in an electrolyte-supported SOFC was not reported [6,8]. One potential limitation to electrodeposition is that this method requires that the substrate material be conductive [6].

In this study, we report a novel and simple method to deposit Cu on Ni/YSZ SOFC anodes using a microwave irradiation process. Previously, microwave irradiation processes have been used for the synthesis of metal nanoparticles (Ni, Pd, Ag) and metal oxides ($\gamma\text{-Fe}_2\text{O}_3$, NiO, ZnO, CuO, Co- $\gamma\text{-Fe}_2\text{O}_3$) [9–12]. This process can be faster than most other processes because microwave irradiation times may be on the order of seconds and a calcination step to remove the precursor is not required. Cu particles can be directly deposited onto a support from a solution of ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with an irradiation time of 15 s. The deposition of Cu particles may follow the reaction pathway shown below, which is based on the mechanism of the polyol reduction of metal ions [13,14].



In this communication, we demonstrate that Cu–Ni/YSZ anodes can be prepared by microwave irradiation and the performance of anodes made by this technique is comparable to that reported for anodes prepared by impregnation.

2. Experimental

2.1. Preparation of button cells

Electrolyte-supported button cells were tested in this study. YSZ disks of 0.3 mm thickness were prepared by sintering YSZ powders (TOSOH, TZ-8Y, Japan) at 1723 K for 2 h. To prepare the

* Corresponding author. Tel.: +1 403 210 9488; fax: +1 403 284 4852.
 E-mail address: jhill@ucalgary.ca (J.M. Hill).

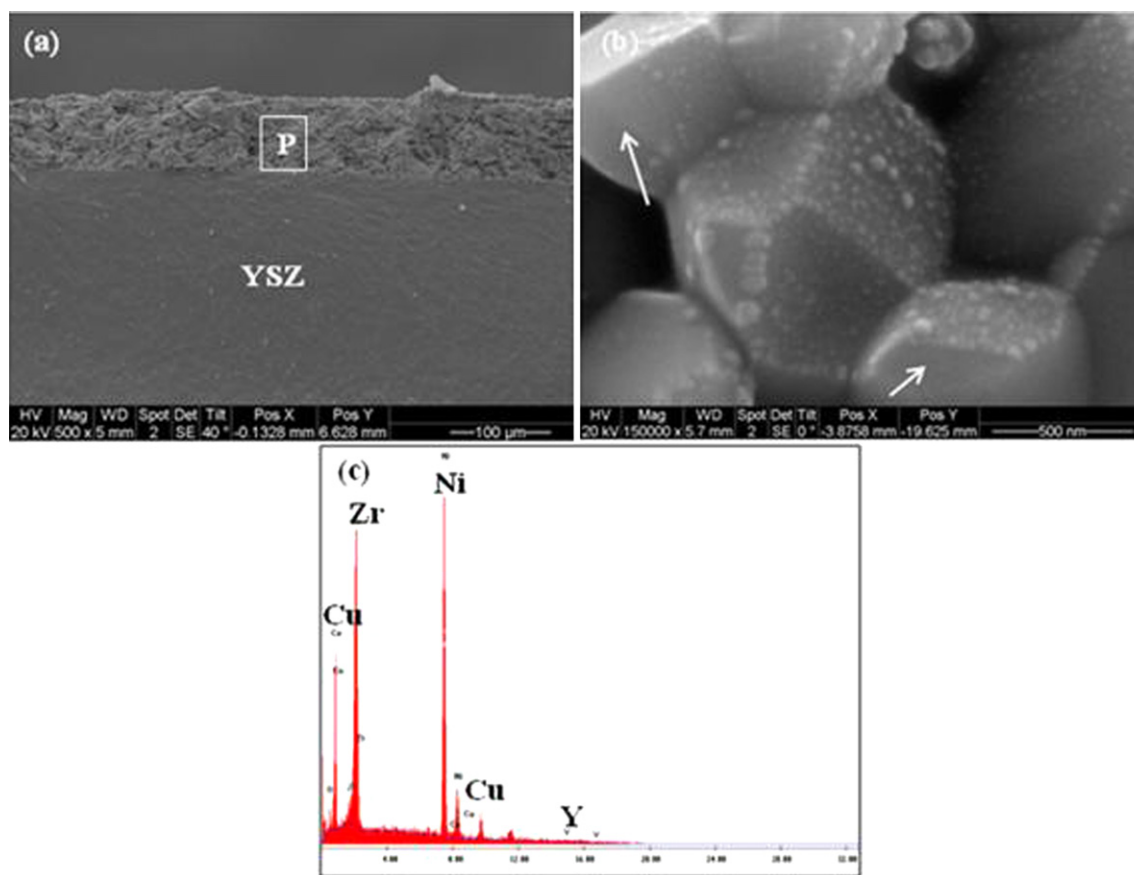


Fig. 1. Cross-sectional SEM images of $\text{Cu}_M\text{Ni}/\text{YSZ}$ cell: (a) anode–electrolyte interface, (b) enlarged image taken from region P and (c) EDS spectra of the anode taken from region P.

anode, a NiO/YSZ slurry was prepared from 56 wt% NiO (Alfa-Aesar, 99%, USA) and 44 wt% YSZ powders mixed by ball milling in acetone for 48 h with zirconia balls. After drying, the NiO/YSZ powder was mixed with glycerol (Alfa Aesar, USA) and the resulting slurry was painted on one side of the YSZ disks, followed by sintering at 1723 K for 2 h. The cathode used in this experiment was a composite of LSM (Praxair, USA) and YSZ . To apply the cathode, a slurry of LSM/ YSZ was prepared by mixing LSM and YSZ powders (50:50 wt%) with glycerol and painting the resulting slurry on the opposite side of the YSZ disk from the anode. The cell was sintered at 1523 K for 2 h, and the geometric areas of both the anode and cathode were $\sim 0.974 \text{ cm}^2$. Before applying the microwave irradiation process to deposit Cu in the anode, the NiO of the anode was reduced to Ni in flowing H_2 (50 mL min^{-1}) at 1073 K for 2 h.

2.2. Microwave irradiation

To deposit Cu onto the Ni/YSZ anode, a 0.033 M solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Alfa Aesar, USA) salt with a reducing agent of ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, Reagent Plus $\geq 99\%$, Sigma Aldrich, USA) was prepared. The solution was stirred for 30 min at room temperature and then ultrasonicated for 5 min to ensure that the salt was completely dissolved in the solution. Vacuum grease was applied to protect the cathode and electrolyte surfaces, and to allow the Cu solution to only access the anode. The button cell was dipped in the solution and then irradiated for 15 s using a household microwave oven (Danby Products Inc., 2.45 Hz, 700 W, USA). The temperature of the irradiated solution was 365 K as measured by a digital thermometer (DiGi-Sense, Type J Thermo-

couple, USA). Preliminary tests with irradiation times up to 60 s indicated that the Cu particles will begin to agglomerate and, thus, a relatively short irradiation time was used. After irradiation, the vacuum grease was removed and the cell was washed several times with ethanol and distilled water before drying in an oven at 383 K for 1 h. The amount of Cu loading was 6 wt% with respect to Ni which was measured using an ultra precision analytical balance.

Ag wire current collectors were attached to both the anode and cathode using Ag paste. Ceramic paste was used to seal the cells in alumina tubes for electrochemical testing. The cathode side of the button cell was exposed to stagnant air. The electrochemical tests were performed in dry H_2 (50 mL min^{-1}) and dry CH_4 (25 mL min^{-1}) at 1073 K and atmospheric pressure. The stability of the $\text{Cu}_M\text{Ni}/\text{YSZ}$ (where “M” denotes preparation by microwave irradiation) cells was tested for 24 h in dry CH_4 at a current density 20 mA cm^{-2} . Temperature programmed oxidation (TPO) was performed on both $\text{Cu}_M\text{Ni}/\text{YSZ}$ and conventional Ni/YSZ cells that were tested in dry CH_4 for 25 h under OCV conditions. OCV conditions are more severe than working conditions. At working conditions, deposited carbon can be removed by O^{2-} , at the triple phase boundary, and/or the steam produced by the electrochemical reaction. The amount of carbon that formed in an electrolyte-supported cell with a Ni/YSZ anode was shown to be 100 times less at a current density of 50 mA cm^{-2} than at OCV [15]. In this study, the cells were tested in dry CH_4 under OCV conditions to accelerate carbon formation so that the difference between carbon formed on $\text{Cu}_M\text{Ni}/\text{YSZ}$ and Ni/YSZ anodes could be better distinguished. A total of 3 cells were prepared and tested. The results shown in the figures are representative of these cells.

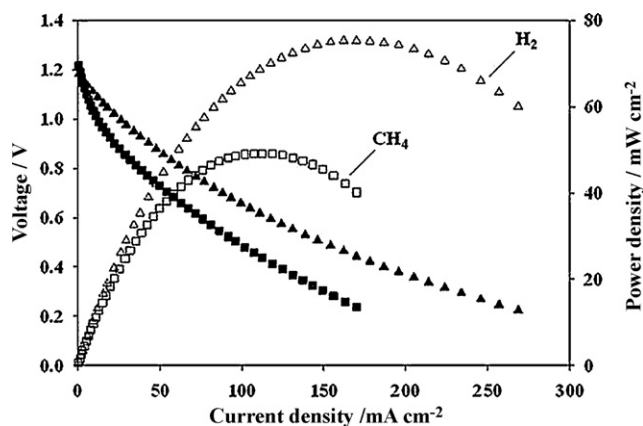


Fig. 2. Voltage (closed symbols) and power density (open symbols) as a function of current density for $\text{Cu}_M\text{Ni}/\text{YSZ}$ anodes tested in dry H_2 (Δ , \blacktriangle) and in dry CH_4 (\square , \blacksquare) at 1073 K.

2.3. Characterization

The microstructure and the morphology of the deposited Cu particles were observed by scanning electron microscopy (SEM, Philips XL30 ESEM). Temperature-programmed oxidation (TPO) was used to characterize any carbon that formed on the anodes. A mass spectrometer (Cirrus 200 Quadrupole) was used to monitor the exit gases during the TPO experiments. Masses 44 (CO_2), 32 (O_2), 28 (CO), 18 (H_2O), and 4 (He) were monitored while the sample was heated at 10Kmin^{-1} in flowing 10% O_2 in He (50mLmin^{-1}).

3. Results and discussion

Fig. 1 shows cross-sectional SEM images of the as-prepared $\text{Cu}_M\text{Ni}/\text{YSZ}$ cell. The thickness of the painted anode was approximately $90\ \mu\text{m}$ (Fig. 1(a)). An enlarged image of the region marked “P” in Fig. 1(a) is shown in Fig. 1(b). This enlarged image shows that the anode was spot coated with Cu but some regions were not covered by Cu as indicated by the arrows. The morphology of the Cu particles was spherical and the average size of the Cu particles was less than 100 nm. The energy-dispersive spectroscopy (EDS) spectrum (Fig. 1(c)) confirms the presence of Cu, Ni, Y and Zr in the anode. The mass change of the samples before and after irradiation indicated that the $\text{Cu}_M\text{Ni}/\text{YSZ}$ anodes contained 6 wt% Cu (with respect to Ni).

Fig. 2 shows the polarization (closed symbols) and power density (open symbols) curves for $\text{Cu}_M\text{Ni}/\text{YSZ}$ anodes obtained in dry H_2 and in dry CH_4 at 1073 K. The performance of the cell was measured first in dry H_2 and then the fuel was switched to dry CH_4 . The OCV of the cell was approximately 1.21 V in dry H_2 . To check the sealing and the quality of the electrolyte, the gas was switched from dry to wet H_2 and an OCV of 1.092 V (not shown here) was obtained. This voltage is very close to the theoretical value of 1.105 V for these conditions indicating that the cell was well-sealed. The maximum power densities were 75mWcm^{-2} in dry H_2 and 49mWcm^{-2} in dry CH_4 after 1 h at OCV at 1073 K. The lower performance of the cell in dry CH_4 compared to dry H_2 , can be attributed to Cu, which is a poor catalyst for C–H bond scission.

Fig. 3 shows the results of galvanostatic tests of the $\text{Cu}_M\text{Ni}/\text{YSZ}$ anodes in dry CH_4 at a current density of 20mAcm^{-2} . The voltage dropped to 0.54 V in the first hour and then increased over 24 h to 0.76 V. The improvement in electrochemical performance for the same cell was also observed in the impedance spectroscopy analysis as shown in Fig. 4. The impedance arcs were measured

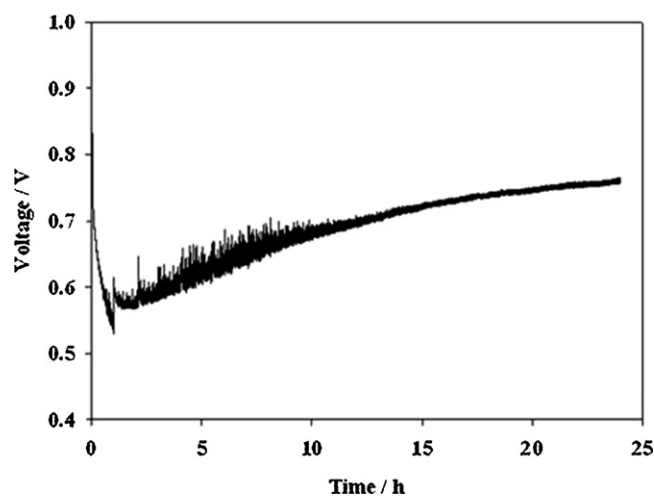


Fig. 3. Stability of the $\text{Cu}_M\text{Ni}/\text{YSZ}$ anode tested at 1073 K in dry CH_4 at 20mAcm^{-2} .

after operating the cell galvanostatically for 1 h and 24 h in dry CH_4 . The high frequency intercept of the impedance arc (R_Q) remained constant at $1.24\ \Omega\text{cm}^2$ between 1 h and 24 h. This consistency indicates that the improvement in electrochemical performance was not related to ohmic losses. The polarization resistances (R_P), as measured by the low frequency intercept of the impedance arc, however, decreased after 24 h of operation in dry CH_4 . There was significant scatter in the measurements at low frequencies, as seen in other systems [16], but the R_P value decreased from $\sim 10\ \Omega\text{cm}^2$ at 1 h to $\sim 7.5\ \Omega\text{cm}^2$ after 24 h. The decrease in polarization resistance indicates that the electrocatalytic process improved with operation time.

TPO studies were conducted to compare the amount and type of carbon formed at OCV conditions in Ni/YSZ and $\text{Cu}_M\text{Ni}/\text{YSZ}$ anodes. Fig. 5 shows the TPO results for Ni/YSZ and $\text{Cu}_M\text{Ni}/\text{YSZ}$ anodes exposed to dry CH_4 for 25 h at OCV and 1073 K. For the Ni/YSZ anode, a single peak of CO_2 was observed at 970 K, which is similar to the value (973 K) reported previously by our group for similar cells [15]. For the $\text{Cu}_M\text{Ni}/\text{YSZ}$ anodes, the CO_2 peak shifted to a lower temperature of 837 K, suggesting that the deposited carbon is more weakly bound when Cu is present. The amount of carbon formed per mol of total metal catalysts as calculated from the

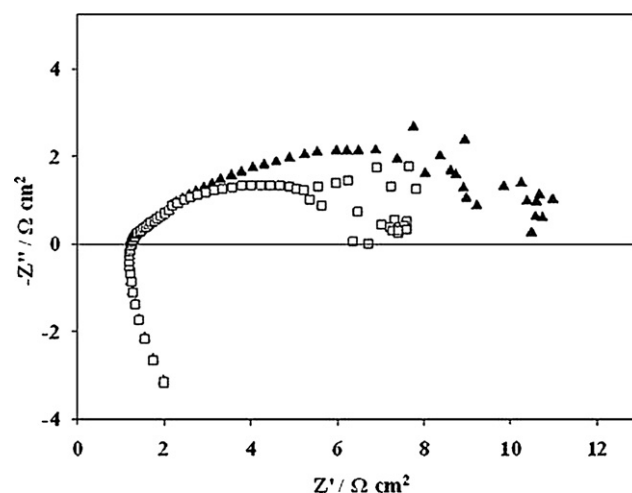


Fig. 4. Electrochemical impedance spectra of $\text{Cu}_M\text{Ni}/\text{YSZ}$ anodes, measured at OCV and at 1073 K after running the cell galvanostatically for 1 h (\blacktriangle) and 24 h (\square) in dry CH_4 .

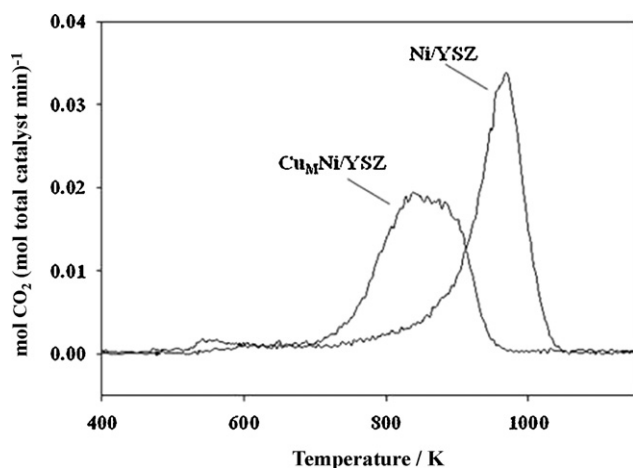


Fig. 5. CO₂ production during TPO of Cu_MNi/YSZ and Ni/YSZ anodes exposed to dry CH₄ for 25 h at OCV and 1073 K.

area under the curve, was slightly lower for Cu_MNi/YSZ than Ni/YSZ anodes.

Kim et al. [4] have reported that the performance of impregnated Cu–Ni/YSZ/CeO₂ anode-supported SOFC increased significantly over a time period of 500 h in dry CH₄ at 1073 K. The amount of Cu to Ni in their study was 4–1, by weight. The increase in performance was attributed to deposited carbon, which helped to link the isolated metal particles to the outside circuit and thus improve electrical conductivity. The authors [4] noted a decrease in both ohmic and polarization resistances over time. In our experiments, we have used electrolyte-supported SOFC with Cu_MNi/YSZ as the anode, and a Cu to Ni ratio of 0.06–1, by weight. The performance trend of Cu_MNi/YSZ anodes was similar to the impregnated Cu–Ni/YSZ/CeO₂ anodes i.e., the performance of Cu_MNi/YSZ anodes in dry CH₄ improved with time. The ohmic resistance of the cell remained constant with time but the polarization resistance decreased, indicating that the electrocatalytic process of Cu_MNi/YSZ anodes improved with time. The maximum power densities for impregnated Cu–Ni/YSZ/CeO₂ anodes (440 and 330 mW cm⁻²), however, were much higher compared to Cu_MNi/YSZ anodes (75 and 49 mW cm⁻²) in dry H₂ and dry CH₄, respectively. The differences in power densities result from differences in the thicknesses of the electrolytes (60 μm vs. 300 μm) and the presence of CeO₂ at the anode, as CeO₂ is known to be an oxidation catalyst for CH₄.

4. Conclusions

Cu particles were directly deposited into Ni/YSZ SOFC anodes using a microwave irradiation process. The irradiation time was 15 s and no calcination step was required. The clear advantage of using the microwave irradiation method is the reduced time required for anode preparation. The irradiation times are on the order of seconds in comparison to impregnation that usually requires multiple steps (because of limited solubility of the metal precursors) and hours if not days for preparation of similar anodes. SEM analysis confirmed that the irradiation technique produced spherical Cu particles that were less than 100 nm in size. The performance of the Cu_MNi/YSZ anodes improved with time when operated with dry CH₄ at 1073 K with a current density of 20 mA cm⁻², which is similar to the behavior of Cu–Ni/YSZ/CeO₂ anodes made by impregnation. Thus, the microwave irradiation process can be used to prepare Cu–Ni/YSZ anodes in significantly shorter time than preparation methods such as impregnation and electrodeposition.

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