



Evaluation of a Cu/YSZ and Ni/YSZ Bilayer Anode for the Direct Utilization of Methane in a Solid-Oxide Fuel Cell

M. A. Buccheri¹, J. M. Hill^{1*}

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

Received February 05, 2013; accepted December 10, 2013; published online February 13, 2014

Abstract

Carbon deposition is an issue when operating solid oxide fuel cells (SOFC) on fuels other than hydrogen, and so a variety of strategies have been used to prevent carbon accumulation on the anodes. In this paper, we describe a bilayer anode that contains a functional layer consisting of Ni/YSZ and a conduction layer consisting of Cu/YSZ. The anode-supported button cells were fabricated using a uni-axially pressing technique to produce the anode, followed by impregnation with Cu. The cells were tested at 1,023 K in

dry CH₄ and their performance compared to that of a typical Ni/YSZ anode. The Cu does not catalyze the cracking of methane and as such less carbon deposits in the conduction layer resulting in anode stability for over 100 h. The limitation with using Cu in the anode is the temperature of operation.

Keywords: Bilayer Anode, Carbon Deposition, Copper, Methane, Solid Oxide Fuel Cell

1 Introduction

In recent years, solid oxide fuel cells (SOFC) have received significant attention because of their high fuel conversion efficiency and their fuel flexibility. Ceramic Fuel Cell Limited (CFCL) [1, 2] has developed a 2 kW SOFC stack and achieved an electrical efficiency up to 60% in natural gas. In the CFCL stack test, natural gas is partially (10%) externally pre-reformed with a steam to carbon ratio (S/C) of 2 to remove larger hydrocarbons [1]. A S/C ratio >2 is generally required because nickel, which is the typical anode material for SOFC, is susceptible to carbon deposition [3–5]. Pre-mixing the fuel with steam may result in thermal gradients in the anode if the endothermic and exothermic reactions are not appropriately balanced throughout the anode [6]. In addition, a lower open circuit voltage (OCV) will be obtained due to dilution of the fuel, and the system complexity is increased [4]. For instance, a water management system must be implemented and failure to supply water to the anode can lead to irreversible damage of the cells due to coking. While Ni-based anodes have shown stable operation in CH₄ in a narrow window of operating conditions – high current densities (>0.8 A cm⁻²) and lower temperature (<973 K) [7] – it is unlikely that Ni can be used in the anode for larger hydrocarbons and low water content without deactivation.

For this reason, several studies have focused on increasing the carbon tolerance of Ni by alloying Ni with various metals including Cu [8–10], Sn [11–13], and Au [14], adding alkali metal oxides (MgO, CaO, SrO, and BaO) to the Ni [15–17], or using alternative materials such as CeO₂–Cu [18, 19], or La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM), and La_xSr_{1-x}TiO₃ (LST) [20–22]. Although some of these different anodes have shown improved carbon tolerance, the electrochemical performance often decreases when the Ni is promoted or replaced [11, 21].

Thus, another approach for developing an anode that is suitable for use with hydrocarbon fuels is the separation of the anode into two layers: a thin (~10 to 20 μm) functional layer (AFL) for the electrochemical reactions and a thicker layer for current collection and support (namely anode conduction layer, ACL) [23–25]. Gross et al. [24] obtained a maximum power density of 0.539 W cm⁻² in CH₄ (3% H₂O) at 1,073 K for a thin (15 μm) 1 wt.% Pd and CeO₂ functional layer with a non-catalytic perovskite, La_{0.3}Sr_{0.7}TiO₃, as the conduction layer. La_{0.3}Sr_{0.7}TiO₃ (LST) was reported to show redox stability, satisfactory electronic conductivity (up to

[*] Corresponding author, jhill@ucalgary.ca

16 S cm⁻¹ in reducing atmosphere) [26], as well as sulfur tolerance [27]. Pillai et al. [25] reported a bilayer anode with a thin (30 µm) Ni/YSZ functional layer and a thicker (~700 µm) La_{0.2}Sr_{0.8}TiO₃ conduction layer that was stable in synthetic natural gas for current densities as low as 0.2 A cm⁻² with little cell voltage degradation (an initial ~120 mV drop) in a fuel mixture of H₂ and 50–100 ppm of H₂S. In further work by this group [28], the superior stability against coking of the Ni-based LST-supported cell was attributed to the thin Ni-cermet layer that was positioned where conditions are least prone to coking: lower CH₄ and higher H₂O and CO₂ partial pressure (see Figure 4 in Ref. [28]).

Cu is relatively inert in terms of breaking C–C bonds, a good electronic conductor and also relatively inexpensive [19]. Thus, we have prepared and investigated a bilayer anode with a thin (~80 µm) Ni/YSZ functional layer and a thicker (~600 µm) Cu/YSZ conduction layer for the direct utilization of dry CH₄. Due to its low melting temperature, 1,356 K, Cu must be added by impregnation of a Cu nitrate solution into a pre-sintered YSZ porous matrix [18]. For the anode functional layer (AFL), Ni/YSZ was chosen due to its good electro-catalytic activity for the H₂ oxidation reaction. Previous studies in our group [29, 30] have also shown that Ni/YSZ at the TPB (in AFL) is less susceptible to carbon formation than the Ni/YSZ in ACL. A recent study [31] has demonstrated that a Ni-interlayer Cu-based anode structure was much more stable (72 h) in dry methane at 1,073 K and no carbon formed under the testing conditions (~300 mA cm⁻², 1,073 K and 72 h).

Our experience is that Cu is not stable at 1,073 K and, thus, we have tested anode-supported button cells with a Cu/YSZ + Ni/YSZ bilayer structure at a lower temperature of 1,023 K. The cells were prepared and tested in H₂ and dry CH₄, and compared to Ni/YSZ cells. The electrochemical behavior of the anodes was determined by linear cyclic voltammetry, stability tests (galvanostatic experiments), and electrochemical impedance spectroscopy (EIS). After electrochemical testing, scanning electron microscopy (Environmental SEM, Philips ESEM-XL30) and energy dispersive X-ray (EDX) analysis were performed to determine the morphology of the bilayer anodes and the elemental composition. The carbon that was formed on the anodes after exposure to dry CH₄ was characterized by temperature programmed oxidation (TPO). Although the Cu/YSZ + Ni/YSZ bilayer was stable in terms of carbon formation, the Cu sintered over 80 h at 1,023 K. Thus, these anodes may only be suitable for even lower temperature applications.

2 Experimental

2.1 Cu/YSZ + Ni/YSZ Bilayer Anode Cells Preparation

Cu/YSZ + Ni/YSZ bilayer anode cells were prepared by uni-axially pressing yttria-stabilized zirconia (YSZ, Tosoh, TZ-8Y, Japan) powder for the electrolyte, nickel oxide (NiO)/YSZ powder for the AFL and a mixture composed of YSZ and

pore former for the ACL. The NiO/YSZ powders were prepared by mixing NiO (51 wt.%, Alfa Aesar, 99% purity, USA), YSZ powder (43 wt.%), and graphite (6 wt.%, Alfa Aesar, conductive grade, 325 Mesh), with zirconia milling media in ethanol for 24 h. After mixing, the powders were dried and ground in a mortar followed by sieving to obtain particles <150 µm in size. The mixture for the ACL was prepared by mixing YSZ and the pore former poly-methyl methacrylate (PMMA, MW of 540,000 g mol⁻¹; Scientific Polymer Products, Inc., USA) in the weight ratio of 60:40 in ethanol for 24 h. After drying, the binder poly-vinyl alcohol (PVA; Alfa Aesar) was added to the powders to increase the mechanical strength of the disks. After uni-axially pressing at 44 MPa, the three-layered structure was sintered in air at 1,623 K for 2 h using a heating and cooling rate of 5 K min⁻¹.

The metal phase, Cu, was incorporated into the porous YSZ matrix of the ACL by impregnation of a 3 M Cu(NO₃)₂ solution prepared by dissolving Cu(NO₃)₂ · 3H₂O (Alfa Aesar) salt in de-ionized water. Before the impregnation procedure, the porosity of the YSZ matrix was determined by water-uptake measurements, as described in Ref. [32], to be approximately 66 vol.% (i.e., the volume of pores is 0.15 ml). A micropipette was used to add a known quantity (0.1 ml) of Cu(NO₃)₂ solution to the YSZ matrix. The Cu loading target was between 36 and 40 wt.% (with respect to the YSZ) for all bilayer anode cells. This loading corresponds to 19–21 vol.% ($V_{Cu}/(V_{Cu} + V_{YSZ}) \times 100$) of Cu, which is well above the percolation threshold of ~10 vol.% [33, 34] required to obtain electronic conductivity but the resistances of five cells with different Cu loadings were measured to verify this value for our microstructure. Because the quantity of the Cu(NO₃)₂ solution added to the YSZ matrix was known, the equation below was used to estimate the number of impregnation and calcination cycles:

$$N^0 = \frac{m_{Cu}}{M_{Cu} C_{sol} v_{sol}} \quad (1)$$

where m_{Cu} denotes the quantity of Cu (g), M_{Cu} is the molecular weight ($M_{Cu} = 63.54$ g mol⁻¹), C_{sol} is the molarity of the solution ($C_{sol} = 3$ mol L⁻¹ Cu(NO₃)₂), and v_{sol} is the volume of the solution that is added at each impregnation step ($v_{sol} = 0.1$ ml). Complete conversion of Cu(NO₃)₂ to Cu upon decomposition and reduction was assumed.

Calcination was done in air at 723 K for 1 h, and the impregnation procedure was repeated on average 10 times, as expected according to Eq. (1), until the Cu loading in the anode was approximately 40 wt.% with respect to the porous YSZ matrix (i.e., $W_{Cu}/W_{YSZ-anode} \times 100$). Finally, the CuO in the conduction layer was reduced *in situ* to Cu during cell testing. Table 1 summarizes the materials and quantities used to fabricate the Cu/YSZ + Ni/YSZ bilayer anode cells.

Typical Ni/YSZ anode-supported cells were prepared by uni-axially pressing YSZ powder for the electrolyte and NiO/YSZ powder for the anode. The NiO/YSZ mixture was prepared as described above and formed both the functional and conduction layers of the anodes in the Ni/YSZ cells. The

Table 1 Materials used to fabricate bilayer anodes and Ni/YSZ button cells.

Cell type	Cathode	Electrolyte	Anode functional layer (AFL)	Anode conduction layer (ACL)
Cu/YSZ + Ni/YSZ YSZ Pt	Pt	YSZ	NiO/YSZ	YSZ/PMMA + Cu
Quantity (g)	0.01	0.5	0.1	0.8 + ~0.2
Ni/YSZ YSZ Pt	Pt	YSZ	NiO/YSZ	
Quantity (g)	0.01	0.5	1.5	

layers of electrolyte and anode powders were co-pressed at 44 MPa, and the resulting structure was sintered in air at 1,623 K for 2 h using a heating and cooling rate of 5 K min⁻¹ [30].

For all Ni/YSZ and the bilayer anode cells, the cathode was made by painting Pt (Engelhard, USA) onto the electrolyte and firing at 1,123 K in air for 1 h. All cathodes had a geometric area of 0.3 cm² and were left open to air. Ag wires (Alfa Aesar) were attached to the electrodes as current collectors. Pt paste (Engelhard) was used to attach the wire to the cathode side and Ag paste (Alfa Aesar) was used to connect the wire to the anode side. A ceramic sealant (Aremco, 552 VFG, USA) was used to seal the cells onto the alumina cell tube (McDanel Advanced Ceramic Technologies, USA). A schematic of the Cu/YSZ + Ni/YSZ bilayer anode cell attached to the alumina tube is shown in Figure 1.

2.2 Electrochemical Testing and Post-Test Analysis

Electrochemical experiments including linear cyclic voltammetry, stability tests (galvanostatic experiments), and EIS were performed using an electrochemical interface (1287 potentiostat + 1260 frequency response analyzer, Solartron Analytical, UK) at 1,023 K. In the galvanostatic tests, the current density was held at 100 mA cm⁻². EIS tests were done at OCV with a voltage amplitude of 20 mV and in the frequency range 10⁶–10⁻² Hz.

The flow rate of humidified H₂ (Grade 5, Praxair, Canada) was 50 ml min⁻¹. Humidification was achieved by bubbling

the gas through de-ionized water at 299 K. The flow rate of dry CH₄ (Grade 3.7, Praxair) was 25 ml min⁻¹. The flow rate of each fuel was fixed by a mass flow controller (Type 1179A, MKS Instruments, USA) previously calibrated with a flow calibrator (Mini-Buck Calibrator; A. P. Buck, Inc., USA) at ambient pressure (88 kPa) and temperature (299 K).

Temperature programmed oxidation was used to analyze the carbon that was formed on the anodes tested with dry CH₄. When cooling the fuel cell, the anode was exposed to He to prevent oxidation of the carbon. TPO experiments were carried out using 10 vol.% O₂ in He with a total flow rate of 50 ml min⁻¹. The temperature in the reactor was ramped from room temperature to 1,173 K at 10 K min⁻¹ and the outlet gases were analyzed with a mass spectrometer (Cirrus™; MKS Instruments). Signals for *m/z* = 44 (CO₂), *m/z* = 28 (CO), *m/z* = 32 (O₂), *m/z* = 18 (H₂O), *m/z* = 2 (H₂), and *m/z* = 4 (He) were monitored during TPO.

After electrochemical testing, scanning electron microscopy (Environmental SEM, Philips ESEM-XL30) and EDX analysis were performed to determine the morphology of the bilayer anodes and the elemental compositions of the AFL, ACL, and electrolyte. The EDX quantification was performed with atomic number, absorption, and fluorescence corrections (ZAF corrections). The EDX analysis was done for a minimum of three different regions (10 × 10 μm² in size) of the AFL.

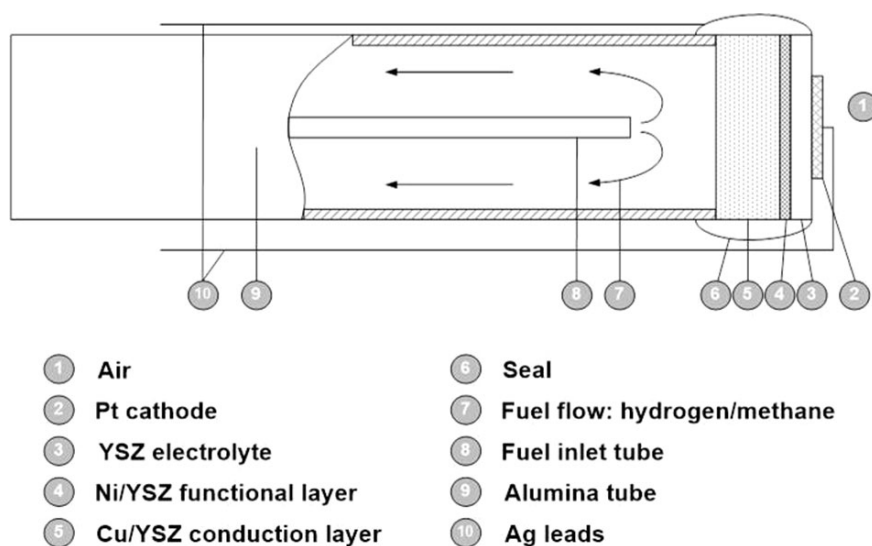


Fig. 1 Schematic of the Cu/YSZ + Ni/YSZ bilayer anode cell attached to the alumina cell holder and its components.

3 Results and Discussion

3.1 Cu/YSZ and Ni/YSZ Bilayer Anode Cell Microstructure and Elemental Analysis

Figure 2 shows SEM micrographs and the EDX analysis for a Cu/YSZ + Ni/YSZ bilayer anode cell after testing in humidified H₂. The morphology of the AFL (Figure 2a) was similar to that of the typical Ni/YSZ anode. Figure 2b shows the EDX results corresponding to the Ni/YSZ AFL. The percentages of the elements O, Y, Zr, Ni, and Cu were 6.3, 11, 40, 31, and 12 wt.%, respectively, in the AFL. Considerably more Y than O was observed, and this was most likely due an artifact resulting from the overlap between the O K α and Y K α peaks in the EDX spectra. Cu was observed in the AFL, suggesting that the Cu(NO₃)₂ solution percolated into the ACL during preparation. Cu is known to form a solid solution with Ni at the typical SOFC temperatures.

The ACL is shown in Figure 2c. Large pores (~100 μ m) were formed in the ACL after burn-off of the pore former PMMA. The particle size distribution of PMMA powders was characterized by a d_{50} of approximately 90 μ m, and d_{100} less than 150 μ m. This hollow structure for the ACL is beneficial for wet impregnation and reducing gas transport resistances to and from the TPB, but it may lack mechanical strength. EDX was done over four areas representative of the ACL and the average elemental analysis is shown in Figure 2d. In addition to elements of O, Y, and Zr, as expected for the YSZ, Cu was detected in the amount of 49.9 wt.%, that is higher than

the expected target of 40 wt.%. The small amount of Ni (1.2 wt.%) in the ACL detected by EDX was most likely due to X-ray background noise that was originated from the Ni/YSZ functional layer.

There are a range of appropriate Cu loadings reported in the literature from 19 wt.% (~10 vol.% w.r.t. YSZ) up to 40 wt.% [33–35] and, thus, the ohmic resistance of five different cells prepared identically except for the Cu loading in the ACL were determined. Figure 3 shows the ohmic resistance (R_{Ω}) of the cells *versus* the Cu loading in the ACL, as mea-

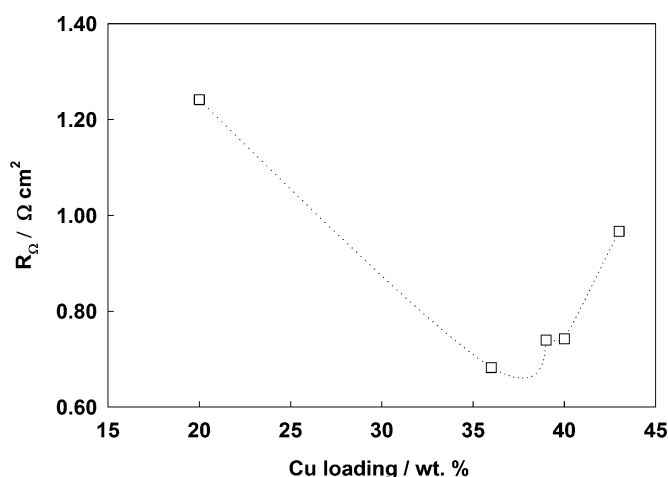


Fig. 3 Ohmic resistance of Cu/YSZ + Ni/YSZ | YSZ | Pt cells as a function of the Cu loading in the conduction layer. Fuel: H₂ (50 ml min⁻¹); $T = 1,023$ K.

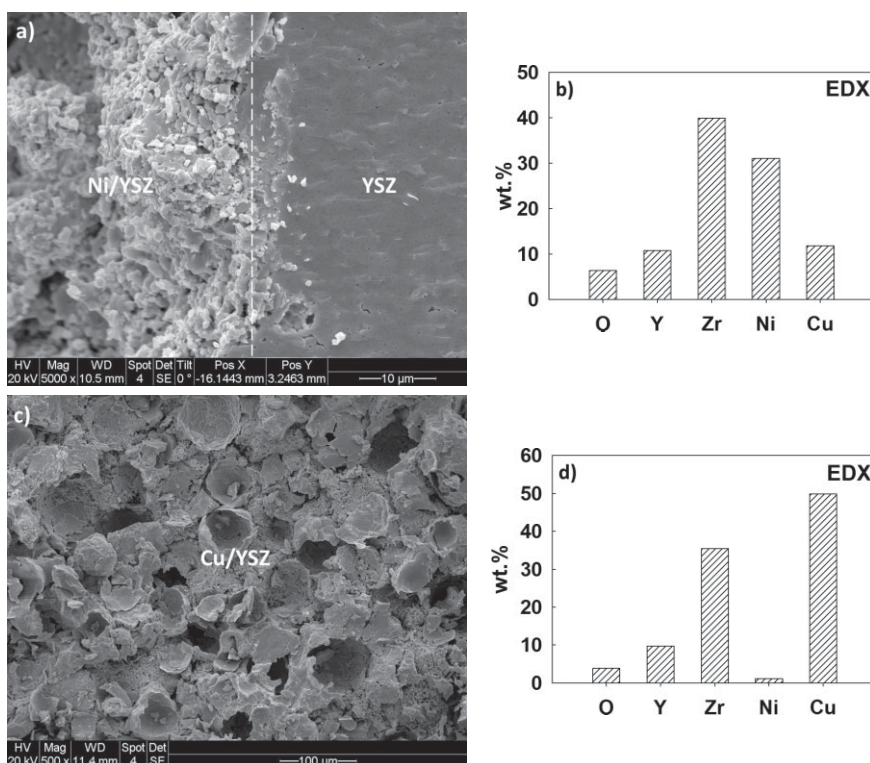


Fig. 2 SEM micrographs and EDX analysis of (a and b) the anode functional layer and (c and d) the anode conduction layer for a Cu/YSZ + Ni/YSZ bilayer anode after testing in humidified H₂.

sured by EIS after 1 h of testing in H_2 at 1,023 K. The R_Ω decreased from $1.24 \Omega \text{ cm}^2$ at 20 wt.% Cu to $0.68 \Omega \text{ cm}^2$ at 36 wt.% Cu. The addition of more Cu, up to 39–40 wt.%, did not change the cell R_Ω within the experimental error of the measurement (standard deviation of $0.110 \Omega \text{ cm}^2$). The thin film theory [34] predicts that the electrical conductivity of a porous Cu/YSZ slab reaches an asymptotic value above 15 vol.%, which is consistent with our results and no improvement being obtained above 36 wt.% of Cu ($\sim 19 \text{ vol.}\%$). In fact, the ohmic resistance increased to $0.96 \Omega \text{ cm}^2$ at a Cu loading of 43 wt.%, which suggests that the Cu did not percolate throughout this cell and an uneven distribution was obtained with parts of the anode having Cu loadings below the required value.

3.2 Electrochemical Characterization and Stability with H_2 Fuel

Figure 4a shows current–voltage characteristics and power density curves with humidified H_2 for a Cu/YSZ + Ni/YSZ|YSZ|Pt cell. Results for the Ni/YSZ|YSZ|Pt cell are also shown for comparison. The cell OCV were 1.078 and 1.051 V for the bilayer anode and the typical Ni/YSZ cell,

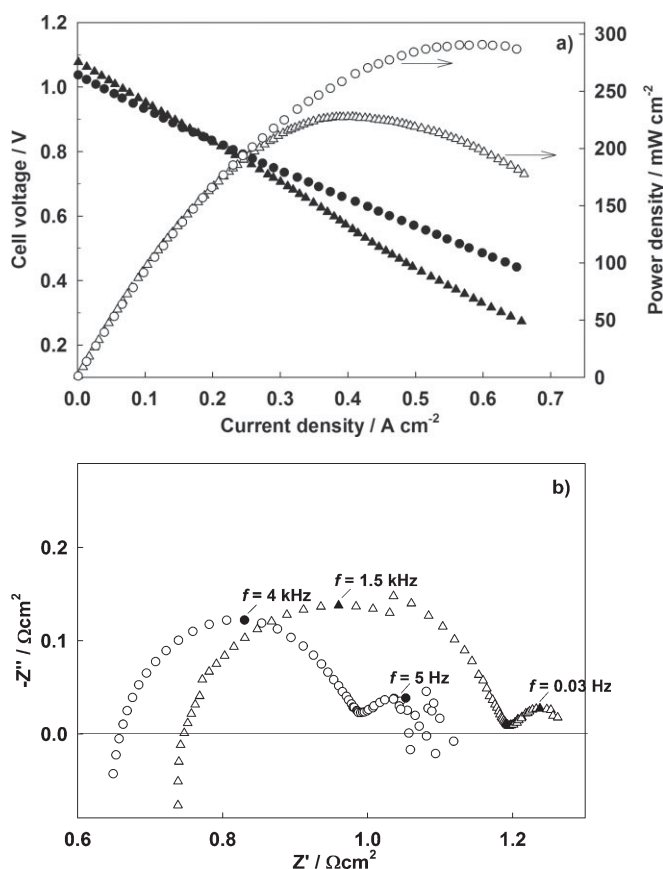


Fig. 4 (a) Cell voltage (filled symbols) and power density (open symbols) curves as a function of the current density for (●, ○) a Ni/YSZ|YSZ|Pt and (▲, △) a Cu/YSZ + Ni/YSZ|YSZ|Pt cells. (b) Nyquist plots in humidified H_2 for the (○) a Ni/YSZ|YSZ|Pt and (△) Cu/YSZ + Ni/YSZ|YSZ|Pt at OCV and 1,023 K. Inlet fuel $\text{H}_2 = 50 \text{ ml min}^{-1}$.

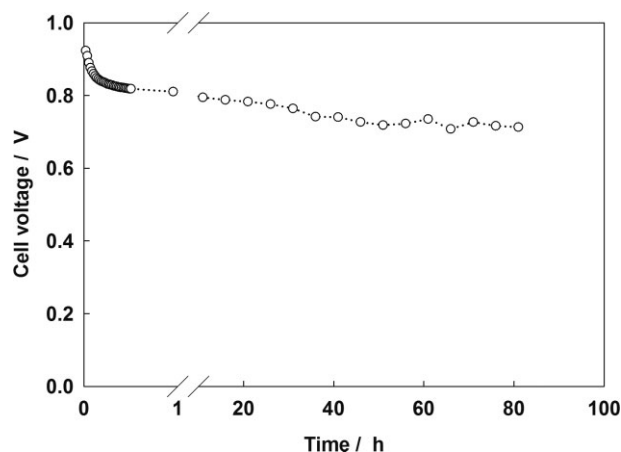


Fig. 5 Cell voltage as a function of time for a Cu/YSZ + Ni/YSZ|YSZ|Pt cell tested in humidified H_2 and 100 mA cm^{-2} at 1,023 K.

respectively. These OCV values are close to the theoretical Nernst potential calculated for a fuel mixture of 96% H_2 and 4% H_2O (1.096 V at 1,023 K), thus indicating that the cells were well sealed. Peak power densities of 228 and 288 mW cm^{-2} were obtained for the bilayer and the Ni/YSZ cells, respectively.

The EIS spectra for these cells are shown in Figure 4b. The EIS spectrum for the Cu/YSZ + Ni/YSZ|YSZ|Pt cell consisted of two arcs: one arc was obtained for the high frequency (peak frequency $f_{\text{peak}} = 1.5 \text{ kHz}$) and a second arc was obtained for the low frequency ($f_{\text{peak}} = 0.03 \text{ Hz}$). Although it is difficult to assign the arcs to a specific process in 2-electrode impedance work, the main arc could be attributed to charge transfer reactions, while the low-frequency arc could be attributed to diffusion through the porous anode [36] and/or cell geometry artifacts (i.e., gas conversion impedance) [37]. Similarly, the EIS spectrum of the Ni/YSZ|YSZ|Pt cell was formed by two arcs: a high frequency ($f_{\text{peak}} = 4 \text{ kHz}$) and low frequency arc ($f_{\text{peak}} = 5 \text{ Hz}$); however, the low frequency arc was difficult to determine due to the noise in the EIS data points for $f < 5 \text{ Hz}$. The polarization resistances, R_p , were 0.42 and $0.52 \Omega \text{ cm}^2$ for the Ni/YSZ|YSZ|Pt and Cu/YSZ + Ni/YSZ|YSZ|Pt cells, respectively. The high frequency x-axis intercepts of the spectra, R_Ω , of the cells were 0.65 and $0.74 \Omega \text{ cm}^2$ for the Ni/YSZ|YSZ|Pt and Cu/YSZ + Ni/YSZ|YSZ|Pt cells, respectively.

Figure 5 shows a galvanostatic experiment for a Cu/YSZ + Ni/YSZ|YSZ|Pt cell tested in H_2 at 100 mA cm^{-2} for 80 h at 1,023 K. After an initial degradation in the first 20 min of testing, the cell voltage was relatively stable at $\sim 0.8 \text{ V}$ with a degradation rate of 1.4 mV h^{-1} over the duration of the experiment. The area specific resistance (ASR) of the cell was also calculated as the ratio between the cell voltage drop from the OCV value to the operating current density of 100 mA cm^{-2} . After 20 min of testing, the ASR was $2.4 \Omega \text{ cm}^2$ and increased to $3.5 \Omega \text{ cm}^2$ after 80 h in H_2 . The ASR degradation rate was calculated to be $14 \text{ m}\Omega \text{ cm}^2 \text{ h}^{-1}$.

3.3 Electrochemical Characterization and Stability with Dry CH₄ Fuel

Figure 6a shows current–voltage characteristics and power density curves for the cells with a Cu/YSZ + Ni/YSZ bilayer anode and a typical Ni/YSZ anode exposed to 25 ml min^{−1} of dry CH₄ at 1,023 K. The OCV of the cell with a Ni/YSZ anode was 1.154 V in dry CH₄, which is slightly higher than the OCV value of 1.13 V reported for a Ni/YSZ anode in humidified CH₄ (with 3% H₂O) [7]. For the cell supported by Cu/YSZ, a lower OCV of 1.042 V was obtained. Similarly, Kim et al. [8] reported an OCV of 1.0 V for a Cu–Ni alloy anode, while Gorte et al. [18] reported an OCV of 0.9 V for a Cu–CeO₂ anode in dry CH₄. A peak power density of 238 mW cm^{−2} was obtained with the Ni/YSZ|YSZ|Pt cell that was higher than the peak power density of 145 mW cm^{−2} observed with the Cu/YSZ + Ni/YSZ|YSZ|Pt SOFC in dry CH₄. As shown in Figure 2, some Cu penetrated into the functional layer and so the number of Ni sites at the TPB is likely reduced in the bilayer anode, which results in a lower performance.

Figure 6b shows the EIS spectra for the two cells in dry CH₄. The ohmic resistances, R_{Ω} , were 0.66 and 0.78 Ω cm² for the Ni/YSZ and bilayer anode cells, respectively. These val-

ues are similar to those obtained in H₂ but the shapes of the spectra were different and consisted of a single depressed-arc. The span of the arc was also larger in dry CH₄ – 2.14 and 1.58 Ω cm² for the Ni/YSZ and bilayer anode cells, respectively.

To investigate the stability of the Cu/YSZ + Ni/YSZ|YSZ|Pt in dry CH₄, a galvanostatic test was performed at 100 mA cm^{−2} and 1,023 K, and the results are shown in Figure 7. In dry CH₄, the cell voltage was essentially stable at approximately 0.6 V and a cell voltage degradation of 1.2 mV h^{−1} was calculated over 117 h. The total area specific resistance (ASR) increased from an initial ($t = 20$ min) value of 3.4–4.8 Ω cm² at the end of experiment, which corresponds to an ASR degradation rate of 12 m Ω cm² h^{−1}, similar to the degradation values that were obtained in H₂ (the results from Figure 5 have been included in Figure 7 for easier comparison). In Figure 7, the cell stability of a typical Ni/YSZ anode-supported cell operated in dry CH₄ and 100 mA cm^{−2} is also shown in the inset. For the Ni-supported cell, the cell voltage degraded rapidly due to coking and dropped to zero within 10 h of operation (but the cell was exposed to methane for 24 h). In anode-supported cells, carbon formation is much more severe than in electrolyte-supported cells [30].

Following the galvanostatic test, TPO experiments were performed to characterize the carbon formed. After testing, the cell was removed from the cell holder, and the entire cell – including electrolyte, cathode, and current collectors – was weighed and introduced into the TPO reactor. Because of the difficulty in recovering all of the catalyst and carbon material from the cell holder, the CO₂ production during TPO was normalized by the weight of sample used in the reactor. The TPO profiles are shown in Figure 8 for the two cells tested in the experiment shown in Figure 7. For the Cu/YSZ + Ni/YSZ anode, a low temperature CO₂ peak was observed between 500 and 800 K, and this peak is much smaller that

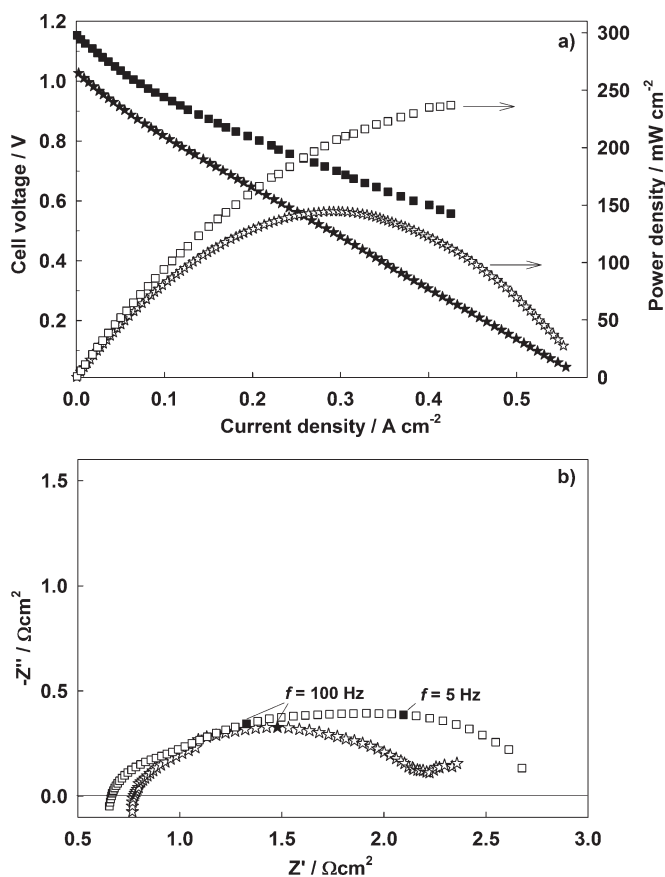


Fig. 6 (a) Cell voltage (filled symbols) and power density (open symbols) as a function of the current density for (■, □) Ni/YSZ|YSZ|Pt and (★, ☆) Cu/YSZ + Ni/YSZ|YSZ|Pt cells. (b) Nyquist plots in dry CH₄ for the (□) Ni/YSZ|YSZ|Pt and the (☆) Cu/YSZ + Ni/YSZ|YSZ|Pt cell at OCV and 1,023 K. Inlet fuel CH₄ = 25 ml min^{−1}.

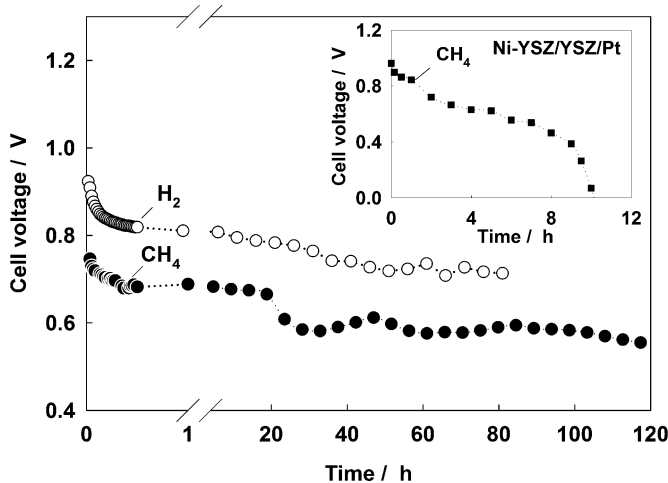


Fig. 7 Cell voltage as a function of time for a (●, ○) Cu/YSZ + Ni/YSZ|YSZ|Pt cell in humidified H₂ (open symbols) and dry CH₄ (filled symbols) tested at 100 mA cm^{−2} and 1,023 K. The inset shows the same experiment (100 mA cm^{−2} and 1,023 K) for a (■) Ni/YSZ|YSZ|Pt supported-cell in dry CH₄.

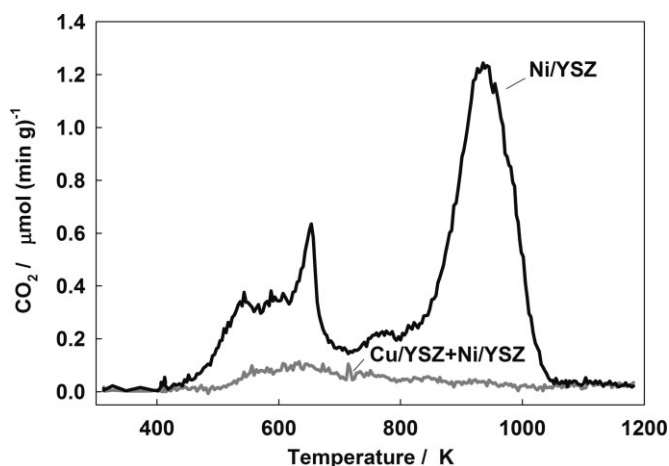


Fig. 8 TPO curves for Cu/YSZ + Ni/YSZ bilayer anode after exposure to dry CH₄ and 100 mA cm⁻² for 117 h at 1,023 K (gray line), and a Ni/YSZ anode after exposure to dry CH₄ and 100 mA cm⁻² for 24 h at 1,023 K (black line).

the peak obtained for the Ni/YSZ anode, consistent with the relative stabilities of these anodes in dry CH₄ (Figure 7). For the Ni/YSZ anode, several CO₂ peaks were observed: one set of peaks between 500 and 700 K and a second set between 800 and 1,050 K. The higher temperature peaks represent a stable type of carbon that was likely formed on the Ni/YSZ conduction layer [30]. The Cu in the ACL reduced carbon formation as has been shown and discussed by the research group of Gorte and Vohs [8, 19]. The Cu in the AFL (Figure 2) will also have decreased carbon formation [8, 31, 38].

The EIS spectra obtained in dry CH₄ are shown in Figure 9 for a different Cu/YSZ + Ni/YSZ | YSZ | Pt cell as a function of time. The ohmic resistance (R_{Ω}) of the cell was initially 0.77 Ω cm² and was reduced to 0.75 Ω cm² after 24 h of testing. Kim et al. [8] tested a 20 wt.% Cu–Ni alloy anode in dry CH₄ and after 168 h of operation observed a significant reduction in the ohmic resistance of the cell, suggesting that the carbon formed at the anode can improve the connectivity of the metal particles. While in this previous work the reduction of R_{Ω} was significant (from 0.9 to 0.6 Ω cm²), the improvement for the Cu/YSZ + Ni/YSZ bilayer anode cell shown in Figure 9 is more modest, most likely due to the higher initial electronic conductivity of our cell (0.77 Ω cm²). Furthermore, the span of the EIS arc (or R_p) at $t = 24$ h also decreased in size from 1.58 to 1.29 Ω cm², and reached a minimum at 1.05 Ω cm² after 12 h of testing (i.e., nearly 30% improvement). A similar behavior was observed by Kim et al. [8] for a Cu–Ni alloy anode, and the improvement was attributed to the carbon formed. The carbon is beneficial to connect isolated metal particles at the triple phase boundary (TPB), resulting in an increase of the electrochemical activity. After 60 h of operation, however, the resistances increased to 1.22 and 2.51 Ω cm² for R_{Ω} and R_p , respectively, most likely due to Cu sintering within the anode, and subsequent degradation of electronic conductivity within the ACL.

The morphology of a Cu/YSZ + Ni/YSZ bilayer anode tested in H₂ for 80 h at 1,023 K and 100 mA cm⁻² (experiment of Figure 5) is shown in Figure 10. Generally, Cu formed a well-connected film within the pores of the ACL that covered portions of the YSZ surface. The labeled structure in the micrograph of Figure 10a was determined by EDX analysis to be mostly Cu (~78 wt.%). Spherical Cu particles were also formed, however, with diameters <1 μm (Figure 10b). McIntosh et al. [34] have suggested that Cu in infiltrated anodes can form isolated particles such that the measured conductivity is lower than the value expected by the thin film theory, which is consistent with our requirement of additional Cu (Figure 3). Tucker et al. [39] reported a rapid cell degradation for a Ni-infiltrated anode due to a coarsening effect of the fine Ni particles, and subsequent loss of electronic conductivity. The Ni particle growth is driven by the associated decrease in surface energy, and Ni surface diffusion on YSZ is believed to be the primary sintering mechanism at elevated temperatures [40,41]. For Cu-infiltrated anodes, this coarsening mechanism is expected to be even more significant because of the lower melting temperature (1,356 K) of Cu, and the presence of the particles of Figure 10b can be explained by Cu sintering, which resulted in an increase of the cell ohmic resistance with time (Figure 9). Similar Cu particles were observed in another study (see SEM micrograph of Figure 3 in [42]) with Cu-infiltrated anodes exposed to H₂ for 2 h at 1,173 K.

3.4 Discussion

From our results, it is evident that Cu–Ni bilayer anodes are effective at reducing carbon accumulation (Figure 8) and, thus, increasing the stability of the SOFC (Figure 7). Cu sintering, however, is still an issue at 1,023 K (Figures 9 and 10). A number of reviews [20–22, 43] have pointed out that it is very difficult to find a material that can satisfy all the strin-

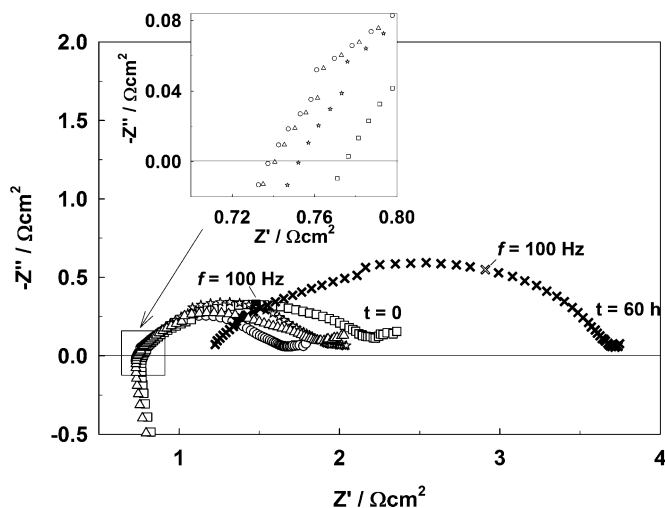


Fig. 9 Nyquist plots at OCV with dry CH₄ for a Cu/YSZ + Ni/YSZ | YSZ | Pt cell after (□) 10 min, (△) 6 h, (○) 12 h, (☆) 24 h, and (x) 60 h of testing in dry CH₄ and 100 mA cm⁻² at 1,023 K.

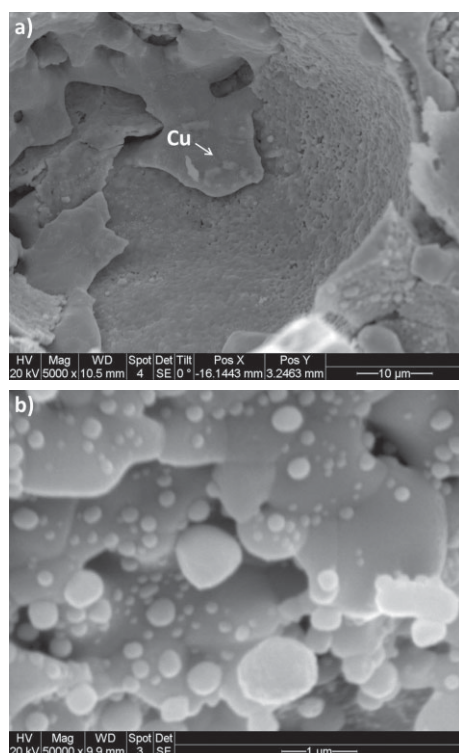


Fig. 10 SEM micrographs of a pore in the anode conduction layer of a Cu/YSZ + Ni/YSZ|YSZ|Pt cell after galvanostatic test shown in Fig. 5 (humidified H_2 for 80 h at 100 mA cm^{-2} and $1,023 \text{ K}$): (a) a large pore with a Cu film and (b) Cu particles within the same pore.

gent requirements for a SOFC anode: (i) redox stability, (ii) chemical and thermal stability with cell components, (iii) electrochemical activity, (iv) electronic conductivity, and (v) carbon tolerance. For this reason, the use of a bilayer anode is a promising strategy because it is possible to separate the issue of conductivity and electrochemical activity by the use of different materials for the AFL and the ACL [23–25].

The preparation of the anodes is not trivial. If the Cu is distributed evenly and forms a continuous thin film then the amount required will be that predicted by the percolation theory. In this work, a single step uni-axial pressing technique was used with a wet impregnation to infiltrate the anode with Cu because they were simple techniques to prepare the anodes and test for cell stability and carbon formation. With this technique, more Cu than that predicted by the percolation theory (19 vol.% *vs.* 10 vol.%) was required to achieve an optimal conductivity (Figure 3). Nevertheless, less Cu was required using the impregnation technique than if a co-sintered Cu/YSZ cermet (requiring ~30 vol.%) had been prepared [46].

Another issue with the impregnation technique is preventing the Cu nitrate solution from percolating into the Ni/YSZ functional layer. The presence of Cu was positive in terms of reduced carbon formation (Figure 8) but negative in terms of reduced performance in both humidified H_2 (Figure 4) and dry CH_4 (Figure 6). The similar shapes of the impedance plots (Figures 2b and 4b), for the Cu/YSZ + Ni/YSZ|YSZ|Pt

and Ni/YSZ|YSZ|Pt cell suggest that the presence of Cu in the AFL is not changing the reaction pathway but just reducing the number of Ni sites and possibly affecting the local gas phase composition. Ni in the ACL will promote the reforming and decomposition reactions of CH_4 [30], thus producing a gas phase composition that can be more easily electrochemically oxidized [44].

Although the power densities in CH_4 are lower for the bilayer anode (Figure 6), the Cu/YSZ + Ni/YSZ anode cells accumulated much less carbon (Figure 8) than the Ni/YSZ anode and, thus, was stable in dry CH_4 and 100 mA cm^{-2} for over 100 h, while the Ni/YSZ anode cell was destroyed within 10 h. During the galvanostatic experiment (Figure 7), the cell voltage degraded with a rate of 1.2 mV h^{-1} , which was actually slightly less (but likely within experimental error) than the degradation rate of 1.4 mV h^{-1} in humidified H_2 (Figures 5 and 7), thus indicating that factors other than carbon formation caused this degradation. Aside from cell to cell variations (delamination at the cathode, quality of sealing, etc.), that affect the degradation rate, the poor thermal stability of Cu is likely the main factor in the degradation of the bilayer cells [10]. The ohmic resistance was the smallest after 12 h of operation and then increased substantially after 60 h of operation (Figure 9). This minimum is likely a result of carbon deposition improving the conductivity initially followed by the sintering of the Cu reducing the conductivity. Gorte et al. [18] have reported that Cu is likely to be sufficiently stable at temperatures $<973 \text{ K}$. At lower temperatures, the ionic conductivity of the YSZ electrolyte decreases. Exchanging the YSZ for a different material (e.g., gadolinium doped ceria) is possible but then other factors are introduced. The problem with the thermal stability of the Cu may be reduced or eliminated by lowering the temperature of operation and/or using a different fabrication technique, such plasma spraying [45], for example.

4 Conclusion

A Cu/YSZ and Ni/YSZ bilayer anode for SOFC was prepared by single step uni-axial pressing to produce the anode support followed by impregnation of Cu into the porous YSZ matrix. This anode exhibited improved tolerance toward carbon and was operated at $1,023 \text{ K}$ in dry CH_4 and 100 mA cm^{-2} for over 100 h. The cell voltage degradation was $<12\%$ during this period. The cell degradation was attributed to a reduction of the cell ohmic resistance due to the sintering of Cu at $1,023 \text{ K}$, and thus these anodes are suitable for lower temperature applications. The stable performance of the bilayer anode toward dry CH_4 was attributed to its improved carbon tolerance. In comparison, a comparable button cell with a Ni/YSZ anode had much higher initial performance but failed within 10 h under the same conditions because of excessive carbon formation.

Acknowledgments

Solid Oxide Fuel Cell Canada Strategic Research Network from the Natural Science and Engineering Research Council (NSERC) and other sponsors listed at www.sofccanada.com. The authors thank Dr. Michael Schoel for assistance with the SEM images and Dr. Anand Singh for helpful discussions.

References

- [1] J. Love, S. Amarasinghe, D. Selvey, X. Zheng, L. Christiansen, *ECS Trans.* **2009**, 25, 115.
- [2] R. J. Payne, J. Love, M. Kah, *ECS Trans.* **2011**, 35, 81.
- [3] K. Ahmed, K. Fogar, *Catal. Today* **2000**, 63, 479.
- [4] M. Mogensen, K. Kammer, *Annu. Rev. Mater. Res.* **2003**, 33, 321.
- [5] H. He, J. M. Hill, *Appl. Catal. A* **2007**, 317, 284.
- [6] K. Nikooyeh, A. A. Jeje, J. M. Hill, *J. Power Sources* **2007**, 171, 601.
- [7] Y. Lin, Z. Zhan, J. Liu, S. A. Barnett, *Solid State Ionics* **2005**, 176, 1827.
- [8] H. Kim, C. Lu, W. L. Worrell, J. M. Vohs, R. J. Gorte, *J. Electrochem. Soc.* **2002**, 149, A247.
- [9] C. M. Grgicak, M. M. Pakulska, J. S. O'Brien, J. B. Giorgi, *J. Power Sources* **2008**, 183, 26.
- [10] S. I. Lee, J. M. Vohs, R. J. Gorte, *J. Electrochem. Soc.* **2004**, 151, A1319.
- [11] A. Singh, J. M. Hill, *J. Power Sources* **2012**, 214, 185.
- [12] E. Nikolla, J. Schwank, S. Linic, *J. Catal.* **2009**, 263, 220.
- [13] E. Nikolla, J. Schwank, S. Linic, *J. Catal.* **2007**, 250, 85.
- [14] I. Gavrielatos, V. Drakopoulos, S. G. Neophytides, *J. Catal.* **2008**, 259, 75.
- [15] D. La Rosa, A. Sin, M. L. Faro, G. Monforte, V. Antonucci, A. S. Aricò, *J. Power Sources* **2009**, 193, 160.
- [16] T. Takeguchi, Y. Kani, T. Yano, R. Kikuchi, K. Eguchi, K. Tsujimoto, Y. Uchida, A. Ueno, K. Omoshiki, M. Aizawa, *J. Power Sources* **2002**, 112, 588.
- [17] L. Yang, Y. Choi, W. Qin, H. Chen, K. Blinn, M. Liu, P. Liu, J. Bai, T. A. Tyson, M. Liu, *Nat. Commun.* **2011**, 2, 357.
- [18] R. J. Gorte, S. Park, J. M. Vohs, C. Wang, *Adv. Mater.* **2000**, 12, 1465.
- [19] R. J. Gorte, J. M. Vohs, *J. Catal.* **2003**, 216, 477.
- [20] J. B. Goodenough, Y. H. Huang, *J. Power Sources* **2007**, 173, 1.
- [21] C. Sun, U. Stimming, *J. Power Sources* **2007**, 171, 247.
- [22] S. Tao, T. S. I. John, *Chem. Rec.* **2004**, 4, 83.
- [23] M. D. Gross, J. M. Vohs, R. J. Gorte, *J. Mater. Chem.* **2007**, 17, 3071.
- [24] M. D. Gross, J. M. Vohs, R. J. Gorte, *Electrochem. Solid-State Lett.* **2007**, 10, B65.
- [25] M. R. Pillai, I. Kim, D. M. Bierschenk, S. A. Barnett, *J. Power Sources* **2008**, 185, 1086.
- [26] O. A. Marina, N. L. Canfield, J. W. Stevenson, *Solid State Ionics* **2002**, 149, 21.
- [27] H. Kurokawa, L. Yang, C. P. Jacobson, L. C. De Jonghe, S. J. Visco, *J. Power Sources* **2007**, 164, 510.
- [28] M. R. Pillai, Y. Jiang, N. Mansourian, I. Kim, D. M. Bierschenk, H. Zhu, R. J. Kee, S. A. Barnett, *Electrochem. Solid-State Lett.* **2008**, 11, B174.
- [29] V. Alzate-Restrepo, J. M. Hill, *Appl. Catal. A* **2008**, 342, 49.
- [30] M. A. Buccheri, A. Singh, J. M. Hill, *J. Power Sources* **2011**, 196, 968.
- [31] V. Sariboğa, F. Öksüzömer, *Appl. Energy* **2012**, 93, 707.
- [32] M. Boaro, M. V. John, R. J. Gorte, *J. Am. Ceram. Soc.* **2003**, 86, 395.
- [33] T. Klemensø, K. Thydén, M. Chen, H.-J. Wang, *J. Power Sources* **2010**, 195, 7295.
- [34] S. McIntosh, H. He, S. I. Lee, O. Costa-Nunes, V. V. Krishnan, J. M. Vohs, R. J. Gorte, *J. Electrochem. Soc.* **2004**, 151, A604.
- [35] S. McIntosh, R. J. Gorte, *Chem. Rev.* **2004**, 104, 4845.
- [36] S. Primdahl, M. Mogensen, *J. Electrochem. Soc.* **1999**, 146, 2827.
- [37] S. Primdahl, M. Mogensen, *J. Electrochem. Soc.* **1998**, 145, 2431.
- [38] S. Islam, J. M. Hill, *J. Power Sources* **2011**, 196, 5091.
- [39] M. C. Tucker, G. Y. Lau, C. P. Jacobson, L. C. DeJonghe, S. J. Visco, *J. Power Sources* **2008**, 175, 447.
- [40] T. Klemensø, M. Mogensen, *J. Am. Ceram. Soc.* **2007**, 90, 3582.
- [41] D. Simwonis, F. Tietz, D. Stöver, *Solid State Ionics* **2000**, 132, 241.
- [42] J. Sukwon, C. Lu, H. He, K. Ahn, R. J. Gorte, J. M. Vohs, *J. Power Sources* **2006**, 154, 42.
- [43] A. Atkinson, S. Barnett, R. J. Gorte, J. T. S. Irvine, A. J. McEvoy, M. Mogensen, S. C. Singhal, J. M. Vohs, *Nat. Mater.* **2004**, 3, 17.
- [44] M. A. Buccheri, J. M. Hill, *J. Electrochem. Soc.* **2012**, 159, B361.
- [45] N. Benoved, O. Kesler, *J. Power Sources* **2009**, 193, 454.
- [46] D. W. Dees, T. D. Claar, T. E. Easler, D. C. Fee, F. C. Mrazek, *J. Electrochem. Soc.* **1987**, 134, 2141.