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An Efficient SOFC Based on Samaria-Doped Ceria (SDC) Electrolyte

Mingfei Liu,[a] Dong Ding,[a] Yaohui Bai,[a] Ting He,[b,*] and Meilin Liu[a,*,z]

[a]*Center for Innovative Fuel Cell and Battery Technologies, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA*
[b]*Research & Development, Technology, ConocoPhillips Company, Bartlesville, Oklahoma 74004, USA*

Doped ceria has been widely studied as electrolyte materials for intermediate temperature solid oxide fuel cells (IT-SOFCs). While high peak power densities have been reported, the electronic conductivity of doped ceria under fuel cell operating conditions reduces the open circuit voltage (OCV) and hence energy efficiency, more so with thinner electrolyte membrane at higher operating temperatures. Here we report a new cell structure: a thin SDC electrolyte membrane supported by a composite anode consisting of a mixed-ion conductor $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) and NiO. The inter-diffusion between BZCYYb and SDC during co-firing results in a thin layer of doped barium cerate and zirconate at the interface, which suppresses the electronic conduction of SDC and enhances the OCV and cell performance. The new cell structure also shows excellent stability when wet hydrogen or methane was used as fuel at 750°C.
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Intermediate-temperature solid oxide fuel cells (IT-SOFCs) have attracted worldwide attention because lowering the operating temperature (from 1000°C to 500–800°C) has potential to considerably widen the selection of less expensive materials to reduce cost while improving the reliability and operational life of SOFC systems.[1–4] It is well known, however, SOFC performance drops rapidly as operating temperature is reduced due to the increased resistances of electrolyte and electrodes. Recently, considerable efforts have been directed to IT-SOFCs based on thin-film electrolyte of doped ceria.[5–8] Compared to the widely used yttria-stabilized zirconia (YSZ) electrolyte, gadolinia-doped ceria (CGO) or samaria-doped ceria (SDC) shows much higher ionic conductivity in the intermediate temperature range. For example, a single cell based on an anode-supported SDC electrolyte membrane has demonstrated remarkably high peak power densities (> 1 W/cm^2) at 600°C.[8] Further, doped ceria electrolytes have excellent chemical and thermal compatibility with the commonly used cathode materials such as $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC), and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF).[5,8,9] However, the electronic conductivity of doped ceria electrolytes reduces the open-circuit voltage (OCV) and hence energy efficiency under typical fuel cell operating conditions,[5–8] more so for thinner electrolyte membranes and at higher temperatures.[10] In addition, the volume expansion associated with partial reduction of ceria (Ce^{4+} to Ce^{3+}) upon exposure to a reducing atmosphere (e.g., on the anode side exposed to the fuel in an SOFC) may result in severe structural and mechanical degradation (such as micro-crack and delamination).

In order to overcome these problems of doped ceria electrolytes, different approaches have been studied to suppress/block the electronic conduction of doped ceria. Eguchi et al.,[11,12] Zhang et al.,[13] and Zhao et al.[14] used a thin layer of ZrO_2-based electrolyte or BZCY on the anode side to form bi-layer structure to suppress the partial reduction of doped ceria. Fox example, the OCV of a cell based on a single layer of SDC electrolyte membrane (~24 μm thick) showed only 0.81 V at 650°C;[7] in contrast, a cell based on a SSZ/SDC bi-layer electrolyte reached an OCV of ~1.02 V below 750°C,[13] indicating that the internal shorting of SDC electrolyte can been eliminated by a thin SSZ layer. However, the formation of a solid solution of $(Ce, Zr)O_{2-x}$ during sintering and the flaws in the bi-layer may significantly increase the electrolyte resistance and hence degrade the performance.[13,14] Hibino and co-workers[15,16] reported a new method for suppressing the reduction of ceria, where a thin $BaCe_{1-x}Sm_xO_3$ layer was grown by a solid state reaction of the SDC electrolyte layer and a thin BaO film deposited previously over the SDC surface at elevated temperatures. Open-circuit voltages of a hydrogen-air fuel cell with the coated SDC electrolyte were close to 1 V at 600–950°C. However, the performance was too low for practical applications. It is also noted that the introduction of a doped-bismuth oxide layer on the top of doped ceria[17,18] or on LDC/LSGM surface[19] has demonstrated some OCV improvement. To date, however, the demonstrated enhancement was relatively small. For example, the OCV for a cell with a GDC/doped bismuth oxide bi-layer electrolyte was less than 0.8 V at 650°C,[17,18] still representing significant energy loss due to internal leaking. Also, the stability of the doped bismuth oxide bi-layer configuration might be a concern. Recently, Sun et al.[20] proposed a composite electrolyte consists of perovskite-type proton conductor $BaCe_{0.8}Sm_{0.2}O_{3-\delta}$ (BCS) and fluorite-type oxygen ionic conductor $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) for SOFC applications. Even though the OCV was significantly enhanced at 700°C and reasonable performance and stability have been demonstrated using H_2 as fuel, the OCV was still much lower than the Nernst potential. In addition, the stability of the composite electrolyte under hydrocarbon fuel/CO_2 condition is also a concern.

Here, we report a more practical and effective cell structure: a dense SDC electrolyte film supported by a composite anode consisting of NiO and $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb),[21] demonstrating high OCV values (hence excellent voltage efficiency) and excellent performance at 500–750°C. In addition, the Ni-BZCYYb supported SDC cells showed good stability under wet methane, offering additional advantages over the Ni-SDC supported SDC cells.

Experimental

SOFC Fabrication.—Preparation of anode substrates.— The NiO-BZCYYb anode support was directly prepared via mixing the precursors of NiO, $BaCO_3$, ZrO_2,CeO_2 Yb_2O_3, Y_2O_3 and starch in a certain proportion to make sure that the BZCYYb composition was $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ and the weight ratio of NiO: BZCYYb: starch was 65:35:10. The mixture was ball milled in an ethanol medium for 24h and dried subsequently to form the anode precursor. The precursor was uniaxially pressed into pellets in a steel die with the size of 1 mm in thick and 13mm in diameter under a pressure of 250 MPa and subsequently calcined at 800°C for 2h in air to get the anode substrates.

Fabrication of SDC film.—Thin electrolyte membrane of SDC was processed by a refined particles suspension coating technique.[7,22] SDC powders, synthesized via carbonate co-precipitation process,[23] were employed to make a suspension. The suspension was coated on the porous NiO-BZCYYb anode supports surface to make SDC

* Electrochemical Society Active Member.
z E-mail: mingfei.liu@mse.gatech.edu; meilin.liu@mse.gatech.edu

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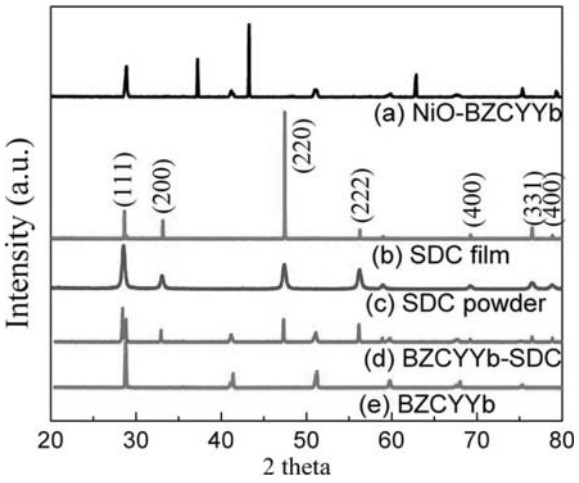

Figure 1. XRD patterns of (a) NiO-BZCYYb anode, (b) SDC electrolyte film on NiO-BZCYYb, (c) SDC powder for the slurry, (d) SDC and BZCYYb co-fired at 1400°C for 5h, and (e) BZCYYb.

electrolyte layers. Finally, the anode supports with SDC coats were co-sintered at 1400°C for 5 h.

Preparation of cathode.—LSCF powder (purchased from Fuelcell Materials Co., US.) was mixed with V-006 and acetone to form a cathode slurry, which was brush-painted on the SDC electrolyte, followed by firing at 1050°C for 2 h to form porous LSCF cathode on SDC.

SOFC Testing.— The whole cell was mounted and sealed on a fuel cell testing fixture, and then tested with humidified hydrogen or methane (3%H_2O) as fuel and ambient air as oxidant. The cell performances and the long-term electrochemical performances of test cells were examined with an Arbin multi-channel electrochemical testing system (MSTAT). Ac impedance measurements were conducted using a Solartron 1255 HF frequency response analyzer, which was interfaced with an EG&G PAR potentiostat (model 273A) with an amplitude of 10mV in the frequency range from 100 kHz to 0.1 Hz.

Materials Characterization.— An X′ Pert PRO Alpha-1 X-ray diffractometer (with Cu Kα radiation) was used for phase identification of the anode substrate and electrolyte film. The microstructure and morphology of the cell was examined using a thermally assisted field emission scanning electron microscope (SEM, LEO 1530) equipped with an energy dispersive X-ray (EDX) spectrometer.

Results and Discussion

Shown in Fig. 1 are the XRD patterns of the as-prepared anode substrate (curve a) and the SDC film (curve b) after sintering at 1400°C for 5 h. It is seen that there were only NiO and peaks corresponding to BZCYYb phase in the anode substrate, indicating that solid state reaction took place in the anode and BZCYYb phase was formed in-situ during the high temperature sintering process. The in-situ synthesis of the BZCYYb phase for the anode not only reduces the energy consumption, but also shortens the processing time, which will reduce the cost. For the electrolyte film, only fluorite phase of SDC was detected. However, it should be noted that the SDC film on NiO-BZCYYb anode shows (220) preferential grain orientation, which is different from the SDC powders, indicating that the substrate might have some influence on the SDC film formation. In addition, the chemical compatibility between BZCYYb and SDC was investigated by examining the XRD patterns for the mixture of BZCYYb and SDC powders (weight ratio of 1:1) calcined at 1400°C for 5 h. No extra peaks or splitting of main reflections were observed in the XRD patterns for the SDC-BZCYYb samples (Fig. 1 curve d), indicating that there was no apparent chemical reactions between BZCYYb and SDC during the high firing temperature. However, it was found that the peaks of BZCYYb in the SDC-BZCYYb were slightly shifted to higher angle, which is attributed to some inter-diffusion between BZCYYb and SDC.

Fig. 2a shows the surface morphology of the as-prepared SDC film on NiO-BZCYYb anode substrate. The SDC film is crack-free, continuous, and quite dense; the grain size is varied from 2 to 6 μm. Shown in Fig. 2b is a cross -sectional view of a tri-layer cell. It can be seen that the SDC film (about 30 μm thick) seems uniform, continuous, and well adhered to the NiO-BZCYYb anode substrate, almost without any cracks or noticeable pores, indicating that the SDC film with good quality was successfully formed on NiO-BZCYYb anode substrate. As to be described later, such a good interface between Ni-BZCYYb and SDC may be responsible for the good long term stability of the cell. However, further analysis of the SDC layer near the interface indicated that some inter-diffusion was detectable by energy dispersive X-ray spectroscopy (EDX), as shown in Fig. 2c and 2d. A clear Ba peak along with the expected Sm and Ce was shown in the SDC film, indicating some Ba was diffused to SDC electrolyte layer from the anode. Other elements, like Yb, Zr and Y, might also diffuse to the SDC layer, but they were under the background level. It is noted that the signal of Au was resulted from the as-deposited Au coating.

It is well known that the electronic conductivity of SDC electrolyte increases with temperature when exposed to a fuel, leading to a larger decrease in OCV (or energy efficiency) at a higher temperature. Thus, anode supported cells with thin SDC electrolyte becomes inefficient at temperatures higher than 650°C.[7,23] However, very high OCV of 0.995 V at 750°C was achieved in our NiO-BZCYYb supported SDC cell, as shown in Fig. 3a. At lower temperatures, the OCV values reached 1.004, 1.029, 1.047, 1.055, and 1.065 V at 700, 650, 600, 550, and 500°C, respectively, which are close to the theoretical values predicted by the Nernst Equation, indicating that there is very low electronic conductivity and few flaws (cracks, pin holes, etc.) in the electrolyte membrane. The achieved OCV values are much higher than those observed for a conventional cell based on doped ceria electrolyte under similar conditions (e.g., ~0.81 V at 650°C).[7] It is well known that the OCVs of cells based on a mixed conducting electrolyte (such as doped ceria) depends also on the thickness of the electrolyte membrane[10] and the catalytic activity of the electrode-electrolyte interfaces.[24–26] Accordingly, it is difficult to achieve high OCVs at 650°C for anode-supported cells because the thicknesses of the SDC or GDC electrolyte membranes are relatively thin.[7,10,23] The significant enhancement in the OCV values of the NiO-BZCYYb/SDC/LSCF cell is attributed to some new phases such as doped barium cerate ($Ba(Ce, Sm, Zr, Y, Yb)O_3$) at the interface due to inter-diffusion between BZCYYb and SDC during firing. It is these new interfacial phases that prevent the reduction of SDC and effectively block the electronic conduction through the SDC electrolyte membrane. Since the thermal expansion coefficients of doped barium cerates (~$11.2 \times 10^{-6}/K$[27] for BZCY and ~$11.6 \times 10^{-6}/K$[28] for BZCYYb) are very close to those of SDC (~$12.8 \times 10^{-6}/K$[29]), the new interfacial phase is thermally compatible with the SDC membrane.

Compared to other approaches to block electronic conduction in SDC electrolyte,[11–18] this new concept is more effective and very simple. Fox example, surface modification of SDC by the deposition of a BaO film at high temperatures (>1500°C) to form a BCS surface layer is difficult to be implemented in an anode supported cell, which may limited the practical application.[15,16]

Fig. 3b shows some typical performances of a single cell, demonstrating peak power densities of 0.86, 0.76, 0.64, 0.5, 0.36, and 0.24 W/cm^2 at 750, 700, 650, 600, 550, and 500°C, respectively, when humidified hydrogen was used as fuel and ambient air as oxidant. The performance achieved in this work is comparable to those of the conventional Ni-SDC supported cell at low temperature range,[7] where peak power densities of 0.59 W/cm^2 at 600°C and 0.31 W/cm^2 at 550°C were obtained in a single cell based on 24 μm thick SDC electrolyte, but the OCV was much lower in the conventional Ni-SDC anode supported cell. It is noted that our cell performance is

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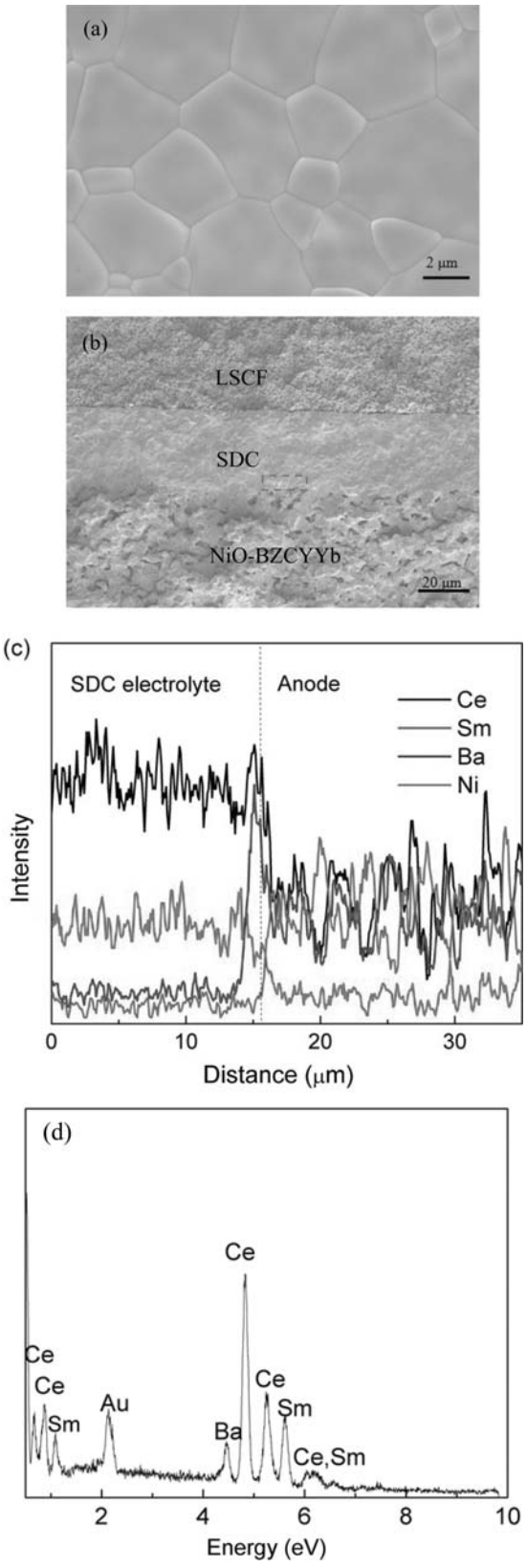

Figure 2. SEM image of (a) surface morphology of the SDC electrolyte; (b) cross sectional view of the as-prepared tri-layer cell, (c) EDS line scan across the SDC and Ni-BZCYYb interface, and (d) SEM-EDX spectra taken from the SDC electrolyte layer close to the Ni-BZCYYb/SDC interface shown in (b).

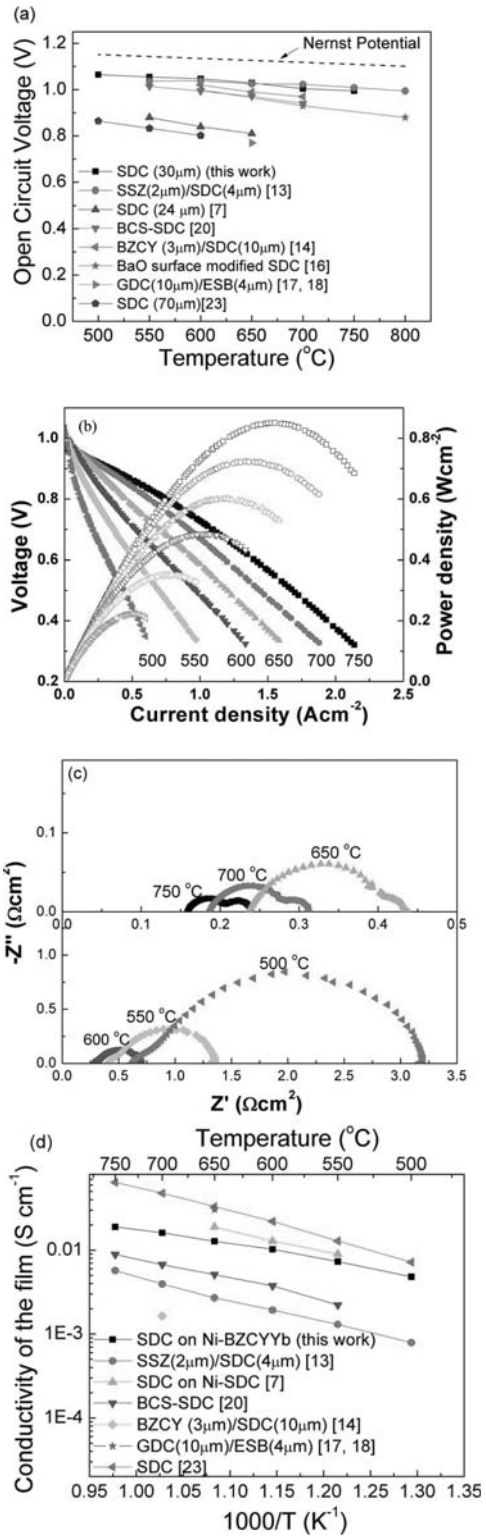

Figure 3. (a) OCVs of the Ni-BZCYYb supported SDC cell; (b) The Typical current-voltage characteristics and the corresponding power densities for SDC based cell measured at 500–750°C when ambient air was used as oxidant and humidified (3 v% H_2O) hydrogen as fuel. The number by each set of data represents the temperature in °C at which the full cell performance was measured; (c) Impedance spectra for the single cell measured under OCV conditions open-circuit conditions at different temperatures and (d) Conductivities of SDC electrolyte film on Ni-BZCYYb anode compared with other data reported in the literature.

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higher than that of reported for BZCY based cells at lower temperature range,[30,31] though the BZCY shows higher ionic conductivity at low temperature range.[1,21] The results suggest that the single cell of Ni-BZCYYb supported SDC is very promising for application in low-temperature SOFCs. Considering the fact that pure LSCF was used as the cathode material in this cell, it is expected that the cell performance can be further enhanced when other highly activity cathode materials are used such as BSCF[8] and SSC-SDC.[5,7]

In order to gain more insights into the new cell structure, impedance spectra of the cells were measured under open circuit conditions at different temperatures, as shown in Fig. 3c. It is clear that the electrolyte resistances, R_Ω, and the electrode polarization resistance, Rp, increased significantly as the operating temperature was reduced from 750°C to 500°C. For example, the R_Ω was increased from 0.16 to 0.62 Ω cm^2, while the Rp increased from 0.08 to 2.53 Ω cm^2. The significant increase in Rp at low temperatures indicates the cell performance is limited more by the slow electrode kinetics at low temperatures. Since the polarization of cathode is believed to dominate the electrode polarization loss. The development of more catalytically activity cathode materials is a grand challenge to further enhancement of the performance. Since doped ceria electrolytes have much better chemical and thermal compatibility than doped zirconia electrolytes with catalytically active cathode materials, SOFCs based on doped ceria electrolytes have better potential to minimize efficiency loss due to cathodic polarization.

Further, the conductivity of the anode supported SDC electrolyte film estimated from L/R_Ω was shown in Fig. 3d, where L is the thickness of the electrolyte film. Obviously, the SDC film on the Ni-BZCYYb anode exhibited a lower conductivity than those reported for bulk SDC electrolyte[23] and Ni-SDC supported SDC films.[7] The low conductivity might result from the different interface between the anode and SDC. In the Ni-BZCYYb supported SDC, the inter-diffusion between BZCYYb and SDC near the interface may reduce the ionic conductivity of the SDC electrolyte film. Still, the conductivity of the SDC electrolyte on Ni-BZCYYb (0.016 S/cm^2 at 700°C) is better than those reported for an SSZ/SDC[13] or BZCY/SDC[14] bi-layer (the average conductivity estimated from the total thickness of the bi-layer) and a BCS-SDC composite[20] (0.004, 0.0017, and 0.0067 S/cm^2 at 700°C, respectively). The relatively low performance achieved in those studies[14,20] is due most likely to the low conductivity of the bi-layer or composite electrolytes. In addition, physical contact of two dense electrolytes layer in a bi-layer structure may cause delamination and cracking due to the thermal stress developed at the interface, leading to failure of the cell.

To evaluate the electrochemical stability of SDC electrolyte membrane on Ni-BZCYYb anode, the durability of the cell was first examined at 750°C under constant voltage of 0.7 V using humidified H_2 as fuel, as shown in Fig. 4. A stable power output was demonstrated up to 70 hrs, indicating that the Ni-BZCYYb anode is electrochemically stable under the testing conditions. More interestingly, this novel cell showed excellent coking tolerance when the fuel was switched from hydrogen to methane. Early studies indicated that the conventional Ni-SDC anode encountered a serious carbon deposition which degraded the cell rapidly in a few hours when methane was used as fuel.[32] In order to overcome the susceptibility to coking in the Ni-SDC anode, a thin film catalyst of SDC was coated on the anode; the nano-structured SDC coating was in suppressing carbon deposition.[32] In this study, a simple and one-step co-fired Ni-BZCYYb/SDC structure showed good coking tolerance with wet methane as fuel. The cell produced an output current of ~0.65 A/cm^2 at 0.7 V. The lower performance in methane is due most likely to lower catalytic activities for reforming/oxidation of the hydrocarbons than for hydrogen. However, there was no observable degradation during the period of testing with wet methane as fuel, suggesting that the Ni-BZCYYb exhibits excellent coking tolerance.[21] It is believed that this anode has tolerance to sulfur poisoning as well.[33,34] The unique properties of this anode are associated with the structures and compositions of the Ni-BZCYYb anode surfaces, which promote in situ reformation of methane on the anode surface and a water-mediated carbon-removal.[34]

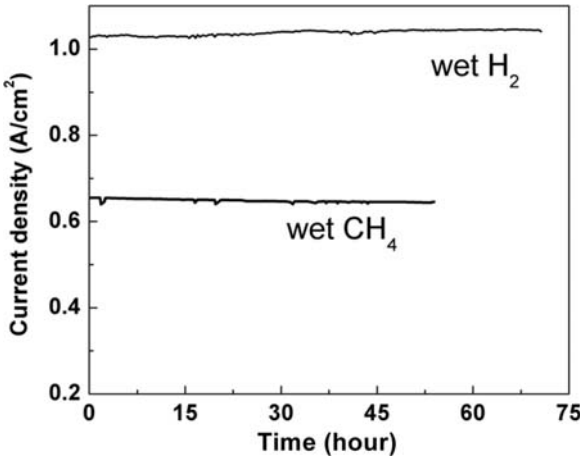

Figure 4. Current density as a function of time for the Ni-BZCYYb supported SDC cell, operated at 750ºC at a constant cell voltage of 0.7 V when wet H_2 or methane (wet gas contained 3 v% water vapor as humidified at 25°C) was used as the fuel and ambient air as the oxidant.

Conclusions

We have demonstrated an efficient IT-SOFC structure based on doped ceria electrolytes. NiO-BZCYYb has been successfully employed as the anode for SDC based electrolyte to effectively block the electronic conductivity while maintaining the high performance. Single cells with LSCF cathode achieved high power densities of 0.86, 0.64, and 0.36 mWcm^2 at 750, 650, and 550°C, respectively. EDX analysis suggests that there is some inter-diffusion between BZCYYb and SDC near the interface, leading to the formation of a new phase that suppresses the internal shorting of the SDC electrolyte and enhances the open circuit voltage. Furthermore, the cell shows stable operation when wet H_2 and methane were used as the fuel at 750°C, indicating that the anode has good coking tolerance. The results suggest that the new cell configuration, LSCF | SDC | Ni-BZCYYb, is very promising for practical applications.

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