The improvement of barium-containing anode for ceria-based electrolyte with electron-blocking layer

Jiafeng Cao^{a,b}, Zheng Gong^a, Chuangang Fan^c, Yuexia Ji^b, Wei Liu*

^a CAS Key Laboratory of Materials for Energy Conversion & Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Hefei 230026, PR China

^b School of Mathematics and Physics, Anhui University of Technology, Maanshan, 243032, PR China

^c School of materials science and engineering, Anhui University of Technology, Maanshan, PR China

Abstract: An original approach aiming at the improvement of barium-containing anode in the reduction of partial internal electronic short circuit for ceria-based electrolyte in intermediate temperature solid oxide fuel cells (IT-SOFCs) was proposed in this research. The improved cells employed by mixed proton-oxide ion-electron conducting composite anodes show efficiently enhanced properties, especially in the effective increase of **power densities**. The electron-blocking layer **can be maintained** with a suitable proportion of $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC) below 20 mol% **at anodes**. Furthermore, a mechanism for barium diffusion and ionic conduction behavior in barium-containing anodes of the improved cells **was proposed**.

Keyword: Ceria-based Electrolyte; Barium diffusion; Polarization resistance; Solid oxide fuel cells

1. Instruction

Intermediate temperature solid oxide fuel cells are extensively researched worldwide considering their mild operating temperature, lower fabrication cost, etc. comparing with the conventional SOFCs demanding an operating temperatures beyond 800°C [1-4]. As a typical oxygen conductor, doped CeO_2 (DCO) has been widely investigated in IT-SOFCs owing to its high ionic conductivity and low operating temperature [5-7]. Sm^{3+} and Gd^{3+} -doped ceria (SDC and GDC) with high ionic conductivity based on an anode-supported electrolyte membrane have exhibit peak power densities in the intermediate temperature range [8,9]. Furthermore,

* Corresponding author. Tel.: +86 0551 3606929; fax: +86 0551 3602586.
E-mail address: wliu@ustc.edu.cn (W. Liu)

ceria-based electrolytes have excellent properties with the commonly used cathode materials such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ - $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (LSCF-GDC), $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC) [8,10,11]. However, the occurrence of $\text{Ce}^{4+}/\text{Ce}^{3+}$ mixed valences associated with the stabilization of oxygen vacancies remains a huge challenge for ceria-based SOFCs operating under high voltages [12,13]. Therefore, ceria-based cells have to be processed at temperatures below 500°C, where the reduction of Ce^{4+} is thermodynamically suppressed [14,15].

In order to overcome the reduction of ceria at anodic side, bi-layered electrolytes were first developed such as depositing a thin $\text{Y}_{0.1}\text{Zr}_{0.9}\text{O}_{2-\delta}$ (YSZ) film on the doped ceria electrolyte membrane [16-18]. Unfortunately, the lower ionic conductivity of YSZ at intermediate temperatures will inevitably increase the ohmic resistance of cells. Bismuth oxide was also employed to reduce electronic conductivity by coating a thin doped bismuth oxide film between electrolyte and cathode [19]. However, the main drawback of Bi_2O_3 is that it is not stable in the blocking layer because the layer can actively react with cathode under high operating temperature [20].

Barium diffusion has been successfully reported to be an effective approach to suppress the reduction of DCO electrolyte by forming a Ba-containing functional layer over the electrolyte surface [14, 21-25]. More recently, $\text{Ni-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (Ni-BZCY) [24,26] and $\text{Ni-BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (Ni-BZY) [25] cermets were reported for SDC pellets with barium ionic diffusion under high temperature. The fuel cells exhibited significantly improved open circuit voltages (OCVs) as well as high energy efficiencies demonstrating barium-containing anodes were significantly materials that can efficiently eliminate internal short circuit for DCO-based SOFCs. Unfortunately, the redox reaction only restrainedly occurs at the interface of anode|electrolyte because of the limited oxygen-ionic conduction of barium-containing anodes. It continues to be a limiting factor for enhanced cells which has not been systematically studied up to now. In our previous work [27], $\text{BaZr}_{0.45}\text{Ce}_{0.45}\text{Gd}_{0.1}\text{O}_{3-\delta}$ at anode was proposed to avoid partial reduction from Ce^{4+} to Ce^{3+} in GDC electrolyte by forming a functional electron-blocking interlayer in situ. The functional interlayer can efficiently reduce n-type electronic conductivity causing enhanced OCVs. However,

the ceria cells with $\text{BaZr}_{0.45}\text{Ce}_{0.45}\text{Gd}_{0.1}\text{O}_{3-\delta}$ anodes were also found particularly blocking the oxygen-ionic conduction than that of the cell with Ni-GDC anode.

As far as we know that the combination between the formation of electron-blocking layer and the enhancement of oxygen-ionic conductor at Ba-containing cells still remain a perplexing problem and has not been clearly clarified in detail up to now. As a consequence, this work is supposed to achieve two aims: 1). Fabricating the electron-blocking layer by metal ions diffusion at the interface of anode and electrolyte. 2). In an effort to enhance the overall efficiency of the cells by increasing the triple phase boundary (TPB) length for ceria-based cells with barium-containing anode after modifying the ions conduction as compared with the traditional anodes. Thus mixed-ionic-electronic conducting materials, forming composite anodes, were employed to fabricate $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC)-based cells by co-pressing method. The relation-ship between barium diffusion and the micro-structure, electrochemical properties of $\text{NiO}-(1-x)\text{BZCG}-x\text{GDC}|\text{GDC}|\text{SSC}-\text{SDC}$ ($0 \leq x \leq 1$) were systemically investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), I-V polarization characterizations and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1 Synthesis scheme

Stoichiometric $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{C}_4\text{H}_6\text{BaO}_4$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ and Gd_2O_3 original anodic powders were used in the experiment to synthesize anodes and electrolyte. Driven by the high oxygen-ionic conduction, GDC has been introduced into anodes as listed in Table 1, which illustrates the compositions of the cells in this research. The powders for anode substrate were labeled as $\text{NiO}-(1-x)\text{BZCG}-x\text{GDC}$ and the weight ratio of $\text{NiO}:(1-x)\text{BZCG}-x\text{GDC}$ was 60:40. The composite anodes in this research were synthesized by a citric acid-nitrate gel combustion process, which can be seen in previous report [27]. Pure anodic powders were obtained after being heated at 1050 °C for 5 hours by a furnace. GDC ash for electrolyte was also synthesized by the same method with a calcined process at 600 °C for 3 hours. The

anode-supported half cells were all obtained by co-pressing, followed by sintering at 1350°C for 5 hours to form dense GDC electrolyte pellets with a size of about 1 mm in thickness and 12 mm in diameter. $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ (SSC-SDC) composite has been reported to be a good cathode for DCO-based SOFCs and was employed as the cathode in this research [28]. The cathodic slurry was then painted onto the GDC membrane and heated at 950°C for 3h in air to form full cells.

2.2 Characterization techniques

X-ray powder diffraction (XRD) patterns of powders were recorded by an X-ray diffractometer (Rigaku TTR-III) in the range of $2\theta = 20\text{-}80^\circ$. Microstructures of the samples were analyzed using a scanning electron microscope (SEM JSM-6700F). Silver paste (Sino-platinum Metals Co.,Ltd PC-Ag-8110) was applied to the cathode surface as a current collector and Ag wires were employed as the conducting wires for fuel cells test. Cells test measurements were evaluated using 3% H_2O humidified hydrogen as fuel and static air at cathode side in the temperature range from 550 to 700°C in a cell testing system. I-V curves of the cells were measured with a DC electronic load based on the two-probe configuration. The electrochemical impedance spectra were obtained under open circuit conditions using a CHI604B impedance analyzer for the frequency dependent observation from 100 kHz to 0.1 Hz. The polarization resistances of the cells under open circuit conditions were determined from the electrochemical impedance spectra.

3. Results and Discussion

3.1 Characterization results

An approach in this research to enhance the properties of ceria cells with barium-containing anodes was carried out by increasing the proportion of GDC powders in the synthetic procedure of anodes. The GDC molar ratios at anodes were selectively studied according to the different electrochemical properties of the cells-improved, and the cells with anodic samples $\text{NiO}-(1-x)\text{BZCG-xGDC|GDC|SSC}$

-SDC ($x=0, 0.2, 0.25, 0.3, 1$) were fabricated and labeled hereafter as Ni-BZCG, 0.8-0.2, 0.75-0.25, 0.7-0.3 and Ni-GDC, respectively. Fig.1 shows the XRD patterns of the composite anodes with different amount of GDC composition. With the increase of GDC amount in NiO-(1-x)BZCG-xGDC composites, the intensity of (111) peak at 28.55° , which is identified as the main peak of the GDC phase, is gradually increased, whereas that of the (220) peak at 29.40° from the BZCG phase is decreased. No other appreciable phase is found in the results, suggesting that there is no chemical reaction between BZCG and GDC.

As is shown in Fig.2, the cell test and electrochemical characterization of the as-sintered samples at 1350°C for 5 h are progressed at different temperatures ranging from 550 to 700°C with humidified hydrogen (3% H_2O) as the fuel fed at a flow rate of 20 ml min^{-1} . As GDC is introduced into the anodes, the OCV values are slightly depressed from 0.982 to 0.947 V for Ni-BZCG and 0.8-0.2 samples, and then obviously reduce from 0.85 to 0.68 V for 0.75-0.25, 0.7-0.3 and Ni-GDC at 700°C , owing to the decreased relative content of BZCG. For the operating temperature at 650°C , the OCVs gradually decrease from 1.012 to 0.975 V for Ni-BZCG and 0.8-0.2, and then further reduce to 0.721 V for Ni-GDC. However, the power densities of the cells demonstrate a different trend. As for the Ni-BZCG anode at 700°C , the maximum value of the power density is 505.38 mW/cm^2 , and the power density is efficiently enhanced to be 763.08 mW/cm^2 for 0.8-0.2, which could be ascribed to the increase of GDC content. Furthermore, enhanced power densities values of 615.69 and 579.49 mW/cm^2 for 0.75-0.25 and 0.7-0.3 samples can be obtained according to our measurement. For comparison, the power densities for Ni-GDC sample at 700 and 650°C are only 358.97 and 205.13 mW/cm^2 , meaning that the addition of GDC content in anodic side with BZCG composition is an efficient approach to improve the properties of the ceria-based cells.

After electrochemical test, the microstructures of as-prepared full cells are examined by SEM. Fig.3 presents that the electrolyte films are fully-dense and show an excellent adhesion with the substrates and the cathodes. The thickness of the GDC films are about 20-25 μm , which is not considered to be the main influencing factor of

the results. As is shown in Fig.3, the cross sections marked by black lines, focusing at the interface, show that relatively good porosity of the composite anode layer **is achieved**. Fig.3 also shows the surface of the electrolytes of the tested cells. The morphology of the electrolytes appears no different than each other. The grain sizes are about 1-4 μm and the pellets are quite dense without pores. Prior to electrochemical measurements, the full cells including composite anodes, GDC electrolytes and SSC-SDC cathodes are synthesized at the same progress, and it can be concluded that the different properties between the as-sintered samples will be mainly ascribed to **the different composition of composite anodes**.

Fig.4 presents the typical electrochemical impedance spectra (EIS) of the cells measuring at elevated temperatures from 550 to 700 $^{\circ}\text{C}$. The high-frequency intercept corresponds to the ohmic resistance (R_o) of the cell, including the ionic resistance of the electrolyte, the electronic resistance of the electrodes and contact resistance between the interfaces of the components. The low-frequency intercept corresponds to the total resistance of the cell when inductive reactance was not induced associated with the different components. The difference between the high frequency and low frequency intercepts with the real axis represents the total interfacial polarization resistance (R_p) of the cell. When inductive reactance is induced in the electrodes, the impedance curve will be negatively reduced and reversed arc can be seen in some cases when the value of inductive reactance is not negligible. As shown in Fig.4, the polarization resistance seriously decreases with the increase of GDC content. The Ni-BZCG presents the largest R_p (0.4512, 1.5256 Ωcm^2) of all the cells mentioned above at 700 and 650 $^{\circ}\text{C}$. However, the 0.8-0.2 pellet at the same temperature **shows** reduced R_p (0.3363, 0.5737 Ωcm^2) values, which declines by about 25.5 and 62.4%. More importantly, the polarization resistance of 0.8-0.2 cell tested at 600 and 550 $^{\circ}\text{C}$ (0.8876 and 1.4194 Ωcm^2) have already been closed to the value of Ni-GDC (0.5918 and 1.6987 Ωcm^2) at the same temperature. As the proportion of GDC powders at anodes increase to 25 and 30%, forming the 0.75-0.25 and 0.7-0.3 samples, the value between the high frequency and low frequency intercepts with the real axis at 700 and 650 $^{\circ}\text{C}$ significantly decrease to 0.0131, 0.0345 Ωcm^2 and 0.0112, 0.0279 Ωcm^2 ,

respectively, which demonstrate much less than the R_p value of Ni-GDC sample (0.0848 and 0.1931 Ωcm^2). For 0.75-0.25 and 0.7-0.3 samples, it should be noted that the impedance spectra show seriously negative plot at low frequency, especially at high operating temperature between 650 and 700 °C. Herein, inductive reactance is induced which will be discussed in the following section. In contrast, the typical anode-supported ceria-based cells including the peak power densities, OCVs and R_p values at 600 °C are shown in Table 2. It can be concluded that the performance of cell-improved in this work is more superior to the best reported performances by far of the ceria SOFCs based on barium diffusion, which is widely considered to be the most promising low-temperature SOFCs [21-25], as shown in Table 2.

3.2 Mechanism analysis

As is illustrated above, 0.8-0.2 pellet shows higher performance than the other samples considering the OCVs, power densities and R_p values. Therefore, the most suitable proportion of GDC is around 20% according to our results. Herein, the proposed mechanism of the cells with composite anodes with different GDC ratios is shown in Fig.5. The composites, made of Ni, an electron conductor, BZCG, a proton conductor under reduction atmosphere, and GDC, an oxygen-ion conductor, have been employed for the anodes because of the multifunctional conduction of electron, proton and oxygen-ion as compared with the traditional anodes. Besides, the BZCG composition can also provide barium ions which can fabricate electron-blocking layer at the interface of anode and electrolyte with co-firing temperature. The oxygen-ionic conduction of GDC at improved anodes can extend more TPB sites for fuel reduction which will promote the rate of redox reaction. Fig.5a shows the un-improved cell with NiO and BZCG powders, which are only the electron and proton conductors. The electron-blocking interlayer can be fabricated in situ at anode|electrolyte interface by barium diffusion in Ni-BZCG. Nevertheless, the redox reactions between proton and oxygen can only be restricted in the interface of anode|electrolyte. Under the circumstances, the GDC composition is then applied to be the third composition at anode. Figure 5b shows the potential paths for proton, oxygen ionic and electronic

transport in 0.8-0.2, typically consisting one hydrogen-ion and one oxygen-ion conduction at anode. It can be seen that redox area can be expanded to the whole anode, which will greatly enhance the properties of the pellets. At the same condition, barium ions can also transmit across anodic side to the interface forming electron-blocking layer under high temperature. However, in the case of 0.75-0.25 and 0.7-0.3 pellets, barium diffusion is restrained by the increased GDC particles, which is the result of the decreased OCV values at 650 and 700 °C.

Nanosized BaO islands on the Ni surface, creating numerous nanostructured BaO/Ni interfaces, were reported facilitating water-mediated carbon removal reactions [29]. Tao [30] also reported the formation of BaO coating on Ni surface which can effectively readily adsorb water and facilitate water-mediated carbon removal at Ni-BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ}-Sm_{0.2}Ce_{0.8}O_{1.9} anode. Considering the previous reports, the results of impedance spectra (Fig.4c.d) can be explained as follows: the inductive reactance may be generated by the corrosion at anodes. Considering 0.7-0.3 sample before cell testing, much BaO dot depositing on the surface of nickel particles will cause the following reaction at anode, which is shown in Fig.6.a:

Hence, the corrosion reaction at anode induced by H₂O (Eq. (1-2)) may be the reason for the respected inductive reactance in Fig.4c.d.

To further confirm the supposed mechanism, electrochemical impedance spectroscopy measurements were performed fed by CH₄ instead of H₂, which is illustrated in Fig.6.b. The reactions at anode are:

Fig.7 shows the impedance spectra before and after fuel switch test of the 0.7-0.3 sample as a function of time. In the beginning ($t=0$), the difference between the high frequency and the low frequency intercept with the real axis displays no negative impedance spectra, which demonstrates that inductive reactance was not induced by CH_4 . When H_2 was fed to the anode instead of CH_4 , the corrosion at anode **was generated**, and the inductive reactance can be seen from $t=10$ mins, amplified at $t=30$ mins, and seriously reversed to the negative arc **at $t=80$ mins**. However, when CH_4 was fed to the anode again, the spectrum with no inductive reactance recovered after 10 minutes (at $t=90$ mins), which demonstrated that $\text{Ba}(\text{OH})_2$ decomposed into BaO and H_2O again.

In order to characterize the structural and compositional properties of the functional electron-blocking layer, the microstructure of the electron-blocking layer were acquired by SEM-EDS. **Fig.8 shows the SEM-EDS images for the cross sections of anode-supported half cells considering diffused elements**. In Fig.8.a, Ba ions have been clearly seen diffusing into GDC electrolyte from anodic side by co-fired process, which is responsible for the high enhancements of the OCVs for Ni-BZCG **sample**. It should be noted that Zr ions can also diffuse to GDC electrolyte, but they are under the background level, which can be seen in [21]. Fig.8.b **demonstrated** that Ba ions **can still gather** at the interface of anode|electrolyte forming the electron-blocking layer. However, it can be seen from the microstructure analysis of Fig.8c and Fig.8d that the functional **electron-blocking** layers have not been sufficiently fabricated considering the low Ba signal at anode|electrolyte interfaces. It should be noted that **Ba diffusion will be restrained when GDC increased** and hence the electron-blocking layer cannot be sufficiently fabricated, which is the main reason for the reduced OCVs of 0.75-0.5 and 0.7-0.3 samples. Meanwhile, **the power intensities of these two samples were improved** for the existence of GDC powders **compared with Ni-BZCG at anodes**. The low power intensity of Ni-GDC can be attributed to the high partial

internal electronic short circuit for GDC electrolyte and single oxygen-ion conducting ability of GDC at anode. On the basis of the results above, barium diffusion is responsible for the enhanced performances of the enhanced OCVs, and the addition of GDC at anode works as oxygen-ionic conduction medium in this research, which can influence the formation of electron-blocking layer and promote the redox reaction.

Conclusions

In summary, composite anodes including mixed-ionic-electronic conducting materials were employed in the improvement of CeO₂-based electrolyte. The systematical results indicated that the introduction of GDC had an enhancement on the performance of the cells with Ba-containing anodes and the as-prepared 0.8-0.2 sample exhibited excellent properties compared with the other pellets. The higher OCVs can be first attributed to the Ba diffusion at anodic side. The high power densities of the improved pellets with composite anodes can be ascribed to the increasement of GDC content, which can extend more TPB sites at anodes. The mechanism for the improved cells with composite anodes including metal diffusion was proposed and the inducement of inductive reactance was ascribed to the corrosion reaction at anodes. Importantly, this research provided a desirable combination of enhanced OCVs and improved power densities for ceria-based SOFCs, which suggested a novel process that can facilitate to prepare ceria cells operating with high activities.

Acknowledgments

This work was supported by the National Science Foundations of China (Grant Nos: 11404004 and 51502004). The project was also supported by the Natural Science Foundation of Anhui University of Technology (Grant No: QZ201417).

References

- [1] E. Fabbri, D. Pergolesi, E. Traversa, Materials challenges toward proton-conducting oxide fuel cells: a critical review, *Chem. Soc. Rev.* 39 (2010) 4355-4369.
- [2] E.D. Wachsman, K.T.Lee, Lowering the Temperature of Solid Oxide Fuel Cells, *Science* 334 (2011) 935-939.
- [3] M.L. Liu, M. E. Lynch, K. Blinn, F. M. Alamgir, Y. Choi, Rational SOFC material design: new advances and tools, *Mater. Today* 14 (2011) 534-546.
- [4] B.C.H. Steele, A. Heinzel, Materials for fuel-cell technologies, *Nature* 414 (2001) 345-352.
- [5] A.B. Stambouli, E. Traversa, Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy, *Renew. Sust. Energ. Rev.* 6 (2002) 433-455
- [6] R.S. Torrens, N.M. Sammes, G.A. Tompsett, Characterization of $(\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2}$ synthesized using various techniques, *Solid State Ion.* 111 (1998) 9-15.
- [7] F. Zhao, Z.Y. Wang, M.F. Liu, L. Zhang, C.R. Xia, F.L. Chen, Novel nano-network cathodes for solid oxide fuel cells, *J. Power Sources* 185 (2008) 13-18.
- [8] Z. P. Shao, S. M. Haile, A high-performance cathode for the next generation of solid-oxide fuel cells, *Nature* 431 (2004) 170-173.
- [9] Q.L. Liu, K.A. Khor, S.H. Chan, High-performance low-temperature solid oxide fuel cell with novel BSCF cathode, *J. Power Sources* 161 (2006) 123-128.
- [10] E.Q. Zhao, Z. Jia, L. Zhao, Y.P Xiong, C.W. Sun, M.E. Brito, One dimensional $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}/\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ nanocomposite cathodes for intermediate temperature solid oxide fuel cells, *J. Power Sources* 219 (2012) 133-139
- [11] C.J. Fu, K.N. Sun, N.Q. Zhang, X.B. Chen, D.R. Zhou, *Electrochemical*

- characteristics of LSCF–SDC composite cathode for intermediate temperature SOFC, *Electrochim. Acta* 52 (2007) 4589-4594.
- [12] M. Nolan, S.C. Parker, G.W. Watson, The electronic structure of oxygen vacancy defects at the low index surfaces of ceria, *Surf. Sci.* 595 (2005) 223-232.
- [13] K. Eguchi, T. Setoguchi, T. Inoue, H. Arai, Electrical properties of ceria-based oxides and their application to solid oxide fuel cells, *Solid State Ionics* 52 (1992) 165-172.
- [14] A. Tomita, S. Teranishi, M. Nagao, T. Hibino, M. Sano, Comparative performance of anode-supported SOFCs using a thin $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ electrolyte with an incorporated $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ layer in hydrogen and methane, *J. Electrochem. Soc.* 153 (2006) A956-A960.
- [15] R. Doshi, R. Von L. Richards, J.D. Carter, X. Wang, M. Krumpelt, Development of solid-oxide fuel cells that operate at 500°C, *J. Electrochem. Soc.* 146 (1999) 1273-1278.
- [16] Q.L. Liu, K.A. Khor, S.H. Chan, X.J. Chen, Anode-supported solid oxide fuel cell with yttria-stabilized zirconia/gadolinia-doped ceria bilayer electrolyte prepared by wet ceramic co-sintering process, *J. Power Sources* 162 (2006) 1036-1042.
- [17] S. Cho, Y.N. Kim, J.H. Kim, A. Manthiram, H.Y. Wang, High power density thin film SOFCs with YSZ/GDC bilayer electrolyte, *Electrochim. Acta* 56 (2011) 5472-5477.
- [18] Z.G. Lu, J. Hardy, J. Templeton, J. Stevenson, D. Fisher, N.J. Wu, A. Ignatiev, Performance of anode-supported solid oxide fuel cell with thin bi-layer electrolyte by pulsed laser deposition, *J. Power Sources* 210 (2012) 292-296.
- [19] J. S. Ahn, D. Pergolesi, M. A. Camaratta, H. Yoon, B. W. Lee, K. T. Lee, D. W. Jung, E. Traversa, E. D. Wachsman, High-performance bilayered electrolyte intermediate temperature solid oxide fuel cells, *Electrochem. Commun.* 11 (2009) 1504-1507.
- [20] J. Hou, F.G. Liu, Z. Gong, Y.S. Wu, Wei Liu, Different ceria-based materials $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ and $\text{Sm}_{0.075}\text{Nd}_{0.075}\text{Ce}_{0.85}\text{O}_{2-\delta}$ for ceria–bismuth bilayer electrolyte

- high performance low temperature solid oxide fuel cells, *J. Power Sources*. 299 (2015) 32-39
- [21] D. Hirabayashi, A. Tomita, T. Hibino, M. Nagao, M. Sano, Design of a reduction-resistant $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ electrolyte through growth of a thin $\text{BaCe}_{1-x}\text{Sm}_x\text{O}_{3-\delta}$ Layer over electrolyte surface, *Electrochem. Solid-State Lett.* 7 (2004) A318-A320.
- [22] M.F. Liu, D. Ding, Y.H. Bai, T. He, M.L. Liu, An efficient SOFC based on samaria-doped ceria (SDC) electrolyte, *J. Electrochem. Soc.* 159 (2012) B661-B665.
- [23] A. Tomita, Y. Tachi, T. Hibino, Blocking of electronic current through a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ electrolyte film by growth of a thin $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ layer, *Electrochem. Solid-State Lett.* 11 (2008) B68-B70. ELECTROCHEM SOLID ST
- [24] W.P. Sun, W. Liu, A novel ceria-based solid oxide fuel cell free from internal short circuit, *J. Power Sources* 217 (2012) 114-119.
- [25] W.P. Sun, Z. Shi, J. Qian, Z.T. Wang, W. Liu, In-situ formed $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}@\text{Ba}(\text{Ce}, \text{Zr})_{1-x}(\text{Sm}, \text{Y})_x\text{O}_{3-\delta}$ core/shell electron-blocking layer towards $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ -based solid oxide fuel cells with high open circuit voltages, *Nano Energy* 8 (2014) 305-311.
- [26] Z. Gong, W.P. Sun, D. Shan, Y.S. Wu, Wei Liu, Tuning the thickness of Ba-containing “functional” layer toward high-performance ceria-based solid oxide fuel cells, *ACS Appl. Mater. Interfaces* 8 (2016) 10835-10840.
- [27] J.F. Cao, Z. Gong, J. Hou, J.F. Cao, W. Liu, Novel reduction-resistant $\text{Ba}(\text{Ce}, \text{Zr})_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ electron-blocking layer for $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ electrolyte in IT-SOFCs, *Ceram. Int.* 41 (2015) 6824-6830.
- [28] W.P. Sun, L.T. Yan, B. Lin, S.Q. Zhang, W. Liu, High performance proton-conducting solid oxide fuel cells with a stable $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Co}_{3-\delta}$ - $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ composite cathode, *J. Power Sources* 195 (2010) 3155-3158.
- [29] L. Yang, Y.M. Choi, W.T. Qin, H.Y. Chen, K. Blinn, M.F. Liu, P. Liu, J.M. Bai,

- T.A. Tyson, M.L. Liu, Promotion of water-mediated carbon removal by nanostructured barium oxide/nickel interfaces in solid oxide fuel cells, *Nat. Commun.* 2 (2011) 357-365.
- [30] Z.T. Tao, G.H. Hou, N. Xu, Q.F. Zhang, H.P. Ding, A mixed proton-oxide ion-electron conducting anode for highly coking-resistant solid oxide fuel cells, *Electrochim. Acta* 150 (2014) 55-61.

Figure captions:

Fig.1 X-ray diffraction **patterns** of the powders for anodes with different BZCG:GDC ratios sintered at 1050°C for 5h and Ni-GDC powder **sintered** at 600°C for 3h.

Fig.2 I-V and I-P curves for full cells of Ni-(1-x)BZCG-xGDC|GDC|SSC-SDC with half-cells processed at 1350°C for 5h: (a) Ni-BZCG, (b) 0.8-0.2, (c) 0.75-0.25, (d) 0.7-0.3, (e) Ni-GDC and (f) Comparison of OCV and power density curves with different cells at the operating temperature of 700 and 650°C. **Open symbols indicate I-V curves, while solid symbols indicate I-P curves.**

Fig.3 Cross-section SEM images of the full cells and SEM micrograph of the micrographs of the cross sections at anode|electrolyte interfaces with Ba-containing anodes annealing at 1350°C for 5 h. (a)(b): Ni-BZCG, (d)(e): 0.8-0.2, (g)(h): 0.75-0.25 and (j)(k): 0.7-0.3. SEM micrographs of the electrolyte surface of the prepared pellets co-fired at 1350°C for 5h. (c): Ni-BZCG, (f): 0.8-0.2, (i): 0.75-0.25 (l): 0.7-0.3.

Fig.4 Impedance spectra plot of the cells on GDC membrane co-sintered with different anodes: (a) Ni-BZCG, (b) 0.8-0.2, (c) 0.75-0.25, (d) 0.7-0.3, (e) Ni-GDC and (f) comparison of R_p values with different cells at the operating **temperatures between 550 and 700 °C.**

Fig.5 Schematic illustration of the mechanism at the anode|electrolyte interfaces:

(a) Ni-BZCG, (b) 0.8-0.2, (c) 0.75-0.25/0.7-0.3 and (d) Ni-GDC.

Fig.6 The schematic of mechanism in Ni-0.7BZCG-0.3GDC anode fed by different fuels: (a) H₂ **and** (b) CH₄.

Fig.7 The impedance spectra of the pellet with Ni-0.7BZCG-0.3GDC anode by fuel switch test at 650°C.

Fig.8 SEM-EDS patterns of cross sections with pellets co-sintered at 1350°C for 5h

by ionic diffusion. (a) Ni-BZCG, (b) 0.8-0.2, (c) 0.75-0.25 and (d) 0.7-0.3.

Table1. Summary of cells with different concentration of GDC at anodes.

Samples	Compositions (anode electrolyte cathode)	Abbr.
1	NiO-BaZr _{0.45} Ce _{0.45} Gd _{0.1} O _{3-δ} Gd _{0.1} Ce _{0.9} O _{2-δ} Sm _{0.5} Sr _{0.5} CoO _{3-δ} -Ce _{0.8} Sm _{0.2} O _{2-δ}	Ni-BZCG
2	NiO-0.8BaZr _{0.45} Ce _{0.45} Gd _{0.1} O _{3-δ} -0.2Gd _{0.1} Ce _{0.9} O _{2-δ} Gd _{0.1} Ce _{0.9} O _{2-δ} Sm _{0.5} Sr _{0.5} CoO _{3-δ} -Ce _{0.8} Sm _{0.2} O _{2-δ}	0.8-0.2
3	NiO-0.75BaZr _{0.45} Ce _{0.45} Gd _{0.1} O _{3-δ} -0.25Gd _{0.1} Ce _{0.9} O _{2-δ} Gd _{0.1} Ce _{0.9} O _{2-δ} Sm _{0.5} Sr _{0.5} CoO _{3-δ} -Ce _{0.8} Sm _{0.2} O _{2-δ}	0.75-0.25
4	NiO-0.7BaZr _{0.45} Ce _{0.45} Gd _{0.1} O _{3-δ} -0.3Gd _{0.1} Ce _{0.9} O _{2-δ} Gd _{0.1} Ce _{0.9} O _{2-δ} Sm _{0.5} Sr _{0.5} CoO _{3-δ} -Ce _{0.8} Sm _{0.2} O _{2-δ}	0.7-0.3
5	NiO-Gd _{0.1} Ce _{0.9} O _{2-δ} Gd _{0.1} Ce _{0.9} O _{2-δ} Sm _{0.5} Sr _{0.5} CoO _{3-δ} -Ce _{0.8} Sm _{0.2} O _{2-δ}	Ni-GDC

Table 2. Some typical ceria-based SOFCs reported in literature including open circuit voltages (OCVs), peak power density (PPD) and polarization resistance (R_p).

Anode	Electrolyte	Cathode	OCVs (600°C)	PPD mW/cm ² (600°C)	R_p (Ω cm ²) (600°C)	Ref.
NiO-SDC	SDC	SSC	1.025	482 (950°C)	0.24 (950°C)	21
NiO-BZCYYb	SDC	LSCF	1.047	500	0.5	22
NiO-SDC	GDC BZ G GDC	SSC	0.96	250	--	23
NiO-BZCY	SDC	SSC-SDC	1.054	511	0.46	24
Ni-BZY	SDC	SSC-SDC	1.053	482	0.8	25
NiO-0.8BZCG -0.2GDC	GDC	SSC-SDC	1.0	566	0.8876	This work

Fig.1:

Fig.2:

Fig.3:

Fig.4:

Fig.5:

Fig.6:

Fig.7:

Fig.8: