



$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}\text{-Sr}_{1.95}\text{Pr}_{0.05}\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ heterogeneous structure composite electrolyte for solid oxide fuel cells

Jihai Cheng[✉], Yifeng Hou[✉], Ming Wang^{✉*}

School of Energy Materials and Chemical Engineering, Hefei University, Hefei 230601 China

Received 18 February 2025; Received in revised form 25 May 2025; Accepted 8 June 2025

Abstract

$\text{Sr}_{1.95}\text{Pr}_{0.05}\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SPFM) powder synthesized by combustion method was uniformly compounded with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) powder obtained by sol-gel route to prepare GDC-SPFM heterogeneous structure composite electrolytes with 10, 15, 20 and 30 wt.% of SPFM. The crystal structure, micro-morphology and electrochemical performance were investigated. Results show that GDC and SPFM have good chemical compatibility and the prepared GDC-SPFM composites have high ionic conductivity at low temperature. The GDC-SPFM composite electrolyte based on 30 wt.% SPFM achieved the best performance at 800 °C and the ionic conductivity of this sample reached 0.07 S/cm.

Keywords: solid oxide fuel cells, $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$, composite electrolyte, heterogeneous structure

1. Introduction

The world's economy, technology and industry have developed rapidly in the past decades. These developments have led to a huge consumption of energy, so people have to explore clean, economic and sustainable energy sources [1]. One example of such source is a solid oxide fuel cell (SOFC) that shows direct conversion of chemical energy into electrical with high efficiency, pollution-free operation and wide fuel adaptability [2,3]. In early studies on SOFCs, yttria-stabilized zirconia (YSZ) with about 8 mol% Y_2O_3 was primarily used as the electrolyte material. However, YSZ fuel cells need to operate at temperatures above 850 °C, which imposes strict requirements for the interconnects, manifolds and seals, necessitating the use of expensive ceramic materials and noble metal alloys [4]. Therefore, in order to use more affordable stainless steel materials, it is essential to lower the operating temperature of the cells [5].

Exploring electrolytes with high ionic conductivity is crucial for the development of low-temperature solid oxide fuel cells. Recently, many researchers have used samarium or gadolinium doped cerium oxide ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC)) to im-

prove its conductivity [6,7]. However, as a commonly used electrolyte materials, doped-cerium based materials have relatively low ionic conductivity at low temperatures, which cannot meet the requirements of low-temperature fuel cells. In recent years, doped-cerium based heterogeneous composite materials have attracted widespread attention due to their high ionic conductivity characteristics [8–10]. For example, semiconductor conductor composite materials, composed of semiconductors and ion conductors in a certain proportion, exhibit excellent ionic conductivity when used as electrolytes [11,12]. Composite electrolytes constructed from carbonates and doped cerium oxide also show much higher ionic conductivity at low temperatures than single-phase doped cerium oxide [13–15]. Therefore, it can be seen that the use of heterogeneous composites is an important method to achieve high ionic conductivity. In order to improve the conductivity of ionic conductors, heterogeneous composite electrolyte materials can be constructed from three aspects: i) electrode material - ion conductor composite, ii) low melting point molten salt-ion conductor composite and iii) electronically conductive low melting point oxide-ion conductor composite [16].

In view of the problem, that the ionic conductivity of traditional $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte material decreases significantly and the ohmic loss increases significantly with the decrease of operating temperature,

*Corresponding authors: tel: +86 551 62158442,
e-mail: wangm@hfu.edu.cn

in this study $\text{Sr}_{1.95}\text{Pr}_{0.05}\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ with high conductivity was introduced into $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ to form a heterostructured composite electrolyte material. Due to the interface effect between SPFM and GDC grains, the interface energy band reconstruction and charge transfer between the two-phase materials form an internal electric field, which promotes the ionic conduction at the interface of SPFM and GDC particles. Therefore, the electrical performance of this electrolyte material is greatly improved.

II. Experimental

2.1. Samples preparation

$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) powder was synthesized via sol-gel method. The stoichiometric amounts of cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99%, Sinopharm Chemical Reagent Co. Ltd), gadolinium nitrate ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%, Sinopharm Chemical Reagent Co. Ltd) and citric acid (99.5%) were dissolved in deionized water. The mixture solution was continuously stirred at 40 °C until a homogeneous sol formed. In this process, citric acid is used as a complexing agent in amount which is 1.5 times higher than the molar ratio of metal ions. The sol was heated and stirred for 2 h to obtain a transparent gel. The gel was heated at 120 °C for 24 h to obtain a dry gel and then calcined at 750 °C to get the final GDC powders.

$\text{Sr}_{1.95}\text{Pr}_{0.05}\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SPFM) powder was prepared by combustion method, which was described in details in our previous study [17]. In this process, $\text{Sr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co. Ltd) were used as raw materials and all these raw materials were analytical reagent grade.

For $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ - $\text{Sr}_{1.95}\text{Pr}_{0.05}\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (GDC-SPFM) composite electrolytes preparation, the SPFM powder and GDC powder were mixed in mass ratios of 10–90, 15–85, 20–80 and 30–70, respectively. The mixtures were ball-milled using anhydrous ethanol as the medium for 5 h to obtain uniform composite samples, which were named SPFM10, SPFM15, SPFM20 and SPFM30.

The composite powders were uniaxially pressed at 200 MPa into discs with the size of $\varnothing 11 \times 1$ mm and then sintered at 1250 °C for 5 h to obtain the dense electrolyte discs for electrochemical testing. The composite powder was also pressed into rectangular bar with the size of $35 \times 4 \times 4$ mm and then sintered at 1250 °C for thermal expansion coefficient (TEC) testing.

2.2. Characterization

The crystal structure of the composite electrolyte was analysed by X-ray diffraction (XRD, Smartlab, Rigaku) with scanning angle of 10°–80° under a scanning speed of 10°/min. The surface morphology of the sintered samples was characterized by scanning electron microscopy (SEM, SU-8010, Hitachi). The elec-

trochemical performance of the samples was measured by electrochemical impedance spectroscopy (EIS) using an electrochemical workstation (CHI604C, China) in air at temperatures ranging from 400 to 800 °C. The sintered discs were evenly coated with conductive glue on both sides and the measurements were conducted in a frequency range of 0.1 Hz–100 kHz with a temperature increment of 50 °C. The impedance spectra were analysed using the ZSimWin software to obtain the resistance which was used to calculate conductivity. The thermal expansion of the samples was measured using a dilatometer (DIL0809PC China) from room temperature to 1000 °C with the heating rate of 5 °C/min.

III. Results and discussion

3.1. Structural characterization

XRD patterns of the composite samples are shown in Fig. 1. The XRD diffraction pattern of each sample is composed of a fluorite phase corresponding to GDC (JCPDS No. 97-018-1224) and a perovskite phase corresponding to SPFM (JCPDS No. 04-004-6426). It can be clearly seen that except for the characteristic diffraction peaks of GDC and SPFM, no other diffraction peaks were detected. This indicates that GDC and SPFM have good chemical compatibility at up to the sintering temperature and there is no significant chemical interaction between GDC and SPFM phases. Therefore, the GDC-SPFM composite electrolyte can remain stable during the operation of the cell.

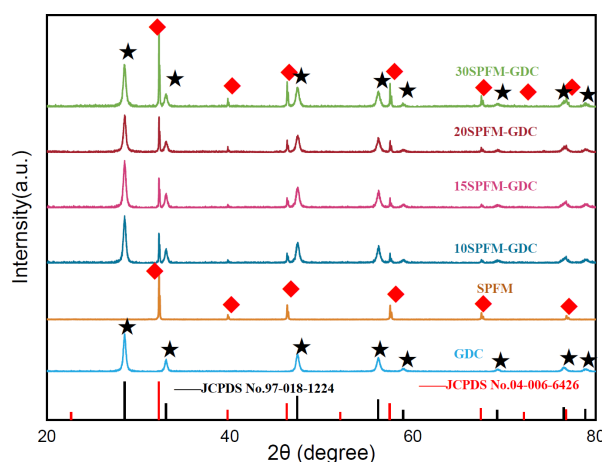


Figure 1. XRD spectra of GDC, SPFM and GDC-SPFM composites with different SPFM content

Scanning electron microscopy images of the sintered GDC-SPFM discs are shown in Fig. 2. The composite with a low SPFM content has a small amount of porosity, as shown in Fig. 2a. The appearance of few pores is due to the adsorption of gases by the particles with different sizes, the extrusion of the powder when pressed into disc and the escape of gases during the sintering process. The formation of pores results in shorter ion conduction pathways and a decrease in oxygen mobility throughout the lattice and thus could cause the decrease

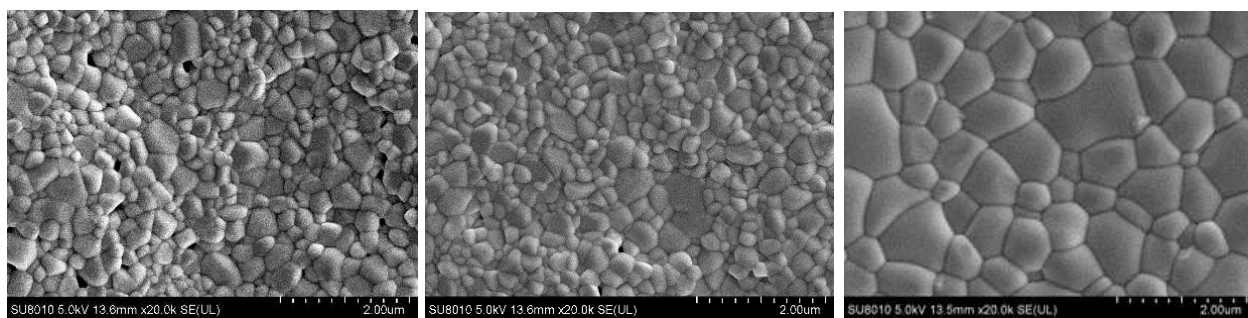


Figure 2. SEM images of: a) GDC-SPFM10, b) GDC-SPFM20 and c) GDC-SPFM30 samples

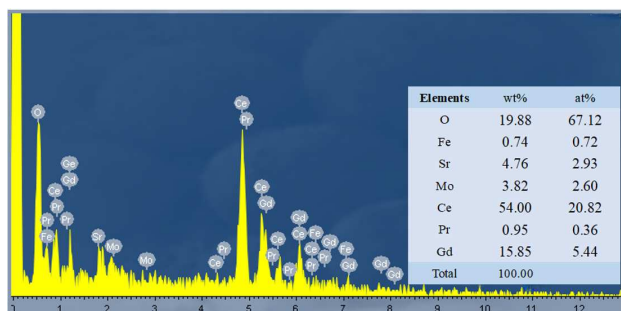


Figure 3. EDS spectrum of the GDC-SPFM30 sample

in conductivity. As the SPFM content in the composite increased, the sample became more dense. Thus, it can be seen that the GDC-SPFM30 electrolyte ceramic sample has a dense structure after sintering at 1250 °C, as shown in Fig. 2c. In this composite electrolyte material grains are uniformly distributed and closely connected, without obvious pores or cracks. This indicates that a hetero-interface was formed between the GDC and SPFM phases during the sintering process, which can effectively block electrons and support ionic conduction. It is previously reported that there is a built-in electric field formed at the interface, which substantially supports the transport of ions conduction [18].

Figure 3 shows the EDS analysis results and it can be concluded that the content of each component is consistent with the theoretical content in the chemical for-

mula, indicating the formation of GDC-SPFM composite phase structure. It can be seen from EDS mapping (Fig. 4) that the presence of each element in the GDC-SPFM composite is evident. In addition, the separate regions rich in Ce, Gd and Sr, Fe, Mo, Pr can be observed, corresponding to the GDC and SPFM phases, respectively. This microstructure indicates that a continuous heterojunction is formed at the contact between GDC and SPFM phase, which can increase the path of ionic conduction [3].

3.2. Electrical properties

The total conductivity (σ) of the GDC-SPFM composite electrolytes is determined from the EIS analysis carried in air. The Nyquist curves of the GDC-SPFM composite electrolyte samples tested at different temperatures are shown in Fig. 5. As it can be seen, the impedance spectra of each sample are composed of a semicircle and the radius of the semicircle gradually decreases as the content of SPFM increases. It is well known that a complete impedance spectrum should include three arcs corresponding to the grain resistance (R_g), grain boundary (R_{gb}) and polarization resistance (R_p). However, in this study electrochemical workstation CHI604C with a maximum frequency of only 100 kHz was used, resulting in incomplete impedance spectra. The spectra were fitted with ZSimpWin software to obtain the grain resistance (R_g) and grain bound-

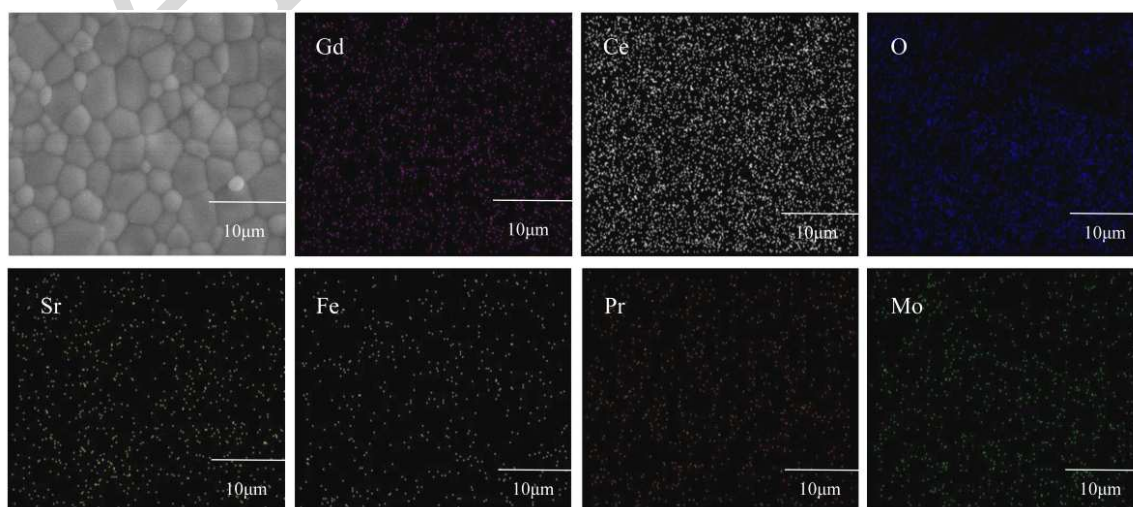


Figure 4. SEM-EDS mapping of the GDC-SPFM30 sample

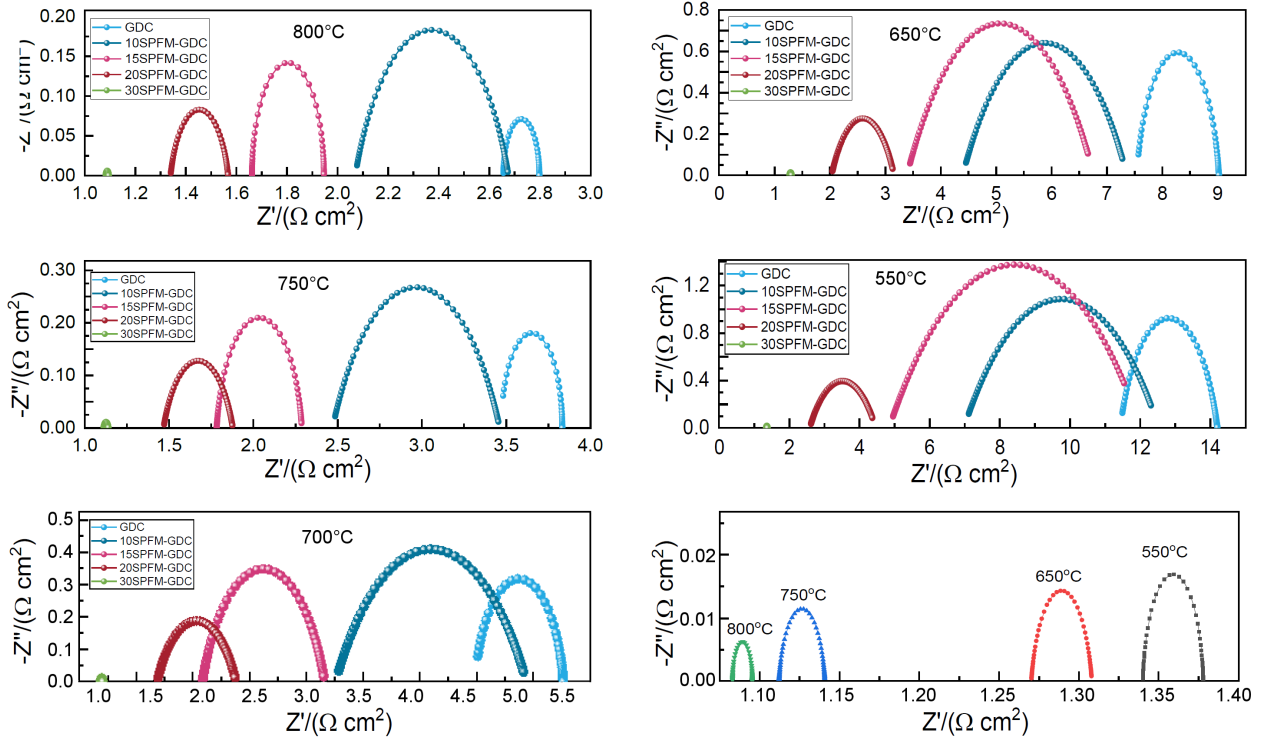


Figure 5. Electrochemical impedance spectra curves of the GDC-SPFM composite samples (a-e) and the GDC-SPFM30 sample tested at different temperatures (f)

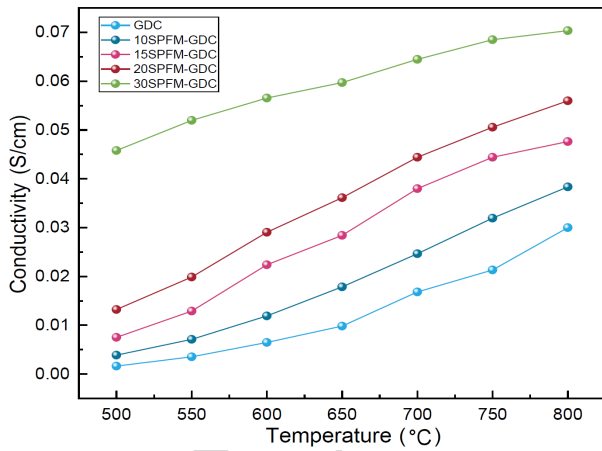


Figure 6. Electrical conductivity of GDC-SPFM composite samples as a function of temperature

ary resistance (R_{gb}). Thus, the total resistance (R_t) can be calculated using the equation [19,20]:

$$R_t = R_g + R_{gb} \quad (1)$$

The sample's total conductivity is then determined as follows:

$$\sigma = \frac{L}{R_t \cdot S} \quad (2)$$

where σ is the conductivity, L is the thickness of the electrolyte discs, S is the surface area of the electrolyte and R_t is the resistance value obtained by fitting at different temperatures.

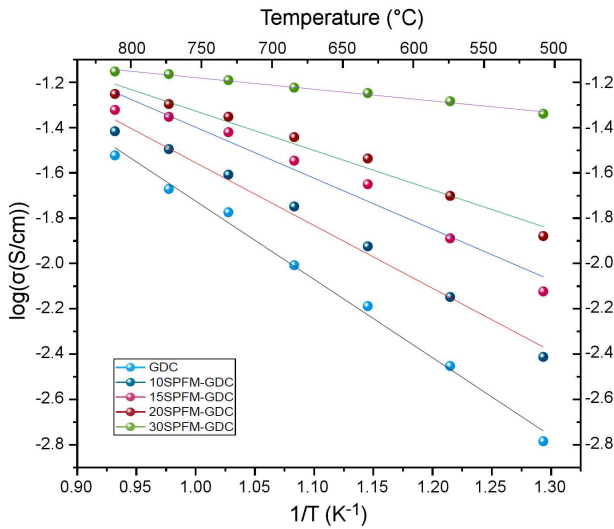
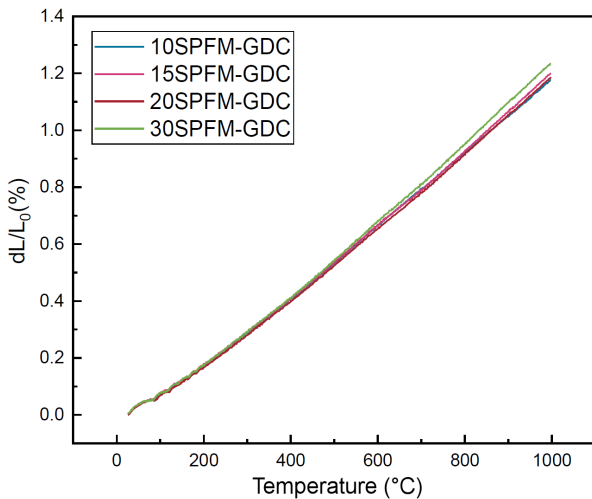
Figure 6 shows conductivities of the GDC-SPFM samples tested at different temperatures. It can be seen that the conductivity of the samples increases with the increase of the testing temperature; at the same time, the conductivity of the samples increases with the increase of SPFM content. It should be noted that a significant increase in ionic conductivity is observed for the SPFM30 composite, which may be attributed to the existence of interfacial conduction mechanism in the composite system [21]. Thus, the maximum ionic conductivity of 0.07 S/cm at 800 °C was obtained for the SPFM30 sample, which is significantly higher than for the pure GDC. This conductivity value is close to that of other CeO_2 -based composite electrolytes as shown in Table 1. The improved ionic conductivity is beneficial to the enhancement of cell performance. The GDC-based composite with appropriate amount of SPFM is promising material which can improve the ionic conductivity of the electrolyte and the related cell performance.

Figure 7 shows the Arrhenius curves of electrical conductivity of the GDC-SPFM composite electrolyte materials. The plots for all the samples are like a straight line and the activation energies are about 0.6 eV in the temperature range from 400 to 800 °C.

According to the temperature dilatation measurements, presented in Fig. 8, it can be seen that the relative displacement of the sample increases with the increase of temperature, showing a good linear relationship without obvious turning points. The average thermal expansion coefficient of the sample is about $11.6 \times 10^{-6} \text{ K}^{-1}$, which matches well with the thermal expansion coefficient

Table 1. Electrical conductivity of CeO₂-based composite electrolytes

Samples	Conductivity [S/cm]	Temperature [°C]	Reference
Ce _{0.8} Sm _{0.2} O _{1.9} (80)-Na ₂ CO ₃ (20)	1.73×10^{-3}	600	[22]
Ce _{0.8} Sm _{0.1} Bi _{0.1} O _{2-δ} -BaCe _{0.8} Sm _{0.1} Bi _{0.1} O _{3-δ}	3.43×10^{-3}	400	[23]
BaO(10)-Ce _{0.8} Gd _{0.2} O _{1.9}	0.036	800	[24]
La _{0.7} Sr _{0.3} Cr _{0.5} Fe _{0.5} O _{3-δ} -CeO ₂	0.093	550	[12]
Ce _{0.8} Gd _{0.2} O _{1.9} -Sr _{1.95} Pr _{0.05} Fe _{1.5} Mo _{0.5} O _{6-δ}	0.07	800	Present work

**Figure 7.** The Arrhenius plots of the GDC-SPFM composite samples' conductivity**Figure 8.** Thermal expansion curves of GDC-SPFM composite samples in air

cient of the commonly used electrode material Ni-YSZ ($11\text{--}15 \times 10^{-6} \text{ K}^{-1}$ [25]). This should ensure the long-term high-temperature stability and the performance of the cell.

IV. Conclusions

In this paper, Sr_{1.95}Pr_{0.05}Fe_{1.5}Mo_{0.5}O_{6-δ} (SPFM) powder synthesized by a combustion method was mixed with Ce_{0.8}Gd_{0.2}O_{1.9} (GDC) powder obtained by sol-

gel route to prepare composite electrolyte materials having high ionic conductivity. The crystal structure, micro-morphology and electrochemical performance of the composites with different GDC/SPFM weight ratios were investigated. GDC and SPFM have good chemical compatibility at the working temperature and the GDC-SPFM composite electrolyte can remain stable during the operation of the cell. The introduction of an appropriate amount of SPFM into GDC can improve the ionic conductivity of the electrolyte and reduce the polarization resistance of the cell. When 30 wt.% of SPFM was incorporated into GDC, the ionic conductivity reached 0.07 S/cm at 800 °C.

Acknowledgement: This work was supported by the Natural Science Foundation of Education Department of Anhui Province (Grant No. 2024AH051532).

References

1. M. Singh, D. Zappa, E. Comini, "Solid oxide fuel cell: Decade of progress, future perspectives and challenges", *Int. J. Hydrogen Energy*, **46** [54] (2021) 27643–27674.
2. B.C. Steele, A. Heinzel, "Materials for fuel-cell technologies", *Nature*, **414** [6861] (2001) 345–352.
3. Y. Xing, S. Rauf, H. Cai, Z. Tayyab, B. Wang, C. Xia, Y. Wu, B. Zhu, "Designing p-n heterostructure of LSCF-CeO₂ material for ionic transportation as an electrolyte for semiconductor ion membrane fuel cell", *Int. J. Hydrogen Energy*, **50** (2024) 428–440.
4. J. Kang, W. Feng, D. Guo, K. Chen, S. Gao, J. Jiang, C. Lu, B. Niu, B. Wang, "Performance optimization of Ca and Y co-doped CeO₂-based electrolyte for intermediate-temperature solid oxide fuel cells", *J. Alloys Compd.*, **913** (2022) 165317.
5. H. Ding, T. Wu, S. Zhao, H. Sun, J. Li, X. Guo, P. Wang, "Grain boundary conduction behaviors of ultra-fine grained CeO₂/BaCeO₃ based electrolytes", *Ceram. Int.*, **48** (2022) 25314–25321.
6. J. Li, M. Yousaf, M. Akbar, N. Asma, E. Hu, M.A.K. Yousaf Shah, A.S. Qadeer, M. Naveed, Y. Lu, "High-performing and stable semiconductor yttrium-doped gadolinium electrolyte for low-temperature solid oxide fuel cells: Electronic supplementary information (ESI) available", *Chem. Commun.*, **59** (2023) 6223–6226.
7. S.Q. Wang, J.H. Geng, X.X. Zhao, Y.Z. Xing, "Elevated sintering capability and electrical conductivity of Fe₂O₃-doped Ce_{0.8}Sm_{0.1}Nd_{0.1}O_{2-δ} as an electrolyte in IT-SOFCs", *Mater. Chem. Phys.*, **309** (2023) 128345.
8. X.Y. Ping, B. Meng, W.K. Liang, Q. Zheng, C. Li, "Electrical conductivity of Y₂O₃-doped CeO₂ based composite ceramics by spark plasma sintering: The effects of a second phase of CeAlO₃", *Solid State Ionics*, **365** (2021) 115653.

9. M. Zhang, L. Yao, Y. Xing, J. Cheng, T. Yang, J. Liu, W. Pan, "Aligned nanofibers incorporated composite solid electrolyte for high-sensitivity oxygen sensing at medium temperatures", *J. Mater. Sci. Technol.*, **181** (2024) 189–197.
10. Z.-Y. Chen, X. Zhang, Y.-N. Liang, Z.U.D. Babar, J.T. Gao, W. Li, S.-L. Zhang, C.-J. Li, C.-X. Li, "Breakthrough in atmospheric plasma spraying of high-density composite electrolytes: Deposition behavior and performance of plasma-sprayed GDC-LSGM on porous metal-supported solid oxide fuel cells", *Int. J. Hydrogen Energy*, **72** (2024) 614–625.
11. N. Mushtaq, Y. Lu, C. Xia, W. Dong, B. Wang, M.A.K. Yousaf Shah, S. Rauf, M. Akbar, E. Hu, R. Raza, M. Imran Asghar, P.D. Lund, B. Zhu, "Promoted electro-catalytic activity and ionic transport simultaneously in dual functional $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Sb}_{0.2}\text{O}_{3-\delta}\text{-Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ heterostructure", *Appl. Catal. B Environ.*, **298** (2021) 120503.
12. Y. Meng, M. Akbar, J. Gao, M. Singh, T.-W. Chiu, B. Wang, C. Xia, L. Fan, "Superionic conduction of self-assembled heterostructural LSCrF-CeO_2 electrolyte for solid oxide fuel cell at 375–550 °C", *Appl. Surface Sci.*, **645** (2024) 158832.
13. M. Anwar, S.A. Ali A. Mughtar, M.R. Somalu, "Synthesis and characterization of M-doped ceria-ternary carbonate composite electrolytes (M = erbium, lanthanum and strontium) for low-temperature solid oxide fuel cells", *J. Alloys Compd.*, **775** (2019) 571–580.
14. Y. Jing, P. Lund, M. Imran Asghar, F. Li, B. Zhu, B. Wang, X. Zhou, C. Chen, L. Fan, "Non-doped CeO_2 -carbonate nanocomposite electrolyte for low temperature solid oxide fuel cells", *Ceram. Int.*, **46** (2020) 29290–29296.
15. S. Casadio, M.C. Díaz Lacharme, A. Donazzi, A. Gondolini, "Role of carbonate amount and synthesis procedure in the conductivity of $\text{SDC-Na}_2\text{CO}_3$ composite electrolytes for solid oxide cells applications", *Int. J. Hydrogen Energy*, **58** (2024) 1324–1331.
16. O. Ettalibi, H. Boumeriame, O. Achak, T. Chafik, "Advanced electrolyte materials based on natural minerals for low-temperature solid oxide fuel cells applications", *Fuel*, **377** (2024) 132848.
17. P. Wang, W. Qian, H. Liang, X. Zhu, J. Cheng, "Preparation and electrical properties of cathode material based on zinc-doped $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ for solid oxide fuel cells", *J. Mater. Sci. Mater. Electron.*, **33** (2022) 21660–21665.
18. Y. Xing, Y. Wu, L. Li, Q. Shi, J. Shi, S. Yun, M. Akbar, B. Wang, J.-S. Kim, B. Zhu, "Proton shuttles in $\text{CeO}_2/\text{CeO}_{2-\delta}$ core-shell structure", *ACS Energy Lett.*, **4** [11] (2019) 2601–2607.
19. S.-Q. Wang, J.-H. Geng, X.-X. Zhao, Y.-Z. Xing, "Elevated sintering capability and electrical conductivity of Fe_2O_3 -doped $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Nd}_{0.1}\text{O}_{2-\delta}$ as an electrolyte in IT-SOFCs", *Mater. Chem. Phys.*, **309** (2023) 128345.
20. Z. Song, L. Yi, C. Li, S. Yang, H. Jiang, "Synthesis & characterization of Ti and Fe co-doped Ta_2O_5 based solid electrolytes for SOFC", *Solid State Ionics*, **312** (2017) 106–111.
21. J. Garcia-Barriocanal, A. Rivera-Calzada, M. Varela, Z. Sefrioui, E. Iborra, C. Leon, S.J. Pennycook, J. Santamaria, "Colossal ionic conductivity at interfaces of epitaxial $\text{ZrO}_2\text{:Y}_2\text{O}_3/\text{SrTiO}_3$ heterostructures", *Science*, **321** (2008) 676–680.
22. S. Casadio, M.C. Díaz Lacharme, A. Donazzi, A. Gondolini, "Role of carbonate amount and synthesis procedure in the conductivity of $\text{SDC-Na}_2\text{CO}_3$ composite electrolytes for solid oxide cells applications", *Int. J. Hydrogen Energy*, **58** (2024) 1324–1331.
23. H. Ding, T. Wu, S. Zhao, H. Sun, J. Li, X. Guo, P. Wang, "Grain boundary conduction behaviors of ultra-fine grained $\text{CeO}_2/\text{BaCeO}_3$ based electrolytes", *Ceram. Int.*, **48** (2022) 25314–25321.
24. A. Venkatasubramanian, P. Gopalan, T.R.S. Prasanna, "Synthesis and characterization of electrolytes based on $\text{BaO-CeO}_2\text{-GdO}_{1.5}$ system for Intermediate Temperature Solid Oxide Fuel Cells", *Int. J. Hydrogen Energy*, **35** (2010) 4597–4605.
25. J.W. Kim, K. Bae, H.J. Kim, J.-W. Son, N. Kim, S. Stenfelt, F.B. Prinz, J.H. Shim, "Three-dimensional thermal stress analysis of the re-oxidized Ni-YSZ anode functional layer in solid oxide fuel cells", *J. Alloys Compd.*, **752** (2018) 148–154.