Solid-State Oxide Fuel Cells

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Abstract. Solid-State Oxide Fuel Cell (SOFC) is an efficient energy conversion device that directly covers fuel's chemical energy into electricity. With a high energy conversion efficiency, it is not limited by the Carnot cycle. Fuel adaptability is wide, clean and pollution-free, all solid structure, do not use precious metal catalyst and other advantages. It is of great significance to achieve the goal of carbon peak and carbon neutrality target in China. However, there are some problems, mainly including: conductivity, relatively low conductivity of medium-temperature solid oxide fuel cells, which limits the performance of batteries, sintering, cost, and stability. To improve the conductivity, researchers are exploring different material combinations and doping strategies to optimize the crystal structure and chemical composition of the electrolyte. Finally, the importance of the electrolyte, the role of the oxygen vacancy, the influence of the doping elements, and the balance of the performance and the cost are drawn.

Keywords: New energy, SOFC, electrolyte, doping, electrical conductivity.

1. Introduction

As an efficient clean energy conversion technology, the performance of solid oxide fuel cell (SOFC) largely depends on the conductivity of electrolyte materials. ZrO_2-Based electrolytes are valued for their good chemical stability and mechanical strength, but there are challenges with low ionic conductivity, poor structural stability and high sintering temperature. This study focuses on the electrical properties of the ZrO_2-based SOFC electrolyte doped with different elements, aiming to improve the oxygen vacancy concentration, structural stability and sintering performance of the electrolyte by using the doping modification. The research progress of unary, binary and multivariate doped ZrO_2 electrolyte is systematically analyzed, discusses the influence of different doped elements and their combinations on the electrolyte performance, and summarizes the relationship between doped metal ions and ZrO_2 electrolyte performance. We study how to optimize the performance of ZrO_2-based electrolyte by element doping, and solve the problems such as insufficient conductivity, structural stability and sintering performance encountered in practical application. This study has important scientific significance and practical application value in promoting the development of SOFC technology, improving energy efficiency, reducing environmental impact and promoting sustainable development, and has a guiding role in realizing the goal of SOFC working at lower temperature and having higher ionic conductivity. The solid oxide fuel cell industry has experienced a series of key technological breakthroughs and advances. These technological advances include improvements of electrolyte materials, optimization of electrode materials, and improvements of system integration technology [1].

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For example, researchers are exploring different material combinations and doping strategies to optimize the crystal structure and chemical composition of electrolytes and improve the conductivity. According to the latest market analysis report, China's solid oxide fuel cell market has shown significant growth in recent years. With the increasing global attention and investment in clean energy technology, as well as the increasing awareness of environmental protection from all walks of life, solid oxide fuel cell, as an efficient and environmentally friendly energy conversion technology, has been gradually promoted in the energy field, and the market size continues to expand. SOFC electrolyte materials face a variety of challenges in reducing the working temperature to improve battery performance and stability; first, high temperature dependence. currently widely used electrolyte materials such as yttrium-stable zirconia (YSZ) need to have a high operating temperature (900-1000°C) to have a high ionic conductivity. Second, electrical conductivity problem. Even at high temperature, the conductivity of some electrolyte materials is still not enough to meet the demand of high efficiency energy conversion. Third, stability issues. Electrolyte materials must be resistant to chemical, electrochemical and thermal stresses when working in a medium-temperature environment. These stresses may cause changes in the properties of the electrolyte material that can affect the performance of the fuel cell. Therefore, improving the stability of electrolyte materials is the key to the development of mesophilic solid oxide fuel cells.

Oxygen vacancies can be created by doping low-valent metal ions, which are the basis of oxygen ion conduction. The oxygen ions migrate from the cathode to the anode. Doping can enhance the structural stability of electrolyte materials. For example, when rare earth metal ions are doped with Zr, because their ionic radius is close to Zr, they do not cause too large lattice distortion, thus maintaining good structural stability. By doping, the sintering temperature of electrolyte materials can be reduced, thus reducing the manufacturing cost and improving the production efficiency. For example, binary doping can improve the sintering performance, reduce the sintering temperature and improve the sintering speed.

The electrolyte improvement can improve the energy conversion efficiency of the SOFC. By developing electrolytes with high ionic conductivity at low temperatures, the operating temperature of SOFC can be reduced and the energy conversion efficiency can be improved. The electrolyte improvements can also help to reduce the operating costs of the SOFC. Traditional SOFC need to operate at higher temperatures, which leads to high heating and energy consumption to maintain temperatures. By reducing operating temperatures, energy consumption can be reduced, thus reducing operating costs. Improving the electrolyte can prolong the service life of the SOFC. Low-temperature working conditions can reduce the thermal stress and chemical erosion of the materials, thus extending the service life of the battery. The improvement of electrolyte meets the goal of environmental protection and sustainable development. By reducing energy consumption and extending equipment life, SOFC can reduce greenhouse gas emissions and other pollutants, helping to combat climate change and environmental protection. The improvement of electrolyte drives the innovation of SOFC technology. The research and development and application of new electrolyte materials have promoted the birth of new technologies, which can be applied to other fields to promote the technological progress of the entire new energy industry chain.

2. Specific cases of the material doping

Take ZrO_2-based solid oxide fuel cell as an example: it can be roughly divided into three kinds: single doping, binary doping and multiple doping. Unary doping can be divided into rare earth metal doping (commonly used rare earth elements include Y (yttrium), Gd (gadolinium), Yb (ytterbium), Dy (dysprosium), Sc (scandium), Ce (cerium), etc.) and alkaline earth metal doping (mainly using Mg (magnesium) and Ca (calcium)). There are two main kinds of binary doping: Y + M doped ZrO_2 and Sc + M doped ZrO_2. Multivariate doping can be divided into three types: Y, Yb, Sc, and Dy co-doped ZrO_2. Ca, Fe, La, Sr, Mg and Y and Ce codoped zirconia. TiO_2-SrO co-doped ZrO_2.

2.1. Parameter summary

Table 1. Battery performance in various kinds doping

	name	electroconductibility	working temperature	Doping percentage (mole)
unitary	The Yb-doped ZrO_2 electrolyte	0.12 S/cm[2]	900℃	8%
	The Gd-doped ZrO_2 electrolyte	0.06837 S/cm[3]	900℃	8%[4]
duality	Nd mix	0.0052 S/cm[5]	800℃	30%
polybasic	Y, Yb, Sc, and Dy were co-doped	0.18 S/cm[6]	1000℃	8%~8.6%
	TiO_2-SrO co-doping	0.14 S/cm[7]	1000℃	7.6%

As shown in Table 1, working temperature and doping percentage of different types of oxide electrolytes are listed in the table. Among these, Yb-doped ZrO_2 electrolyte has the highest conductivity (0.12S / cm), operating temperature of 900°C and doping percentage of 8%. The Gd-doped ZrO_2 electrolyte has a low conductivity (0.06837S / cm), and the working temperature and doping percentage are the same as the Yb-doped ZrO_2. The Nd mixture has the lowest conductivity (0.0052S / cm), an operating temperature of 800°C and a doping percentage of 30%. The Y, Yb, Sc and Dy have a high conductivity (0.18S / cm), an operating temperature of 1000°C, and a doping percentage between 8% and 8.6%. The TiO_2-SrO co-doped electrolyte has a moderate conductivity (0.14S / cm), an operating temperature of 1000°C and a doping percentage of 7.6%.

2.2. Analysis of advantages and disadvantages

There are some advantages of rare earth metal doping (unary doping). First, structural stability. When rare earth metal ions (such as Y, Gd, Yb, Dy, Sc, Ce) are doped with ZrO_2, because the ionic radius is similar to Zr, it will not cause large lattice distortion and maintain good structural stability. Second, high conductivity. Some rare earth metal ions doped (such as Sc) can significantly improve the oxygen ion conductivity. Disadvantages, for example, the price of Sc is high, which may affect its cost performance in commercial applications. Besides, undoing may have low conductivity and density at low temperatures.

Advantages of alkaline soil metal doping (one yuan doping): increasing oxygen vacancy: alkaline soil metal ions (such as Mg, Ca) doping can create more oxygen vacancies, helping to improve ionic conductivity. Disadvantages: Lattice distortion. Except for Mg and Ca, other alkaline soil metal ions differ greatly from Zr ion radius, which may cause large lattice distortion and reduce structural stability. Conductivity problem: The conductivity of Ca doping is usually lower than that of Y doping, because the lattice distortion caused by Ca is larger, which reduces the space of oxygen vacancy migration [8].

Binary doping: Advantages: reducing the sintering temperature: Through binary doping (such as Y + M or Sc + M), a higher ionic conductivity can be obtained at a lower temperature [9]. Improving the conductivity: some binary doping combinations (such as the co-doping of Y and alkaline soil metals) can further improve the oxygen ion conductivity of the electrolyte.

Disadvantages: complex influencing factors: binary doping may involve more complex interactions, and more research is needed to optimize the combination and proportion of doping elements.

Multiple doping: advantages: improving the mechanical properties and thermal stability: multiple doping can improve the sintering performance and density of the electrolyte, to improve the mechanical properties and thermal stability. Disadvantages: the conductivity may be reduced. Compared with unary and binary doping, the multivariate doped electrolyte usually has a low oxygen ion conductivity. Less research: multivariate doping is relatively few, and the understanding of the mechanism of its performance is not sufficient.

Advantages and disadvantages of specific element doping: For Yb doping, it can improve the ionic conductivity, but the cost may be high. Gd doping: the electrolyte synthesized by solution combustion method has a high oxygen ion conductivity. Ca doping: possible reduced conductivity, but higher oxygen ion conductivity and lower activation energy at high temperatures. Al and Bi as ners: can improve density and mechanical properties, but may reduce conductivity.

2.3. Future research directions

Based on the above advantages and disadvantages analysis, the following research directions can be proposed: Optimization of unary doping: Synthesis of nano-doped zirconia powder with narrower particle size distribution range and higher sphericity by improving the process. Study the influence law and mechanism of unitary doping to improve the induced density and ionic conductivity of the electrolyte. Development of binary doping:. while reducing the cost of ScSZ, doping alkaline soil or transition metal on the basis of ScSZ to explore new binary doping combinations to improve the electrolyte performance. To study the potential of Y and alkaline soil metal co-doping to improve the oxygen ion conductivity. Research on the mechanism of multiple doping: systematically study the influence of multiple dopant ions on the electrical performance, mechanical properties and thermal stability of the electrolyte. Explore the combination of Ce, Al or transition metal ions doping on the basis of Mg and Y ion doping to achieve ideal electrolyte properties. Comprehensive improvement of the performance of electrolyte materials: nano-powder materials with high oxygen vacancy concentration and narrow particle size distribution range are prepared, and the electrolyte is prepared into compact thin films. Development of new electrolyte materials: Explore new electrolyte materials, such as the co-doping strategies of CeO_2-based electrolytes, and new composite electrolyte systems. Improvement of sintering technology: to improve the density of electrolyte and crystal phase stability. Interface research between electrolyte and electrode: study the chemical matching between electrolyte and electrode material, optimize the interface performance, and improve the overall performance of the battery. Study on long-term stability and aging mechanism: Study the long-term stability and aging mechanism of doped electrolyte to improve the service life of SOFC. Computational simulation and theoretical design: using first-principle calculation and calculation simulation to predict and optimize the doping effect. Environmental and cost-benefit analysis: considering environmental impact and cost-effectiveness, seeking environmentally friendly and cost-effective doping strategies.

3. Results

The importance of electrolytes: Electrolyte is the core component of SOFC, and its performance directly affects the overall performance of the battery.

The role of oxygen vacancies: Oxygen vacancies in the ZrO_2-based electrolyte are the basis of oxygen ion conduction, which can be created by doping low-valent metal ions.

Dant classification: According to the number of doped elements, it is divided into three categories: unary, binary and multivariate doped ZrO_2 electrolyte.

Rare earth metal doping: rare earth metal ions (such as Y, Gd, Yb, Dy, Sc, Ce) doping ZrO_2 can improve the ionic conductivity of the electrolyte, and because their ionic radius is similar to that of Zr, the structure stability is good after doping.

Improvement in ionic conductivity: Sc-doped ZrO_2 (ScSZ) shows a higher ionic conductivity than YSZ at low temperatures.

Alkaline soil metal doping: alkaline soil metal ion doping ZrO_2 can create more oxygen vacancies, but may lead to poor structural stability, Mg and Ca doping is the main research direction.

Binary doping: Adding the binary doping of a second metal ion M on the basis of Y or Sc doping can reduce the sintering temperature and improve the ionic conductivity.

Multivariate doping: Although multivariate doping can improve the sintering performance and induced density of the electrolyte, the oxygen ion conductivity is usually lower than that of monary and binary doping.

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The relationship between electrolyte performance and doped metal ions: The study summarizes the relationship between the performance of ZrO_2 electrolyte and doped metal ions, as well as the advantages and disadvantages of different metal ions doping.

Future development trend: In order to realize SOFC working at low temperature and have high ionic conductivity, it is necessary to prepare nano-powder materials with high oxygen vacancy concentration and narrow particle size distribution range, and prepare electrolyte into dense film. Research focus: The influence law and mechanism of unary doping are relatively clear, and the future research will focus on improving the process and synthesize nanometer doped zirconia powder with narrower particle size distribution range and higher sphericity. The potential of binary doping: alkaline soil or transition metal on the basis of ScSZ, and Mg and Zn ions or the appropriate amount of Al ions have great development potential. These findings provide an important theoretical and experimental basis for further optimizing the properties of SOFC electrolyte materials and indicate the way for the commercial development of SOFC.

The importance of this study lies in its deep exploration of the electrical properties of solid oxide fuel cell (SOFC) electrolyte materials, especially for the progress of ZrO_2-based electrolyte doped with different elements. As an efficient clean energy technology, the performance of SOFC largely depends on the ionic conductivity, structural stability and sintering properties of electrolyte materials. ZrO_2-based electrolytes have been widely studied and applied for their good chemical stability and mechanical strength, but there are challenges of low ionic conductivity, poor structural stability and high sintering temperature. The different elements doped with ZrO_2-based electrolyte, including monary, binary and multivariate doping, can help solve the above problems, improve the performance of the electrolyte, and thus improve the overall performance and reliability of SOFC. Specifically, the importance of this study is reflected in several aspects:

Technological innovation: Through the doping of different elements, the lattice structure of ZrO_2-based electrolyte can be adjusted to produce more oxygen vacancies, thus improving the conductivity of oxygen ions.

Performance optimization: The study reveals the influence of doping of different metal ions on ZrO_2 electrolyte performance, and provides theoretical basis and experimental data for optimizing electrolyte materials.

Cost effectiveness: By exploring more cost-effective doping elements, such as Y (yttrium) doped ZrO_2, the cost can be reduced and the commercial application of SOFC technology can be promoted. Environment-friendly: As a clean energy technology, the development of SOFC helps to reduce the dependence on fossil fuels and reduce greenhouse gas emissions, which is of great significance to environmental protection [10].

Energy security: Improve the performance and reliability of SOFC, help to improve energy conversion efficiency, and enhance the security and stability of energy supply.

Academic contribution: This research provides new insights and research directions for the research field of solid electrolyte materials, and promotes the development of related scientific fields. Technology application: The research results can help promote the application of SOFC technology in power production, combined heat and power generation, transportation and other fields, and broaden its application scope.

In conclusion, this research is of great scientific significance and practical application value for promoting the development of SOFC technology, improving energy efficiency, reducing environmental impact, and promoting sustainable development.

4. Conclusion

Optimization of onary doping: onary doping has been systematic, especially rare earth element doping. Nanodoped zirconia powder with narrower particle size distribution and higher sphericity can be prepared by improving the synthesis process to improve the induced density and ionic conductivity of the electrolyte.

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Cost-effectiveness of Sc doping: Although Sc doping can significantly improve the oxygen ion conductivity, its cost is high. Future studies could explore ways to reduce costs or develop doped elements with similar effects but lower cost.

Co-doping of alkali soil metal ions: under the premise of ensuring structural stability, an appropriate amount of co-doped alkali soil metal ions (such as Mg and Ca) can improve the conductivity of oxygen ions. Studies should further explore the optimal doping ratio and process conditions.

Intensive study of binary doping: binary doping shows great potential in improving electrolyte performance. In particular, the codoping of Y and Sc, can significantly improve the conductivity. Future studies should focus on optimizing the combination and proportion of doped elements, as well as exploring new binary doping systems.

System study of multivariate doping: Although multivariate doping can improve sintering performance and density, its conductivity is usually lower than that of monary and binary doping. The mechanism of the influence of different element combinations on electrolyte properties is needed systematically studied to discover multivariate doping systems that can improve the conductivity.

Improvement of the preparation process: It is pointed out that the intrinsic oxygen ion conductivity of YSZ can be improved by adjusting the doping amount and changing the preparation process. Future work should include optimizing the molding and sintering process to obtain high-density electrolytes.

Electrolyte film technology: In order to achieve SOFC operating at lower temperatures and having high ionic conductivity, research should focus on the development of dense electrolyte film technology.

References

[1] Peng Suping. Status and Prospect of Fuel cells in China (English) [J]. Engineering, 2023,21 (2): 20-23.

[2] BorikM A,Zaharov D M ,Kulebyakin A V, et al.Single crys-talsolid state electrolytes based on yttria,ytterbia and gado- linia doped zirconia[J] . Materials Chemistry and Physics, 2022,277:125499.

[3] Madhusudhana H C,ShobhadeviSN, Nagabhushana B M , etal. Structural characterization and dielectric studies of Gd doped ZrO2 nano crystals synthesized by solution combustion method[J] . Materials Today: Proceedings, 2018, 5 (10) : 21195-21204.

[4] Lu Zhengang, Guo Ruisong, Yao Fei, et al. Effect of composite doping on sintering properties and electrical properties of YSZ electrolyte materials [J]. Rare Metal Materials and Engineering, 2005,34 (12): 1961-1964.

[5] Jin Y J,Liu ZG,Cao G,etal.Order-disordertransition and e- lectricalperformance of (Nd1-Y) $2Zr_2O_7$ solid solutions[J] . JournalofAlloys and Compounds,2019,811:151974.

[6] Cheng Huicong, Wang Yalei, Li Axin, et al. Dy 2 O 3-ZrO_2 nano-powder synthesis by parallel flow co-precipitation [J]. Material Engineering, 2022,50 (6): 97-106.

[7] Liu Xiaoying, Huang Xiaowei, Wu Xingxing, et al. Multiple 8 YSZ, electrolyte performance research [J]. Material Guide, 2010,24 (S1): 284-287.

[8] Buc'koM M. Ionic conductivity of CaO-Y_2O_3-ZrO_2 materials with constantoxygen vacancy concentration[J] .Journalofthe European Ceramic Society,2004,24(6) :1305-1308.

[9] Yeh T H ,ChiangCM ,LoW C,etal.Co-doping effectofdiva- lent (Mg^{2+}, Ca^{2+}, Sr^{2+}) and trivalent (Y^{3+}) cations with different ionic radii on ionic conductivity of zirconia electro- lytes[J] . Journal of the Chinese Society of Mechanical Engi- neers,Transactions of the Chinese Institute of Engineers-Se- ries C,2009,30(2) :151-157.

[10] WangY P,Gao JT,Chen W ,etal.DevelopmentofScSZ elec- trolyte by very Low pressure plasma spraying for high-per- formance metal-supported SOFCs[J] . Journal of Thermal Spray Technology,2019,29(1-2) :223-231.