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A Systematic Review of SOFC Electrolyte Materials: Classification, Ionic Conduction Mechanism and Performance Regulation

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Abstract. Driven by the global carbon neutrality goal and the traditional energy crisis, solid oxide fuel cells (SOFC) have attracted much attention as an efficient and clean energy conversion technology. The performance of the electrolyte is the core factor determining its efficiency and stability. This article systematically reviews the research progress of four types of electrolytes in solid oxide fuel cells (SOFC): oxide ceramics, sulfides, polymers, and composite electrolytes. It focuses on analysing the crystal structure, ion conduction mechanism, and performance control strategies of each type of electrolyte. It also discusses the influence of defect control and interface engineering on the performance of the electrolyte. At the same time, it clarifies the key role of lattice matching and thermal expansion coefficient compatibility in improving interface stability. The research shows that strategies such as doping modification and composite design can effectively optimize the ion conduction efficiency and stability of the electrolyte, providing technical support for the mid-temperature and long-life development of SOFC and offering references for subsequent research in this field.

1 Introduction

In recent years, under the dual impetus of the global carbon neutrality goal and the crisis of traditional energy sources, the development of clean and sustainable energy conversion technologies has become crucial and has become a key research direction in the energy field. The combustion of traditional fossil energy not only leads to the massive emission of greenhouse gases such as CO_2 and SO_2, causing climate change and environmental problems, but also exacerbates global energy security risks due to its inherent resource scarcity. However, renewable energy sources such as wind energy and solar energy have inherent defects such as intermittency and volatility, and there is an urgent need for efficient and stable energy conversion technologies to achieve a continuous energy supply and efficient utilization. SOFC as a clean power generation technology that directly converts fuel chemical energy into electrical energy, has outstanding advantages such as high energy conversion efficiency, zero pollution emissions, and wide fuel adaptability, and has become a key breakthrough to solve the energy crisis and environmental problems [1].

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As the core component of SOFC, the performance of the electrolyte directly determines the energy conversion efficiency and long-term stability of the battery. The related research in this field has become a core focus. In recent years, scholars both at home and abroad have conducted extensive research on the mechanism of electrolyte systems, achieving a series of landmark achievements. In the field of basic mechanism research, researchers have revealed the intrinsic laws of ion transport and defect behaviour in electrolytes at the atomic scale, providing theoretical support for the targeted design of high-performance electrolytes. In the field of material modification, through strategies such as hetero-interface construction and element doping, the ion conductivity performance of traditional electrolytes in specific temperature ranges has been effectively improved, laying the material foundation for the development of SOFC at medium and low temperatures. Significant breakthroughs have also been achieved in the development of new electrolyte material systems. For example, perovskite-type solid solution electrolytes have successfully enhanced proton conductivity efficiency and chemical stability through component optimization. In the polymer electrolyte field, functional modification and microstructure regulation have effectively solved the problems of mechanical performance degradation and conductivity efficiency decline under high temperatures, promoting the development process of flexible SOFC. Moreover, the composite electrolyte system, leveraging the synergistic effect of multiple phases, integrates the performance advantages of different materials, demonstrating unique advantages in improving ion conductivity efficiency, mechanical stability, and environmental tolerance, providing a new path to break through the performance bottleneck of single-component electrolytes. These research results collectively promote the gradual advancement of SOFC technology towards practical and industrialization directions. However, at present, the core mechanisms and optimization strategies of different electrolyte systems still lack systematic integration, and it is urgently necessary to comprehensively review to clarify future research directions.

Although significant progress has been made in the field of SOFC electrolytes, there is still a lack of comprehensive and systematic reviews and summaries on the performance regulation mechanisms of different electrolyte systems and the interface synergy effects, which hinders the cross-system innovation and industrialization promotion of the technology. Based on this, this paper focuses on the application of SOFC technology and the research progress of core technologies, including the ionic conduction mechanism of solid electrolytes in SOFC and the principles of interface stability between electrodes and electrolytes. The research objective of this paper is to provide technical references for future research in the SOFC field, help the SOFC technology achieve the core development goals of medium-temperature operation, long lifespan, and low cost, and accelerate its industrialization application process in fields such as combined heat and power supply.

2 Overview of solid fuel cell electrolytes

2.1 Core mechanism of electrolytes

Electrolytes are the core components of solid oxide fuel cells (SOFC), with their primary function being ion conduction. The efficiency of these cells directly determines the output performance of SOFCs. The oxygen ion-conducting type is typically represented by yttria-stabilized zirconia (YSZ), and the conduction mechanism involves the directional migration of oxygen vacancy defects. At high temperatures, the intensification of lattice vibrations can reduce the energy barrier for oxygen ion migration, and this mechanism has been verified through first-principles calculations [2].

It is also possible to enhance the proton conductivity of the electrolyte by incorporating additional components. For instance, YSZ, a typical oxygen ion conductor, has relatively poor ionic conductivity at lower temperatures (500-800 degrees Celsius). To improve the proton conductivity of the electrolyte based on YSZ, a semiconductor ZnO is introduced into the YSZ electrolyte layer, creating a heterojunction between the semiconductor and the ionic conductor. This effectively enhances the proton conductivity of the electrolyte based on YSZ [3].

2.2 Classification of solid electrolytes

Based on the composition and structure of the materials, SOFC electrolytes can be classified into four types: oxide ceramics, sulfides, polymers, and composite electrolytes.

Firstly, oxide ceramic electrolytes are currently the mainstream in commercialization. The crystal structures mainly include fluorite structure, perovskite structure, and roxite structure. The fluorite structure (such as YSZ, GDC) has a face-centered cubic arrangement, with cations forming a dense lattice, and oxygen ions filling the gaps and having many migratable oxygen vacancies. The smooth oxygen vacancy migration path makes its ion conductivity excellent at high temperatures. The perovskite structure (such as $BaZrO_3$-based solid solutions) is of the ABO_3 type structure, with A sites mostly being rare earth or alkaline earth metal ions and B sites being transition metal ions. The ion substitution flexibility is high, and through doping, proton sites can be introduced to form conducting channels. The roxite structure (such as $La_2Zr_2O_7$) is of the $A_2B_2O_7$ type defective fluorite structure, with oxygen vacancies arranged in an ordered manner, and the rigid lattice gives it outstanding high-temperature stability. The dense lattice of the fluorite structure enables YSZ to have excellent mechanical strength and chemical stability, but oxygen vacancy migration is hindered at medium and low temperatures, resulting in a decrease in conductivity; the ion substitution property of the perovskite structure can flexibly regulate the proton concentration, but it has the drawback that pure-phase materials are prone to react with CO_2 to form carbonates; the ordered oxygen vacancies of the roxite structure optimize the conducting path, but its intrinsic oxygen vacancy concentration is lower than that of the fluorite structure, and the room-temperature conductivity is relatively low. Overall, this type of electrolyte has outstanding high-temperature stability and chemical compatibility, is suitable for different temperature ranges and working conditions, and remains the core choice for current high-temperature SOFCs.

The sulfide electrolytes exist mainly in the form of glass-ceramic and crystalline states. Glass-ceramic sulfide materials (such as Li_2S-P_2S_5) exhibit an "amorphous matrix and crystalline nanoparticles" composite structure. The amorphous phase provides a flexible framework, while the crystalline phase (such as Li_3PS_4) forms continuous ion-conducting channels. The crystalline sulfide materials are mostly in tetrahedral or octahedral coordination structures. The cations can migrate easily in the lattice gaps, and this structural feature determines that their ionic conductivity at room temperature is much higher than that of oxides. The flexible amorphous matrix also makes it excellent in processing. The thin films can be prepared through simple processes such as mechanical ball milling and hot pressing. The amorphous-crystalline transformation in the Li_2S-P_2S_5 system can be precisely controlled by low-temperature heat treatment. An increase in crystallinity can further widen the ion-conducting channels, allowing the ionic conductivity at room temperature to reach the order of 10^{-3}S/cm. However, the chemical bond energy of S^{2-} in sulfides is relatively low, and the lattice lacks a dense protective structure, making it prone to react with water vapor and CO_2 to form toxic H_2S. CO_2 can also catalyse this hydrolysis process [4-6]. Although elements such as Sb and Bi can be doped to construct thermodynamically stable structures to inhibit hydrolysis [7], the environmental stability remains the core bottleneck restricting its industrialization. Its high conductivity and good processing properties provide the possibility for the development of low-temperature SOFCs, but it requires a strict operating environment as a support.

Polymer electrolytes are classified into proton-conducting type and lithium-ion conducting type. The proton-conducting type is represented by Nafion, while the lithium-ion conducting type includes polymer ionic liquid block copolymers. Through the micro-phase separation of flexible segments and rigid segments, they balance mechanical properties and ion conductivity efficiency [4]. The flexibility of polymer molecular chains makes them excellent in film-forming properties, suitable for the packaging requirements of flexible SOFCs. However, due to the inherent problem of organic phase being prone to oxidation and degradation at high temperatures, they are more suitable for medium and low-temperature environments. Their lightweight and easy-processing characteristics have unique advantages in the field of flexible devices.

Other electrolytes include composite electrolytes, which compensate for the deficiencies of a single system through multi-phase synergy. Common types include ceramic-ceramic composites, polymer-ceramic composites, and MOF-based composites. After Nafion is combined with silicon sulfide layered materials (sSLM), the power density is increased by 2 times at 120 ℃ and 20% relative humidity [8]. Through the complementary and synergistic enhancement of the performance between different phases, composite electrolytes achieve comprehensive improvement in conductivity efficiency, stability, and mechanical properties, providing a new path for the performance breakthrough of SOFC electrolytes [8, 9]. This type of electrolyte compensates for the deficiencies of a single system through multi-phase synergy, achieving comprehensive improvement in conductivity efficiency, stability, and mechanical properties, becoming an important direction to break through the performance bottleneck, but the control of interface compatibility remains a key technical difficulty to be overcome.

3 Research progress on different SOFC electrolyte systems

3.1 Oxide ceramic electrolyte

The research on oxide ceramic electrolytes focuses on low-temperature modification, stability improvement, and low-cost preparation. In fluorite-based structural materials, the oxygen vacancy migration path is regulated through lattice distortion to achieve a synergistic improvement in ion conductivity and structural stability. Sc^{3+} doped YSZ (ScYSZ) optimizes the oxygen vacancy migration path through lattice distortion, and its ionic conductivity at 800 ℃ is 30% higher than that of traditional YSZ [5].

In the perovskite system, the breakthrough lies in the design of solid solutions and doping optimization. Through element substitution, a balance is achieved between proton conductivity and chemical stability, significantly improving the long-term operational stability of the material in complex atmospheres. The $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ solid solution, with the introduction of Ce elements, balances proton conductivity and chemical stability, and its proton conductivity reaches 0.03 S/cm at 600 ℃, with a performance attenuation rate of less than 5% after immersion in CO_2 atmosphere for 100 hours [5].

The greenstone-structured materials can significantly improve the oxygen ion conductivity efficiency while maintaining excellent high-temperature stability. Their unique crystal structure makes them potentially valuable in extreme conditions, and the related research provides new material options for the development of SOFCs in special environments. Taking $La_2Zr_2O_7$ as an example, after Gd doping, the oxygen ion conductivity at 700 ℃ increased from 0.01 S/cm to 0.02 S/cm, and the high-temperature stability was significantly enhanced, making it suitable for extreme conditions [5]. Table 1 shows the performance comparison of different oxide structures discussed in Section 3.1. In the fluorite structure, YSZ has excellent high-temperature stability, and ScYSZ has a 30% increase in conductivity after lattice distortion optimization compared to YSZ. In GDC, the low-temperature conductivity has an advantage, but the electron conductivity is prone to increase in reducing atmosphere. The perovskite structure $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ balances proton conductivity and chemical stability. The $La_2Zr_2O_7$ structure of the greenstone has outstanding high-temperature stability, and the oxygen ion conductivity doubles after Gd doping. The ionic conductivity and stability of various materials are closely related to their crystal structures and are suitable for different temperature working conditions.

Table 1. Comparison of Core Performance of Different Structural Oxide Ceramic Electrolytes.

Material system	**Crystal structure**	**Testing temperature (°C)**	**Ionic conductivity (S/cm)**	**Performance characteristics**
YSZ (Yttria-stabilized Zirconia)	Fluorite structure	800-1000	~0.1(800°C)	Excellent chemical stability and mechanical strength
ScYSZ (Sc^{3+} doped YSZ)	Fluorite structure	800	~0.13 (30% higher than YSZ)	Optimized lattice distortion for oxygen vacancy pathways, increased conductivity
GDC (Gadolinium doped Cerium oxide)	Fluorite structure	600	0.01	Higher proton conductivity at medium and low temperatures; increased electron conductivity in reducing atmosphere
$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$	Perovskite structure	600	0.03	Proton conductivity balanced with chemical stability
$La_2Zr_2O_7$ (undoped)	Crystobalite structure	700	0.01	Excellent high-temperature stability
Gd-doped $La_2Zr_2O_7$	Crystobalite structure	700	0.02	Enhanced high-temperature stability

3.2 Sulfide electrolyte

The Li_2S-P_2S_5 system was prepared as a glass-ceramic sulfide electrolyte through mechanical ball milling combined with low-temperature heat treatment. Its room-temperature ionic conductivity can reach 10^{-3} S/cm. High-resolution TEM observations confirmed that the high conductivity is attributed to the precipitation and connection of crystalline nanoparticles in the amorphous matrix [10]. By doping elements such as Sb and Bi, a thermodynamically stable tetrahedral structure can be constructed, effectively inhibiting hydrolysis reactions and enhancing the air stability and interfacial compatibility of the electrolyte [7].

The high ionic conductivity of this electrolyte is mainly due to the continuous conducting channels formed by the amorphous-crystalline composite structure. The process has been done, and temperature conductivity is good. But still very sensitive to water soluble strength. CO2 reacts strongly with H2O, but even if we use dopants to make our structure more stable, it will have to become better at being environmentally resistant if we ever want this thing out in the wild-conductive as always.

3.3 Polymer electrolyte

Functional Modification of Proton Conductive Polymers introduces proton receptor sites on the polymer, so it can enhance acid doping level as well as high temperature stability but prevent oxidation degradation and extend its usage time [11].

This field of research pays attention to achieving an appropriate balance between heat withstanding ability and ion transport competency. Functionality modification really solves well the high-temperature decrease issue which exists among those proton-carrying polymers. Meanwhile we can also combine with other material and make our Lithium-ION conduction system more durable by fusing it together. However, there is still an inherent high temperature oxidation degradation of the polymer that cannot be removed. Further research will continue to concentrate on collaborative optimization of mechanical property and conductivity efficacy at the medium – high temperature region.

3.4 Composite electrolyte

The central new development within the composite electrolyte is developing an architecture based on multiphase composites. By taking advantage of interface engineering and structural complementarities, we can avoid the inefficiencies of a single system as well as its instability or lack of mechanical strength. Ceramic-ceramic composite electrolyte creates plenty of oxygen vacuums by doing some work on its interfaces, making better travel routes for ions without making problems worse about stuff from different parts getting into each other too much. This makes the ion conductive efficiency and interface stability to get some boost together, which can give us the support needed in the long run in a stable working environment for high temp SOFCs. Polymer-ceramic composite system, the electrolyte membrane synthesized by Nafion and GDC is 0.07S/cm proton conductivity at 80 ℃, and the tensile strength is 30MPa [4]. Optimization of the interface compatibility of organic phase and inorganic phase, at this point, both the efficiency and the property of conductive material and mechanical properties as well as the processing performance met with the requirement of packaging used on flexible SOFC's. And when you think about MOF base electrolyte, there was a bit like an innovation, and here, what happened, because the ordered porosity from the MOF and those unsaturated metal sites from the MOFs that came about by being added either with polymers or ceramics, and they created these channels that were pretty much set up, right? The system can greatly increase ion conducting effectiveness and anti-hydrolysis stability and give a kind of fresh thinking on how to solve the issue by limiting the traditional electrolytes' efficiency. All three composite systems had superior results compared to a single system with the multi -phase synergistic effect. The essence of everything is trying to be precise with respect to structure and performance benefits of different phases so that maximum benefit may come out of such things through controlling the interface and thus this is going to become a major area where a lot of progress will take place when talking about improvements towards improving SOFC performance in general terms.

4 Challenges and prospects

Nowadays some basic challenges with SOFC electrolytes still exist that prevent the broad use of the tech. The environmental stability of sulfide electrolytes is poor; sulfide electrolytes may react with water vapor and carbon dioxide to produce toxic hydrogen sulfide gas. Their preparation, their storage, and then the battery assembly all need to happen in this super dry setting, which makes things very costly if we want to start making this a bigger thing. Polymer electrolytes typically exhibit a reduction in mechanical strength and a drop in ion conductivity when the temperature exceeds 100 degrees centigrade, which cannot meet the operational requirements of medium-temperature SOFCs. In the composite electrolyte system, different physical and chemical properties between different parts are prone to cause stress concentration, microcracks and element interdiffusion, thereby affecting the long-term reliability of the battery. And now we're doing complicated preparation of high-temp resistant special things. And more complicated modifications. And very specific structure engineering. And these have made what's already expensive (initial) costs even more prohibitive for SOFC systems compared with traditional power-generating means, thus continuing to slow down efforts toward broader usage.

In the future, these issues must be dealt with by going into them more deeply. For a mechanistic study using DFT calcs and in-situ characterizations to get exact info about which paths of vacancies & protons take for ion migration and charge trans at boundaries; this will help choose which dop elements, ratio optimization, & structuring. As far as the material modification goes, we also must keep improving the stability of the sulfide electrolyte and keep developing these technologies to be non-destructively able to do things like the exterior surface protection from water as well as the oxidation but still maintain the ionic conductivity that we want. While that's happening, pay attention to MOFs, 2D materials, and the likes of function-bearing carriers, create multi-scale composite structures that can help boost ionic conductivity, mechanical strength, and environmental resistance together, concentrate efforts on surmounting polymer-ceramic composite electrolytes' under-performance issues across medium temperatures.

In terms of the procedure and applications, design an effective buffer layer and combination electrode structures based on the main standard of the thermal expansion coefficients to ease stress and element diffusion at interfaces. To prepare the electrolyte film at low cost and scale, thin and defects free films are required for the reduction in the overall cost of SOFC system. And when it comes to places like datacenters or where both heating and electricity get produced together, there need to be evaluations done all around on stuff like staying stable over a long time and how they take heat cycles into account in order to make sure that electrolyte-research is getting linked up nicely enough so we can see SOFC tech actually moving out past test labs into the real world and offer good help toward the worldwide push for cleaner forms of fuel.

5 Conclusion

In this article make an overview for the research which was done by 4 types of electrolytes in Solid oxide fuel cell (SOFC), those include ox ceramic electrolyte, sulfide, polymers and composites. Electrolyte type: crystal structure & ion transport; how it changes & what it affects. The oxide ceramic electrolytes which are widely used for commercial purposes have a lot of connections with their structure that can change its form according to temperature if you make some changes like structural optimization and doping. Sulfide electrolytes also have good ion transport ability, but they have worse constraints from the environment; the polymers, we need the modification on its function or the microstructure, and thus it shows good properties when there is flexibility; composite electrolytes make up for the shortcomings of each system through mutual enhancement of various phases, and it has become an important direction for improving performance. Interface stability is the core guarantee for the long-term operation of SOFCs, and its improvement depends on the precise matching of lattice matching degree and thermal expansion coefficient. The optimization of all these systems requires considering both body modification and interface regulation.

This study integrates the structure-performance correlations and regulation strategies of the four types of electrolytes, builds a complete knowledge framework, provides clear guidance for subsequent research in the field, and is of great significance for promoting the development of SOFCs towards medium temperature, long lifespan, and low cost, and facilitating the global clean energy transition. In the future, it is necessary to deepen the research on ion transport and interface interaction mechanisms, promote material innovation and process optimization, and accelerate the industrialization of SOFC technology.

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