

Advance in the Electrolyte Material System and Optimization Strategies of Solid Oxide Electrolysis Cells

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Abstract. Solid oxide electrolysis cells (SOECs) are a new type of highly efficient water electrolysis technology for hydrogen production, showing great potential for converting and storing renewable energy and mitigating the greenhouse effect. Electrolytes are key components of SOECs, but single and unmodified electrolytes currently have certain limitations in terms of efficiency and stability. This paper reviews the basic principles of SOECs, the types of electrolytes corresponding to the two ion conduction modes, and related doping modification optimization strategies. By introducing heteroatomic ions such as Gd^{3+} and Y^{3+} through doping modification to regulate oxygen vacancy concentration and optimize ion migration channels, the performance of the electrolyte can be comprehensively enhanced. A comprehensive summary of the various types of electrolytes and doping modification schemes for SOECs can help new researchers get started. Proton-conducting (H-SOEC) is a key area of future research, as it offers significant conductivity at lower operating temperatures, which is crucial for extending device life and reducing manufacturing costs. This will enable the large-scale commercialization of SOECs.

Keywords: Solid oxide electrolysis cell, Hydrogen production, Optimization Strategies, Electrolyte material.

1. Introduction

Electrolysis of water to produce hydrogen is an efficient hydrogen production technology that can convert excess renewable electricity, solving the temporal and spatial dilemmas of transporting and storing renewable electricity, as well as converting electricity into easily storable hydrogen. Solid oxide fuel electrolysis cells (SOECs) are a new type of solid-state electrolysis hydrogen production technology that can overcome the limitations of traditional water electrolysis technology, which requires noble metal catalysts. Their energy efficiency is higher than that of traditional liquid electrolysis systems such as alkaline electrolysis cells (AEC) and polymer electrolyte membrane electrolysis cells (PEMFC), and the theoretical voltage of H cracking at high temperatures is 20%-30% lower than at normal temperatures [1]. In addition, industrial facility waste heat can be utilised, making it suitable for large-scale deployment. SOEC also has advantages such as zero pollution and low raw material purity requirements [2]. SOEC fuels include H_2O , CO_2 , and methane and other hydrocarbons. It reduces low-value H_2O or CO_2 to more valuable H_2 and CO , which is

considered green hydrogen. SOEC's high-efficiency hydrogen production and CO₂ reduction capabilities provide a new approach to mitigating the greenhouse effect and decarbonising global heavy industry.

However, the overall technical maturity of SOEC is relatively low at present. The main issues include poor long-term stability of individual components, a lack of advanced material manufacturing methods, the need to address material degradation issues, and the challenge of balancing battery life with performance improvements. Therefore, there is a need to develop more efficient and stable electrode and electrolyte materials.

Electrolytes are an important component of SOECs. One of the key steps in solving the problem of electrolyte degradation and developing new electrolyte cells is to develop new electrolyte materials, which requires finding novel doping strategies. The SOEC electrolyte material system is highly diverse, with different electrolytes suitable for various operating temperatures and principles, and doping strategies are extremely complex. To better study and understand SOECs, this paper will comprehensively categorise and summarise the various electrolyte material systems of SOECs and their optimisation and modification strategies. The SOEC electrolyte material system is highly diverse, with different electrolytes suitable for various operating temperatures and principles, and doping strategies are extremely complex. To better study and understand SOECs, this paper will comprehensively categorise and summarise the various electrolyte material systems of SOECs and their optimisation and modification strategies.

2. SOEC electrolyte material system

SOEC consists of three main components: cathode, anode, and electrolyte. The electrolyte plays a role in conducting ions and isolating electrons, requiring high ionic conductivity and extremely low electronic conductivity. It also serves to isolate gas flow, so the electrolyte must be dense. Due to the high operating temperature, it must also maintain long-term chemical, mechanical, and thermal stability to withstand material degradation and battery damage caused by different thermal expansion coefficients. From a performance perspective, low ohmic resistance is also required to maintain low voltage, preventing electrolyte ageing and cracking, thereby extending electrolyte life and improving energy efficiency [2]. Therefore, it is also necessary to reduce the thickness of the electrolyte. Currently, SOECs have not yet been commercialised on a large scale, primarily due to battery lifespan and cost not yet meeting requirements. Therefore, when designing electrolyte materials, it is also necessary to consider material durability and reliability, as well as reducing the use of high-cost, low-reserve metals. SOECs are primarily categorised into two types: O-SOEC, H-SOEC, and hybrid types. However, research on hybrid types is currently limited. The first two types represent electrolytes that conduct oxygen ions and protons, respectively. Below, this paper will provide a detailed introduction to the electrolyte types used in each based on the above requirements.

SOEC electrolyte materials are typically not pure oxide materials, but rather materials that have been modified through doping strategies, i.e., the addition of other elements to optimise their properties. This treatment improves the performance of the materials at certain temperatures, such as high ionic conductivity and low electronic conductivity.

2.1. Oxide ion conducting electrolytes

Oxygen ion-conducting SOEC (O-SOEC) is the basic type of SOEC. Compared with H-SOEC, it has been studied for a longer period of time and is more technically mature. Oxygen ions are

conducted to the anode through the electrolyte and oxidised into oxygen at the anode. The schematic diagram of the principle of O-SOEC is as follows:

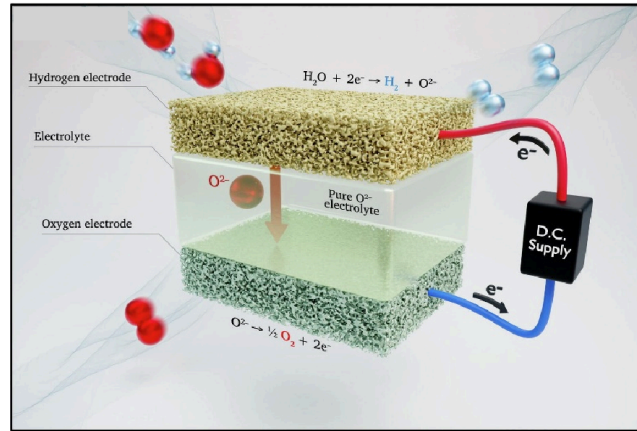


Figure 1. The working principles of Oxygen-SOECs [3]

As shown in the figure above, the reactions at the two electrodes are as follows:
Cathode:



Anode:



O-SOECs typically operate at temperatures between 700 and 1000°C. The core function of the electrolyte material is to conduct oxygen ions, and it must meet basic requirements such as high oxygen ion conductivity. Commonly used electrolyte materials can be primarily categorised into the following types: zirconia-based materials, ceria-based materials, and lanthanum gallate-based materials.

Yttria-stabilised zirconia (YSZ) is the most commonly used electrolyte material in O-SOEC. It has excellent oxygen ion conductivity and mechanical strength, is compatible with many electrode materials, and has outstanding chemical stability. At high temperatures, its conductivity can reach 0.1 S/cm. Yttria-stabilised zirconia (YSZ) is the most commonly used electrolyte material in O-SOEC. It has excellent oxygen ion conductivity and mechanical strength, is compatible with many electrode materials, and has outstanding chemical stability. At high temperatures, its conductivity can reach 0.1 S/cm [4].

Cerium oxide-based materials exhibit excellent performance under medium-temperature conditions (500–800°C). Through appropriate doping and modification treatments, the electrical conductivity can reach the order of 10^{-2} S/cm at operating temperatures [5].

Lanthanum gallium oxide-based materials (doped LaGaO₃) can operate at medium temperatures and exhibit good ionic conductivity, with higher conductivity than traditional YSZ. At 800°C, it can reach 0.17 S/cm, and when the temperature is reduced to 600°C, the advantages of LSGM become even more pronounced. Lanthanum gallium oxide-based materials (doped LaGaO₃) can operate at medium temperatures and exhibit good ionic conductivity, with higher conductivity than traditional YSZ. At 800°C, it can reach 0.17 S/cm, and when the temperature is reduced to 600°C, the

advantages of LSGM become even more pronounced [3]. The sintering time of the material affects the microstructure, which has a significant impact on the electronic conductivity of LSGM. Increasing the sintering time can effectively reduce the electronic conductivity [6].

2.2. Proton conducting electrolytes

Proton-conducting solid oxide fuel cells (H-SOEC) are a new type of SOEC and an iterative technology route for O-SOEC. Protons produced by the anode electrolysis of fuel are transferred to the cathode through the electrolyte and then reduced to hydrogen gas. H-SOEC produces pure, dry hydrogen gas that does not require secondary processing and has a high overall energy conversion efficiency. In addition, there is no steam at the hydrogen electrode, making it easier to maintain electrode stability [7]. The principal diagram is as follows:

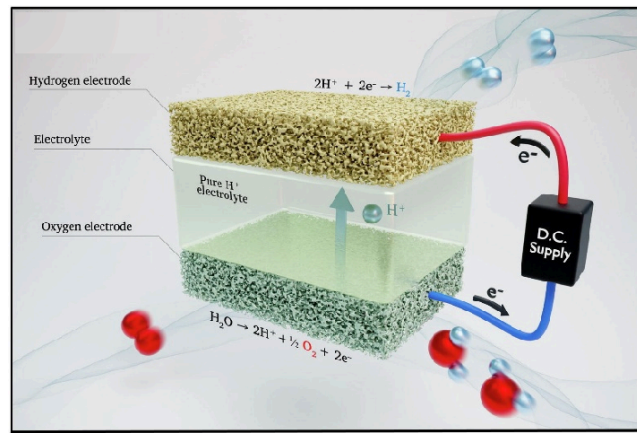


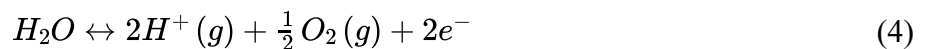
Figure 2. The working principles of Proton-SOECs [3]

As shown in the figure above, the reactions at the two electrodes are as follows:

Cathode:



Anode:



The radius of a proton is much smaller than that of an oxygen ion, which makes it easier for protons to move within the electrolyte lattice. Protons can migrate in two ways: by continuously hopping through adjacent oxygen ions or by rapidly diffusing directly through lattice defects. This results in the activation energy for proton conduction through the electrolyte being much lower than that for O^{2-} , approximately 0.4 eV [8]. Only half of the latter, so a lower operating temperature can meet the requirements for electrolytic efficiency. Therefore, H-SOEC demonstrates significant advantages, combining the advantages of traditional high-temperature SOEC and low-temperature proton exchange membrane fuel cells (PEMFC), with characteristics of lower heat loss and higher energy efficiency [9]. At lower operating temperatures, chemical reactions between components, component degradation, and thermal stress can be reduced, which are the key factors limiting the lifespan of O-SOEC. Additionally, the reduced complexity of thermal management can also simplify the design complexity and manufacturing costs of the stack structure. Combined with the lower

operating temperature, this enables faster startup and shutdown of the equipment, making it suitable for the variable conditions of renewable energy generation. This expands the application scenarios and attracts customer selection, contributing to the large-scale commercial application of H-SOEC.

To meet the above requirements, compared with O-SOEC, the electrolyte of H-SOEC needs to be redesigned to have high proton conductivity while meeting other basic requirements of SOEC electrolytes, such as extremely low electronic conductivity. Currently, research on H-SOEC electrolytes is mainly focused on perovskite materials.

The most widely studied are various types of doped and modified perovskite materials based on BaCeO_3 (BCO) and BaZrO_3 . BCO has higher proton conductivity and sinterability but is unstable in strong reducing environments and humid conditions, while BaZrO_3 has better chemical stability [10]. The two substances are mutually soluble, so they are usually combined to form a solid solution that possesses the properties of both [10]. The BCZY series of perovskite materials are the most commonly used electrolytes in H-SOEC [11]. Depending on temperature requirements, BCO and its solid solution materials perform better at medium and low temperatures, while BaZrO_3 -based materials, such as the BZY series, are suitable for high-temperature environments. Poor sintering performance and high grain boundary resistance are the two main factors hindering BaZrO_3 -based oxides from becoming ideal electrolyte materials for H-SOEC [12]. Strontium-based perovskite materials can also be used as electrolyte materials, such as the SZCY series (SrCeO_3 and SrZrO_3), but they have low proton conductivity. Combining them with BaZrO_3 -based materials can achieve better conductivity [13].

3. Electrolyte optimization strategies

Doping modification is the primary modification method for SOEC electrolyte materials, which can enhance sintering and electrochemical performance. It can increase crystal structure stability and electrical performance for both perovskite and fluorite structure materials.

For Yttria-stabilised zirconia (YSZ), the molar concentration of Y_2O_3 is typically in the range of 7%–10% mol, with the best ionic conductivity at 8% mol. However, a slight increase in concentration can reduce material degradation [5]. Since the ionic radii of Sc^{3+} and Zr^{4+} are very similar, Sc_2O_3 is often doped at a concentration of 8%–10% mol to form stable zirconia [5]. This strategy results in a high ionic conductivity of the electrolyte, allowing the operating temperature to be lowered appropriately to increase service life and reduce energy loss.

For cerium oxide-based materials, the oxygen ion conductivity of CeO_2 can be enhanced by doping with cations such as Gd^{3+} , Sm^{3+} , and Y^{3+} , exhibiting good performance under medium-temperature conditions (500–800°C). Reducing the radius difference between ions can improve conductivity. A doping concentration range of 15–25% mol is commonly used, with electrical conductivity reaching the 10^{-2} S/cm level at operating temperatures [5]. The electrical conductivity first increases and then decreases with increasing doping concentration, reaching a maximum at 20% mol [5].

The perovskite structure allows various ions to enter the lattice, so the properties of the material can be changed by adjusting the ionic composition at two positions [14]. The doping modification of perovskites can be mainly divided into three categories: A-site doping, B-site doping, and AB-site co-doping. This article will mainly introduce these three categories. In addition, recent studies have also introduced F^- into the O^- site, which also exhibits excellent electrochemical performance [9]. By doping with low-cost cations, the vacancy concentration can be effectively increased, improving ionic conductivity and effectively increasing the reaction rate [9].

3.1. A-site doping and B-site doping

When rare earth or alkaline earth metal ions occupying the A site are doped with low-valent (+2 valence) cations, the ionic migration energy barrier can be reduced by altering the radius of the A-site ions, while inducing the formation of additional vacancies in the lattice. This optimises the width of ionic conduction pathways within the lattice and increases the concentration of mobile ions, ultimately enhancing ionic conductivity and reducing internal resistance; Meanwhile, B-site doping with transition metal ions primarily optimises oxygen ion conductivity by regulating oxygen vacancy concentration and oxygen ion migration pathways. Additionally, since proton radius is significantly smaller than that of oxygen ions, this also reduces the proton migration energy barrier, resulting in a substantial increase in proton conductivity.

The same position can be doped with one element or co-doped with multiple elements, such as $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY), which uses double doping at the B site (Zr and Y jointly replacing Ce) [15]. $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb5311) uses three-element co-doping at the B site (Zr partially replaces Ce, Y and Yb as stabilisers) to enhance stability by utilising the high entropy effect [16].

3.2. Co-doping

In addition to separate doping at positions A and B, co-doping at both positions can be employed to more comprehensively regulate the performance of electrolyte materials, particularly H-SOEC electrolytes, which typically utilize co-doping strategies. Additional doping elements such as Y and Yb can replace the original tetravalent Ce or Zr elements, with five metals utilizing the high-entropy effect to enhance stability and increase hydrogen conductivity. $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb), which uses Y and Yb elements for co-doping [17]. By simultaneously altering the ion types at both the A and B sites, synergistic optimization can be achieved in terms of crystal structure, defect concentration, and ion migration pathways. The co-doping strategy overcomes the limitations of single doping, reducing the electrolyte's internal resistance while enhancing ionic conductivity, which facilitates the low-temperature operation of the electrolyte. Multi-element doping also leverages the high-entropy effect to maintain lattice structural stability, helping the electrolyte remain stable under high-temperature and strong reducing conditions.

LaGaO_3 is a perovskite material that is typically co-doped with Sr and Mg elements to form LSGM, the typical example is $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$, which exhibits optimal performance when the doping content is between 15 and 20 mol% [3]. Other doping schemes, such as doping with small amounts of Co or Fe, can only enhance the low-temperature performance of LSGM. Continuing to increase the Co concentration will result in the increase in ionic conductivity being less than that of hole conductivity [18, 19].

4. Conclusion

SOEC is a new type of electrolytic water hydrogen production technology with extremely high energy conversion efficiency. It is compatible with renewable energy systems and contributes to further innovation in renewable energy systems and the control of the greenhouse effect. In addition to its extremely high efficiency, SOEC does not rely on precious metal catalysts or high-purity raw materials, produces low pollution, and generates dry, pure hydrogen. This paper summarizes the basic principles of SOEC, provides a detailed introduction to the types of electrolytes required for efficient hydrogen production based on two conduction mechanisms, and outlines optimization

strategies for electrolyte materials. The primary challenges in designing new electrolytes include enhancing ionic conductivity, suppressing electronic conduction, and reducing electrolyte internal resistance. H-SOEC is a highly promising SOEC solution, as it enables lower operating temperatures through reduced conduction energy barriers, effectively suppressing degradation, which helps address the scaling challenges of SOEC.

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