



Validating the technological feasibility of yttria-stabilized zirconia-based semiconducting-ionic composite in intermediate-temperature solid oxide fuel cells



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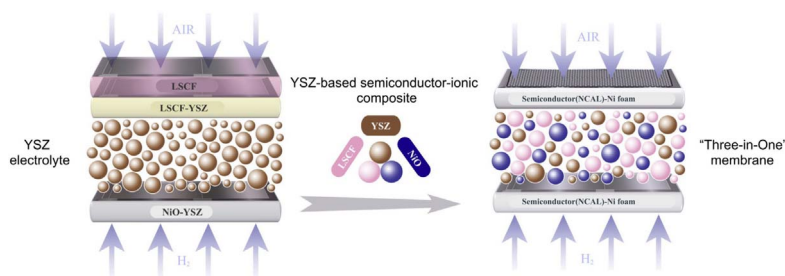
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HIGHLIGHTS

- YSZ-based semiconductor-ionic composites are studied for the first time in SOFCs.
- Experimental data from different YSZ-based composite fuel cells is used for validation.
- Detailed properties of the NiO-YSZ-LSCF composite are investigated by STEM-EELS.
- Significant performance enhancement is achieved by the NiO-YSZ-LSCF-based device.

GRAPHICAL ABSTRACT



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ABSTRACT

YSZ as the electrolyte of choice has dominated the progressive development of solid oxide fuel cell (SOFC) technologies for many years. To enable SOFCs operating at intermediate temperatures of 600 °C or below, major technical advances were built on a foundation of a thin-film YSZ electrolyte, NiO anode, and perovskite cathode, e.g. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF). Inspired by functionalities in engineered heterostructure interfaces, the present work uses the components from state-of-the-art SOFCs, i.e. the anode NiO-YSZ and the cathode LSCF-YSZ, or the convergence of all three components, i.e., NiO-YSZ-LSCF, to fabricate semiconductor-ionic membranes (SIMs) and devices. A series of proof-of-concept fuel cell devices are designed by using each of the above SIMs sandwiched between two semiconducting $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_{2-\delta}$ (NCAL) layers. We systematically compare these novel designs at 600 °C with two reference fuel cells: a commercial product of anode-supported YSZ electrolyte thin-film cell, and a lab-assembled fuel cell with a conventional configuration of NiO-YSZ (anode)/YSZ (electrolyte)/LSCF-YSZ (cathode). In comparison to the reference cells, the SIM device in a configuration of NCAL/NiO-YSZ-LSCF/NCAL reaches more than 3-fold enhancement of the maximum power output. By using

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spherical aberration-corrected transmission electron microscopy and spectroscopy approaches, this work offers insight into the mechanisms underlying SIM-associated SOFC performance enhancement.

1. Introduction

The solid oxide fuel cell (SOFC) is a promising technology that is capable of converting chemical energy directly into electrical energy [1–3]. Since Nernst first demonstrated that yttrium-stabilized zirconia (YSZ) possessed high oxygen-ion conductivity in the late 1930s, YSZ has been used as the electrolyte material in SOFCs. From the 1980s–1990s, milestones were achieved in a range of architectures with planar and tubular SOFCs [4]. To date, YSZ is still the electrolyte of choice for the commercialization of SOFCs.

Notwithstanding its advantages, development potential of YSZ has been constrained by the bottleneck of high-operating temperatures. Design of oxide-ion conductors have been proposed as a solution to this intractable problem, which indicates that it is necessary to develop alternative oxide-ion conductors at a sufficiently lower temperature in order to be technically useful [5]. Tremendous research and development activities on ceria-based fluorite materials have emerged from this insight in order to realize the desired ionic conductivities [6–8]. However, it is widely recognized that ceria, either pure or doped, is less stable under reduced atmospheres. The conversion of Ce^{4+} ions to Ce^{3+} ions gives rise to n-type electronic conductivity, which induces a partial internal short-circuit that deteriorates the open-circuit voltage (OCV) and energy conversion efficiency [9,10]. To tackle this problem, Ni- Sc_2O_3 stabilized ZrO_2 (ScSZ)- $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-8}$ (GDC) [11], $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-8}$ (LSGM)- $\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_{2-8}$ (LDC) [12], YSZ-Sm-doped ceria (SDC) [13], and so on heterostructured/bi-layered electrolytes [14,15] were successively invented, which demonstrated much improved stability performances.

The search for practical technologies to enhance oxide ionic conductivity is pivotal. For SOFCs using YSZ-based oxygen conductors, typically, the most common approach is fabricating YSZ into thin-film-based devices to reduce their resistance. Therefore, the dimensional thickness is minimized to micro-meters [16–19] or even nano-meters [20–22]. Concomitant with prior technical breakthroughs was the emerging interest in coherently strained interfaces. Garcia-Barriocanal et al. found that the ionic conductivities of YSZ and SiTiO_3 (STO) heterostructures were enhanced by eight orders of magnitude, compared with pure YSZ [23]. Another study revealed the incompatibility of the oxygen positions at the YSZ-STO interface planes, which led to high levels of ionic conductivity [24]. Moreover, Lee et al. developed a type of cell geometry using epitaxial nanocomposite film that contained a ~20 nm-diameter YSZ nano-column strain coupled with an STO matrix. This work enhanced ionic conductivity by two orders of magnitude [25]. Strongly enhanced oxygen ion transport, which consisted of Sm-doped CeO_2 (SDC) embedded in STO-supporting matrices, was also found on the vertical nano-columns [26]. The authors surmised that the interface, as well as the SDC nano-columns, contributed to the fast ion-conducting channels. The aforementioned studies suggest the possibility to develop SOFCs based on the co-existence and collaboration between a semiconductor (e.g., STO) and ionic conductors (e.g., YSZ or SDC). Although there is no consensus on the mechanism responsible for the origin of ionic conductivity enhancement, it is clear that tuning the electronic states at interfaces of the semiconductor and ionic material heterostructure can lead to the modification of oxygen-ion-conducting properties. In this scenario, we have reason to believe that the oxide interfaces with enhanced ion conductivity would be favorable for the optimization of materials that target SOFC development at reduced temperatures.

Perhaps the most difficult obstacle to overcome in conventional SOFC technologies, when designing an YSZ/STO- or SDC/STO-centered

fuel cell system, is that the significant electronic conduction obtained by the STO would not make it a competent electrolyte material. It is noteworthy that with the proposal of electrolyte-layer-free fuel cells (EFFCs) [27], a non-electrolyte separator/layer is needed in a single cell configuration. Instead, a single nanocomposite-based component, which combines the function of a semiconductor and an ionic conductor, enables the realization of the fuel cell operation. To better understand the working principle of EFFCs, a Schottky junction model based on a metal-semiconductor configuration has been proposed as a decisive factor [28], which indicates the junction between metal that forms at H_2 supply side and p-type semiconductor is advantageous because the built-in field is directed from the metal surface to the p-type semiconductor. This can facilitate the ion transportation crossing the metal/semiconductor–ionic material interface through ionic conductor, and prevent the electrons passing through the junction. Meanwhile, the ionic conductor sustains fast ion transport and redox reactions, which synergistically contributes to the enhancement of fuel cell performance. These efforts spawned our interests in the exploitation of heterostructure composite materials and their roles in energy and chemical conversions.

Based on the methods described above, this work aims to employ state-of-the-art component materials from current SOFCs in order to validate our proposal regarding the semiconductor-ionic membrane (SIM) and device. SIM-associated devices are compared with two typical SOFCs at 600 °C, a critical comparison for evaluating SOFCs at intermediate temperatures. In addition, we utilize spherical aberration-corrected transmission electron microscopy and spectroscopy approaches to investigate the interfacial properties of semiconductor and ionic materials. We expect this paper will promote a better understanding of SIM-associated fuel cell technologies by providing evidence of performance enhancement from semiconductor-ionic interfacial structures and energy band characteristics.

2. Experimental

2.1. Materials preparation

The heterostructure composite materials, including $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-8}$ (LSCF)-YSZ, NiO-YSZ, and NiO-YSZ-LSCF, were prepared and used as SIMs in a fuel cell device. The LSCF-YSZ composite was fabricated using a wet chemical method. Commercial-type LSCF (Sigma Aldrich, USA) powders were mixed with YSZ (Y_2O_3 7–9 mol %, Mel Chemicals) powders at a weight ratio of 3:2. The mixture was then added to the nitric acid in a diluted solution and stirred for 30 min. The molar ratio of nitrate acid to YSZ was 2:1. The solution was dried at 300 °C for 1 h and then sintered at 800 °C for 4 h. The resultants were thoroughly ground to obtain homogenous LSCF-YSZ powders. The NiO-YSZ composite was prepared in the same fashion. To prepare the NiO-YSZ-LSCF composite, 60 wt% YSZ-20 wt% NiO (Sigma Aldrich, USA), and 20 wt% LSCF were added to a nitric acid solution and then sintered at 800 °C for 4 h.

2.2. Structural and electronic characterization

The morphologies were studied by a scanning electron microscope (SEM, Zeiss Merlin) equipped with Aztec energy-dispersive X-ray spectroscopy (EDX). The crystal structures were analyzed by a Bruker D8 advanced X-ray diffractometer (Germany, Bruker Corporation) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) as the source. The Brunauer-Emmett-Teller (BET) specific surface areas were determined by N_2 physisorption using an ASAP 2020 automated system (Micromeritics). Electron

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