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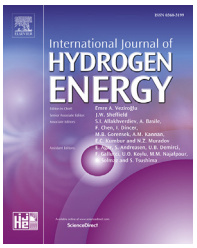

Experimental and physical approaches on a novel semiconducting-ionic membrane fuel cell

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ABSTRACT

Semiconducting-ionic membranes (SIMs) have exhibited significant superiority to replace the conventional ionic electrolytes in solid oxide fuel cells (SOFCs). One interesting phenomenon is that the SIMs can successfully avoid the underlying short-circuiting issue and power losses while bringing significantly enhanced power output. It is crucial to understand the physics in such devices as they show distinct electrochemical processes with conventional fuel cells. We first presented experimental studies of a SIM fuel cell based on a composite of semiconductor $LiCo_{0.8}Fe_{0.2}O_2$ (LCF) and ionic conductor Sm-doped CeO_2 (SDC), which achieved a remarkable power density of 1150 mW cm^{-2} at 550 °C along with a high open circuit voltage (OCV) of 1.04 V. Then, for the first time we used a physical model via combining a semiconductor-ionic contact junction with a rectifying layer which blocks the electron leakage to describe such unique SIM device and excellent performance. Current and power are the most important characteristics for the device, by introducing the rectifying layer we described the SIM physical nature and new device process. This work presented a new view on advanced SIM SOFC science and technology from physics.

Introduction

In recent years, a new approach in the research of solid oxide fuel cells (SOFCs) was introduced by using a semiconducting-ionic membrane (SIM) to replace the conventional ion-conductive and electron-insulating electrolytes. Though the SIM possesses both ionic and electronic conductivities, neither power losses nor reduction of open circuit voltage (OCV) is observed. On the contrary, the SIM fuel cells exhibit normal OCV values above 1.0 V and impressive power output at low operating temperatures without any short-circuiting problem [1–5]. This is a new twist in the long history of the electrolyte-based fuel cell R&D since invented by Grove in 1839.

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The SIMs are commonly in a composite form consisting of two phases, an ion conductor and a semiconductor [1–10]. The latter usually contains transition metal oxides of perovskite or layered structures [9–15]. It is naturally to understand that such SIM materials have a high ionic conductivity along the grain boundaries and ionic phase, and a high electronic conductivity through the semiconductor phase. However, some promoted effects such as higher fuel cell performance and significantly enhanced ionic conductivity are always found when the SIM materials are applied in fuel cells. Thereby, the use of the SIM instead of a conventional solid electrolyte membrane in a fuel cell requires theoretical understanding and physical explanations, especially for two principal phenomena: i) The OCV of SIM-based SOFC is sufficiently high, superior to that of the fuel cell using conventional mixed electronic and ionic conductor (MIEC) electrolyte, e.g. ceria, which causes partial electronic short-circuiting issue to the device [16,17]; ii) The power output of SIM-based SOFC is enhanced due to enhancement of ionic conductivity in the SIM via unique physical mechanism. The high OCV indicates that the internal electron current flow through the SIM layer is successfully blocked. This has been proved as a result of a Schottky junction formed between the semiconductor and anode [5,18], which establishes a Schottky barrier in depletion layer to restraint the electron transporting from anode zone to membrane layer. Moreover, from technology perspective, the SIM fuel cell devices are also remarkably different from the conventional SOFC devices. Typical SOFC technology normally uses perovskite semiconductor oxide as the cathode which is mixed with the ionic electrolyte material to form the composite cathode component [11–13], while in the new SIM fuel cells, an analogous composite made of a cathode semiconductor and an ionic conductor serves as the principle component, electrolyte membrane layer. Therefore, new scientific understanding from the device point of view is also demanded to understand this new SOFC technology.

In this work, from experimental aspect, we prepared a transition metal oxide, $LiCo_{0.8}Fe_{0.2}O_2$ (LCF) and a heterogeneous composite of $LiCo_{0.8}Fe_{0.2}O_2$ and Sm-doped CeO_2 (LCF-SDC) for demonstration of the physical principle of SIM fuel cell. The LCF has an intrinsic nature of the semiconducting property, and more importantly it has a layered structure. According to previous report, layered-structure $LiCo_{0.5}Al_{0.5}O_2$ is able to incorporate protons in the interlayers to allow extremely high proton conductivity, e.g. 0.1 S cm^{-1} at low temperature of 500 °C [6]. Therefore, it is expected that the developed LCF possesses an considerable proton conductivity in addition to its inherent excellent electronic conductivity, and further compositing with the typical oxygen-ion conductor SDC can thus result in a triple $O^{2-}/H^{+}/e^{-}$ conducting property, which is beneficial for rapid fuel cell hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) and device performance optimization [14]. Hereby, with a specific semiconducting-ionic conductor LCF-SDC and the corresponding fuel cell as demonstration case, we make a validation study of a new theoretical model to interpret the SIM physical nature and device process. The physics plays a significant important role to make the device possible by building a rectifying layer to block the electrons passing through internally the device.

Experimental

Synthesis of LCF

All the chemicals used in this work were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). The chemicals of analytical grade were used in this work without further purification. $LiCo_{0.8}Fe_{0.2}O_2$ was synthesized by a sol-gel method. Li_2CO_3, $Co(NO_3)_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ with molar ratio of Li:Co:Fe = 1:0.8:0.2 were mixed in die-ionized water and prepared into a 1 M Li-Co-Fe aqueous solution. Citric acid with an mole amount of 1.3 times as that of the metal ion was dissolved in 70 ml die-ionized water and then stirred for 30 min to obtain a citric acid solution. This solution was further added into the Li-Co-Fe solution, and subsequently heated at 80 °C with continuous stirring until a dense gel mixture was formed. The mixture was then put in an oven at 120 °C for overnight, so that a dried puff gel with a reddish brown colour was attained. Finally, the dried gel product was sintered at 900 °C for 6 h to get a black powder of $LiCo_{0.8}Fe_{0.2}O_2$.

Synthesis of SDC

SDC was synthesized through the solution route by a co-precipitation method. Cerium nitrate and samarium nitrate were dissolved in die-ionized water to prepare 1 M solution individually. The two solutions were then mixed at a molar ratio of Ce:Sm = 0.8:0.2. Sodium carbonate, which served as a precipitating agent with a molar ratio of Ce^{3+}/Sm^{3+}:CO_3^{2-} = 1:1.5, was prepared in a 1 M solution. It was added into the mixed Ce^{3+}/Sm^{3+} solution to form the corresponding carbonate precipitate. The pH value of the solution was then adjusted to 12 by using sodium hydroxide. Afterwards, the precipitate was rinsed several times with die-ionized water followed by washing thoroughly with ethanol to remove the water from the particle surfaces. It was dried overnight in an oven at 120 °C and then calcined at 750 °C for 2 h to obtain the SDC product.

Synthesis of LCF-SDC membrane and electrode

The prepared LCF and SDC were ground completely to obtain powders, on basis of which, the composite material LCF-SDC was prepared by mixing LCF and SDC powders into a homogeneous mixture in a mass ratio of 4:6, followed by thorough grinding. Additionally, the electrode material, $Ni_{0.8}Co_{0.15}Al_{0.05}LiO_{2-\delta}$ (NCAL) was processed into a slurry by mixing the NCAL powder with terpineol solvent. The obtained slurry was then pasted onto nickle foam and desiccated at 150 °C for 0.5 h to form NCAL-pasted Ni (NCAL-Ni) electrodes.

Material characterizations

X-ray diffraction (XRD) measurements were performed on the powder samples using Bruker D8 advanced X-ray diffractometer (Germany, Bruker Corporation) with Cu Ka radiation (λ = 1.54060 Å) as the source. The morphologies, microstructures and chemical compositions were detected by field emission scanning electron microscope (FESEM) equipped

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