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Semiconductor electrolyte for low-operating-temperature solid oxide fuel cell: Li-doped ZnO

Chen Xia ^{a,b,1}, Zheng Qiao ^{a,c,1}, Liangping Shen ^{a,**}, Xueqi Liu ^a,
Yixiao Cai ^d, Yang Xu ^a, Jinli Qiao ^d, Hao Wang ^{a,*}

^a Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Faculty of Physics and Electronic Science, Hubei University, Wuhan, Hubei, 430062, PR China

^b Department of Energy Technology, KTH Royal Institute of Technology, Stockholm, SE-10044, Sweden

^c College of Mechanical and Electrical Engineering, Huanggang Normal University, Huanggang, Hubei, 430062, PR China

^d State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Textile Pollution Controlling Engineering Centre of Ministry of Environmental Protection, College of Environmental Science and Engineering, Donghua University, Shanghai, 201620, PR China

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ABSTRACT

Semiconductors have been successfully demonstrated as the electrolytes for solid oxide fuel cells (SOFCs) in recent years. Many such semiconductors have shown their potentials as a competent ionic conductor for fuel cell operation, indicated by the appreciable ionic conduction and electrochemical performance. In the present study, we depart from traditional electrolyte concept to introduce a new semiconductor electrolyte, Li-doped ZnO to low-operating-temperature SOFCs. The used material was synthesized via a co-precipitation method and investigated from phase structure, morphology and UV–vis absorption perspectives. Utilizing Li-doped ZnO as electrolyte layer, we found the corresponding fuel cell exhibited a remarkable maximum power density of 443 mW cm⁻² along with open circuit voltage (OCV) of 1.07 V at 550 °C, and represented a lower-temperature operation feasibility with power outputs of 138–165 mW cm⁻² at 425–450 °C. Besides, high ionic conductivities of 0.028–0.087 S cm⁻¹ and low activation energy of 0.5 eV were also found in the synthesized Li-doped ZnO at 425–550 °C. Our investigation in terms of electrochemical impedance spectra (EIS) analysis manifested that Li-doped ZnO as the electrolyte layer boosted the electrode reactions of the device, which resulted in rather small polarization resistances and eventually realized good low-temperature performances. Further study based on the rectification characteristic of Ni/Li-doped ZnO contact verified the Schottky junction formation of Li-doped ZnO with anodic Ni, which can avoid the underlying electronic short-circuiting problem. These findings show a profound significance of using doped semiconductor for the future exploitation of SOFC electrolytes.

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* Corresponding author.

** Corresponding author.

E-mail addresses: soso1979@sina.com (L. Shen), nanoguy@126.com (H. Wang).

¹ C. X. and Z. Q. contributed equally to this work.

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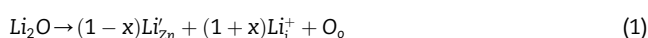
Introduction

Since the first demonstration of semiconducting electrolyte membrane in solid oxide fuel cell (SOFC) at 2011 [1], semiconductors have gained substantial interest in recent years as a new type promising electrolyte for SOFCs, because of their considerable ionic conductivity, catalytic activity and specific semiconductor properties involving electron/hole conduction and energy band structure. The successful application of semiconductors in fuel cells has led to a fresh perspective and new strategy on the development of low-temperature feasible electrolytes. Therefore, a sequence of semiconducting electrolytes have emerged in the past seven years for SOFCs [2–10]. Such new generation of electrolytes typically consist of three categories in the light of ionic conduction mode. The first category is single-phase mixed ion-electron semiconductors, such as hematite ($\alpha\text{-Fe}_2\text{O}_3$), which is well-known as a typical electronic conductor but simultaneously possesses good ionic conductivity due to the long-range-ordering structures of oxygen vacancies in specific planes [2,3,11]. The second category covers the semiconductors that gain an ionic conductive ability induced by hydrogen. Representatives are $\text{LiAl}_{0.5}\text{Co}_{0.5}\text{O}_2$ and SmNiO_3 , which can transit from semiconductors to proton conductors in fuel cell operational atmosphere [4,5]. The third one includes a number of mixed semiconductor-ionic conductors that relying on hetero-phase interfacial conduction [6–9], such as a composite of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and $\text{Ca}_{0.04}\text{Ce}_{0.80}\text{Sm}_{0.16}\text{O}_{2-\delta}$ (SCDC), which reveal an extraordinarily high ionic conductivity of 0.188 S cm^{-1} at $600\text{ }^\circ\text{C}$ that primarily originates from the LSCF/SCDC interface regions [8,10]. It turns out that these semiconductors are all capable to support a low-temperature operation of SOFCs with promising performances when serve as the electrolyte layers.

Different from conventional electrolyte concept of using ions conductive but electrons insulating materials, these explored semiconducting electrolytes possess multiple transport paths for oxygen ions, protons as well as electrons/holes. More importantly, the semiconducting electrolytes are able to form Schottky junction and/or p-n heterojunction with other components under fuel cell conditions, which separate electrons and holes to prevent internal short circuit or electrochemical leakage of fuel cell [12,13]. Consequently, the corresponding fuel cell devices can benefit from such mixed conduction characteristic to attain a significantly activated electrode reaction at the membrane/electrode interface, instead of suffering the short circuiting problem caused by electrons [14]. Following this line, our latest study has introduced a new member, zinc oxide (ZnO) to the semiconductor electrolyte family [15]. As a typical multi-function semiconductor, ZnO has attracted enormous attention in optoelectronics and photocatalytic applications [16]. When operated in fuel cells, ZnO electrolyte exhibited a decent ionic conductivity of 0.09 S cm^{-1} at $550\text{ }^\circ\text{C}$, which enabled the fuel cell to achieve encouraging power densities of $158\text{--}482\text{ mW cm}^{-2}$ at $450\text{--}550\text{ }^\circ\text{C}$. These results are comparable to the newly reported thin film SOFCs using purely ionic conducting yttria-stabilized zirconia (YSZ) electrolyte deposited by atomic layer deposition [17,18]. The initial

demonstration of ZnO in SOFC therefore gives a new electrolyte view from semiconducting and physical aspect to develop advanced electrolytes based on multi-function semiconductor.

It has been pointed out that the substitution of Zn^{2+} by metal ions in ZnO crystal would significantly affect the concentration of the oxygen vacancies, interstitial Zn and Zn vacancies, which causes variations to the concentration and mobility of carrier, and the type of semiconductor [19,20]. This would probably lead a higher ionic conduction and consolidated junction effect to the materials. Thereby, it can be anticipated that a promoted functional material can be obtained from ZnO by doping approach for fuel cell electrolyte membrane uses. Lithium (Li) has been frequently used for doping ZnO as it can be readily incorporated into ZnO. There have been a few reports on the synthesis and semiconducting properties of p-type ZnO doped with Li [21,22]. The process of doping is commonly explained in a Kröger-Vink notation (1) as [21]:



in which, Li^+_{i} and Li'_{Zn} represent Li occupying of an interstitial site and a substitutional site in ZnO lattice, respectively, and O_o is oxygen on lattice site. In the present study, to further optimize the performance of ZnO-based fuel cell, a new electrolyte candidate Li-doped ZnO (LZO) was synthesized by a facile co-precipitation method, and sandwiched between two $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_{2-\delta}$ (NCAL) electrodes to assemble fuel cell devices. Particular attentions with respect to the material properties were given to the phase structure, particle morphology and ultraviolet–visible (UV–vis) absorption perspectives. The electrochemical performances of the corresponding SOFCs were investigated based on current-voltage (I–V) characteristics and electrochemical impedance spectra (EIS) measurements. The junction effect correlated to Li-doped ZnO was also studied to explain the high open-circuit voltages (OCV).

Experimental section

The used LZO was synthesized via a co-precipitation method aiming at reaching a chemical composition of $\text{Li}_{0.15}\text{Zn}_{0.85}\text{O}$. The precursors were zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), lithium nitrate (LiNO_3), and sodium carbonate (Na_2CO_3) of analytical grade without further purification. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and LiNO_3 were dissolved in deionized water to form a 1 M solution in a metal ions mole ratio of $\text{Li}:\text{Zn} = 15:85$. The resultant solution was vigorously stirred at 600 rpm and heated at $60\text{ }^\circ\text{C}$ for 0.5 h. Subsequently, a 1 M Na_2CO_3 solution as the precipitation agent was added into the above nitrate solution under continuous magnetic stirring for 1 h to form a white precipitate, followed by drying the product at $120\text{ }^\circ\text{C}$ for 3 h. The resultant precipitate was then filtered and washed with deionized water for three times, followed by further drying at $120\text{ }^\circ\text{C}$ overnight. Finally, the dried precursors were sintered in air at $600\text{ }^\circ\text{C}$ for 2 h to obtain white powders, which is then collected and ground in an agate mortar to form the eventual sample $\text{Li}_{0.15}\text{Zn}_{0.85}\text{O}$. Since the

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