



Short communication

Detonation nanodiamond introduced into samarium doped ceria electrolyte improving performance of solid oxide fuel cell



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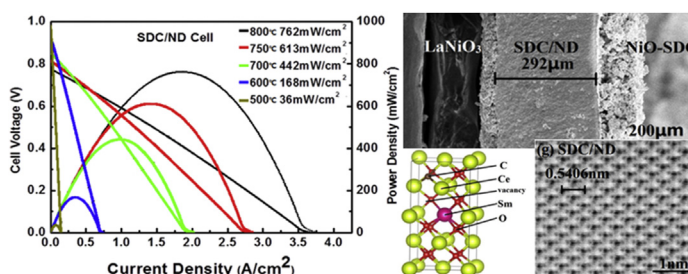
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HIGHLIGHTS

- The high performances of DNDs introduced into the SDC electrolyte.
- DNDs increases electrolyte grain size to enhance the ionic conductivity in grain internal.
- DNDs caused an increasement of the number of Ce^{3+} , generated more oxygen vacancies.
- Power density of SOFC with SDC/ND electrolyte reaches 762 mw cm^{-2} at $800 \text{ }^\circ\text{C}$.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel electrolyte materials of introducing detonation nanodiamond (DNDs) into samarium doped ceria (SDC) is reported here. 1%wt. DNDs doping SDC (named SDC/ND) can enlarge the electrolyte grain size and change the valence of partial ceria. DNDs provide the wider channel to accelerate the mobility of oxygen ions in electrolyte. Larger grain size means that oxygen ions move easier in electrolyte, it can also reduce the alternating current (AC) impedance spectra of internal grains. The lower valence of partial Ce provides more oxygen vacancies to enhance mobility rate of oxygen ions. Hence all of them enhance the transportation of oxygen ions in SDC/ND electrolyte and the OCV. Ultimately the power density of SOFC can reach 762 mw cm^{-2} at $800 \text{ }^\circ\text{C}$ (twice higher than pure SDC, which is 319 mw cm^{-2} at $800 \text{ }^\circ\text{C}$), and it remains high power density in the intermediate temperature ($600\text{--}800 \text{ }^\circ\text{C}$). It is relatively high for the electrolyte supported ($300 \text{ } \mu\text{m}$) cells.

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1. Introduction

Solid oxide fuel cells (SOFCs), one of the most versatile clean energy technologies, possess high conversion efficiency and fuel

flexibility of converting chemical energy to electrical energy. The function is high-efficiency via molecular O_2 reacted with electrons at cathode side to produce oxygen anions, which transports sequentially through an oxygen-ion-conducting electrolyte to the

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anode interface, and the electrons transported through outer circuit [1–3]. Much more efforts have been directed toward fabrication of high performance of SOFCs. The most mature SOFC systems, such as the Siemens-Westinghouse tubular system [4], have the electrical efficiency up to 75%. The fuel can be not only the hydrogen, but also the methane and marsh gas [5]. The electrolyte material, which is the important part of SOFC, is generally required a dense structure, high ionic conductivity, low electronic conductivity, excellent chemical stability with the fuel and oxidant, non-reaction with electrode materials, small mismatch of thermal expansion coefficient to electrodes. At present Ytria substituted zirconia (YSZ) as a traditional electrolyte, has a good mechanical strength and easy sintering properties. However, its ionic conductivity is weakness until the temperatures is above 750 °C and react with Co based cathode [6]. strontium & magnesium doped LaGaO₃ (LSGM) is a new electrolyte material with a stable performance and high ionic conductivity at intermediate temperatures [7]. Unfortunately, it is arduous to realize pure LSGM because of the possible phase transformation and complex preparation process. In comparison, samarium doped ceria (SDC) has been widely investigated and applied due to its advantages at the intermediate temperature (600–800 °C) [8]. It is stability and easy preparation. Importantly, the ionic conductivity relative to the electronic conductivity is dominated in SDC.

Recently the nanostructured solid-state ionic electrolyte, coined as nanoionics [9,10], has become a hot research, due to the advanced energy conversion and storage applications [11,12], such as 1D nanowire SDC [13]. On the other hand, the doping and substitution manners are consistent with M₂O₃ solution in CeO₂ via an oxygen vacancy compensation mechanism. The size of dopant ion has a strong function to the charged defects and binding energies. Small size dopants show greatest binding energies when the oxygen vacancy is in a first neighbor site, and large size dopants prefer the oxygen vacancy to be in a second neighbor site. Furthermore, the crossover point occurs for the dopant that exhibits the lowest binding energy and high ionic conductivity [14]. Size effects are very important in reducing the activation enthalpy for oxygen transport. It is necessary to optimize the dopant size with respect to the host ion it replaces [15].

As we know that the tetravalent elements influences the diffusivity of oxygen ions in two ways: by decreasing the migration barrier close to the solute ions and forming bound defect complexes with the oxygen vacancies [16]. For instance, the cations of Ce_{1-x}Sn_xO₂ change from 8 fold coordination to 4 + 4 coordination identified by the presence of longer Ce–O and shorter Sn–O bonds in comparison to their pure oxide, which implies that these oxygen are loosely held by the surrounding cations in the lattice and contributes to the high OSC observed for Ce_{1-x}Sn_xO₂ solid solution [17]. The formation of metastable clusters of tetravalent solute ions decreases the vacancy formation energy significantly, which is important for ceria that contains Si⁴⁺ and Ge⁴⁺ ions [16]. For the carbon, such as graphite, graphene and amorphous carbon, they have excellent performance and well applications. However, they are not suitable as doping in electrolyte because of high electronic conductivity. Another point is the sheet structure of Nano-carbon, which will impede the transportation of oxygen ions. Most important of all, carbon deposition is completely dangerous to the cathode [18] and anode [19] performance. While we research on another carbon materials, detonation nanodiamond (DNDs), which own high ion and low electronic conductivities, high temperature & corrosion resistant and catalytic activity. So DNDs have favourable properties in ceria. DNDs with diameters of 4–5 nm can produce on a large scale by a controlled detonation of carbon-containing explosives [20,21], which is much cheaper than the price of SDC. Here we report a novel introducing 1% wt. DNDs into the SDC electrolyte,

as SDC/ND. It shows the relatively better performance than pure SDC. The electrical investigation of DNDs reveals that the ionic mobility of SDC electrolyte strengthens the double, and consequently the power of SOFC increases twice. The SDC/ND electrolyte supporting with NiO-SDC as anode and LaNiO₃ as cathode SOFC reaches 762 mW cm⁻² at 800 °C (SDC sample is 319 mW cm⁻² at 800 °C). The DNDs doping can enlarge the grain size of SDC. It also increase the number of Ce³⁺, and thus increases the number of oxygen vacancies in the SDC electrolyte. Both of them enhance the transportation of oxygen ions in the SDC/ND electrolyte. Finally, the DNDs may provide the transportation of hydrogen proton, it makes SDC/ND into the dual ionic conduction mechanism. This new method of introducing detonation DNDs will open-up new vistas in the research for high performance of electrolyte materials for application in SOFCs.

2. Experimental section

The SDC electrolyte was synthesized by glycine-nitrate combustion method [22]. The raw materials were Ce(NO₃)₄·6H₂O (AR) of 18.454 g, Sm₂O₃ (3N) of 1.308 g, glycine (AR) of 7.072 g and HNO₃ (AR) of 1.8 ml (The Moore ratio of Ce, Sm and glycine was 7:3:15). The as-synthesized SDC powder was doped by DNDs of 1% wt. with an average size of 5 nm (denoted SDC/ND) [23]. Because the tiny DNDs can easily reaction with H₃O⁺ at low temperature and become monodisperse colloidal state, while it won't happen with DNDs of diameter larger 20 nm [24]. (we also have tried the 2%wt. doping, denoted SDC/2ND. While the mechanical strength and AC impedance spectra of SDC/2ND dramatic declined. The reason might be the existence of plentiful tiny crevices in electrolyte because of the thermal expansion difference between SDC and DNDs). The SDC sample and SDC/ND sample were both calcined at 800 °C in air for 4 h to form the perovskite structure. Then the powder was dry pressed into wafers under 6 MPa and sintered into ceramics at 1400 °C in the air. Electrical performance measurements were conducted with an electrochemical analyzer (SI1287&1260 solartron UK). AC impedance spectra were recorded in a frequency range of 0.1 Hz–1*10⁵ Hz, and the signal amplitude was 10 mV. Silver paste was used as current collector on the electrolyte and was measured in air between 800 and 650 °C in 50 °C intervals.

The microstructure was indicated by SEM (SSX-550 SAIMADZU Japan) and TEM (JEM-2200FS JEOL Japan). The crystal lattice structures of samples were showed by XRD (D/max-2550 Rigaku Japan) and HRTEM (JEM2010 JEOL Japan), and they also showed the chemical compatibility between electrolyte and electrode. The density of oxygen vacancy was improved by XPS (ESCALAB 250 Thermo Electron Corporation USA), which depends on the valence state of Ce and O elements. For the electrical properties, the electrolyte was tested by alternating current impedance spectra (SI1287&1260 solartron UK), and cell performance was tested by current-voltage and current-power density (CHI-614D CHI China). The crystal model of SDC sample and the SDC/ND sample are calculated by VASP (Vienna Ab-initio Simulation Package) code.

For the cell unit, electrolyte (thickness: 0.3 mm) supported electrodes and single cells were fabricated by scraping. The cathode materials is LaNiO₃ [25], made by sol-gel method and sintered at 1350 °C for 4 h. Then it mixed up with terpinol and ethocel. The mixture scraped on electrolyte as a circle with 6 mm diameter. Then both the electrolyte and cathode were sintered in air at 1350 °C for 4 h. The ingredients of anode was NiO-SDC [26], which including 60%wt of NiO and 40%wt of SDC. It also mixed up with terpinol and ethocel, afterwards, it scraped on the other side of electrolyte (their corresponding position) and sintered in air at 1100 °C for 4 h. Electrical performance measurements were conducted with an electrochemical analyzer (CHI-614D CHI China). AC impedance

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