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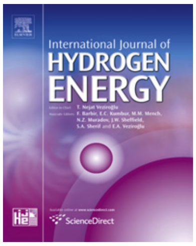

Oxide ion and proton conduction in doped ceria–carbonate composite materials

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ABSTRACT

The direct current four-probe method has been employed to investigate the conduction of oxide ion and proton in a doped ceria–carbonate composite electrolyte for fuel cells. The measurements are conducted in oxygen and in hydrogen atmospheres in the temperature range of 425–650 °C. The conductivities of both of O^{2-} and H^+ increase with the increase of carbonate content above the melting point of the carbonate. The ionic conductivities of the composite electrolytes have also been simulated using the effective medium percolation theory. The deviations between experimental results and simulated values of O^{2-} conductivity are caused by the associating effect of ceramic and carbonate phases, which leads to a higher O^{2-} migration energy through the phase interface. According to the comparison of experimental data and simulated values, the conduction mechanisms of O^{2-} and H^+ have been proposed.

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1. Introduction

Solid oxide fuel cells (SOFCs) operated in the intermediate temperature (IT, 500–800 °C) range have been developed extensively throughout the world in recent years [1,2]. The lower operating temperature, which brings a high resistance of the electrolyte layer, requires new electrolyte materials with effective ionic conductivity in the IT range [3]. Comparing to conventional ceramic oxide ionic conductors, a sort of composite electrolyte consisting of one oxide phase and one molten salt phase possess an improved overall ionic conductivity [4–6]. Among them, doped ceria (DCO)–carbonate composite electrolyte is one of the most promising materials which has attracted much attention in recent years [7–9]. The composite electrolyte is exactly the combination of the electrolytes for the solid oxide fuel cell and the molten carbonate fuel cell. The enhanced ionic conductivity brings an excellent performance of the single cell based on the composite electrolyte at 500–650 °C [10,11].

It is widely believed that the simultaneous conduction of H^+ and O^{2-} in the DCO–carbonate composite electrolyte brings excellent performances of corresponding single cells [12,13]. The observation of water condensed in both of the anode and cathode chambers during the cell operation is the earliest evidence of this opinion [14]. In addition, Zhu et al. [15] employed the composite electrolyte in a water electrolysis cell to investigate the conduction of H^+ and O^{2-}. Recently, the dual ionic conduction in the composite electrolyte was also proved by the Fourier transform infrared spectrum and Raman spectrum analysis of the electrolyte, and the H_2/O_2 electrochemical pumping method over the composite electrolyte membranes [16,17].

Until now, the mechanism of H^+ and O^{2-} conduction in the composite electrolyte has not been revealed clearly. The

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electrochemical impedance spectroscopy (EIS) is used commonly to obtain the ionic conductivity of the electrolyte [18,19]. However, the H^+/O^{2-} conduction in the DCO–carbonate composite electrolyte cannot be measured directly with the EIS, because the total conductivity obtained by EIS includes the conductivities of the ions in the carbonate simultaneously, such as Li^+, Na^+ and CO_3^{2-}, especially above the melting point of the carbonate. Other methods which based on the quantitation of the anode and cathode outlet gases, such as the electrolysis of water, the analysis of cell reaction products and gas concentration cells, cannot provide results with high precision since the composite electrolyte membrane is not dense enough [17]. Therefore, more accurate studies on the ionic conduction mechanism in the DCO–carbonate composite electrolyte are still needed.

The four-probe direct current (DC) method is widely used to measure the conductivity of a certain ion [20–22]. In this work, the four-probe DC method is employed to investigate H^+ and O^{2-} conductions in the samarium doped ceria ($Ce_{0.8}Sm_{0.2}O_{1.9}$, SDC)–$(Li_{0.52}Na_{0.48})_2CO_3$ composite materials. The obtained ionic conductivities are modeled with the effective medium percolation theory (EMPT). Based on the comparison of experimental data and theoretical values, the ionic conduction mechanisms are discussed.

2. Experimental

2.1. Preparation of the composite electrolyte

The SDC–$(Li_{0.52}Na_{0.48})_2CO_3$ composite electrolyte was prepared as described in our previous work [8]. The electrolytes with various weight ratios of the SDC powder and the carbonate are listed in Table 1. The composite electrolytes were pressed at 300 MPa followed by sintering at 650 °C for 1 h.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of the composite electrolytes were recorded using a D8 Focus diffractometer (Bruker Corp., Germany) at room temperature. The microstructure of sintered pellets was observed by the scanning electron microscopy (SEM, S-4800, HITACHI). To characterize the morphology of the SDC frame in the samples, the pellets were leached in a dilute nitric acid solution for 3 h at 80 °C to remove the carbonate in them, and then also detected by the SEM.

Table 1 – The composite electrolyte samples used in this work.

Composite name	Weight ratio SDC:$(Li_{0.52}Na_{0.48})_2CO_3$	Volume ratio SDC:$(Li_{0.52}Na_{0.48})_2CO_3$
SDC-10LN	90:10	71.5:28.5
SDC-20LN	80:20	52.7:47.3
SDC-30LN	70:30	39.4:60.6
SDC-40LN	60:40	29.4:70.6

2.3. Electrical conductivity measurement

The conductivities of the samples were measured using the four-probe DC method in the temperature range of 425–650 °C. The experimental apparatus is shown in Fig. 1. All the sintered samples were cut into a rectangular shape with a size of 5 × 2 × 25 mm for measurement. Silver wires with silver paste were applied as the probes at respective places of the samples. The DC conductivity measurements were carried out in pure H_2 or pure O_2 atmospheres, respectively. The gas flow rate was 100 ml min^{-1} (STP). A small constant direct current was applied on the sample through the two outer silver wires by an electrochemical workstation (VersaSTAT 3, Ametek). The voltage drop between the two inner silver wires was measured by another electrochemical workstation. Since the current in the voltage measuring circuit was at a level of several pA, almost the whole electrode polarization concentrated at the two outer probes and the electrode polarization at the two inner probes is negligible. Therefore, the conductivity of the sample can be calculated according to Eq. (1).

$$\sigma = \frac{IL}{US} \tag{1}$$

where σ is the conductivity of the sample (S cm^{-1}); I the current applied through the sample (A); L the distance between the two inner probes (cm); U the voltage drop between the two inner probes (V); and S the cross-sectional area of the sample (cm^2).

To subtract the possible electronic conductivity of the sample, the Hebb–Wagner measurement was also carried out under H_2 or O_2 atmospheres with Pt paste as the reversible electrode and Ag foil as the blocking electrode, as mentioned in other literatures [20]. The conductivities of H^+ and O^{2-} in the pure $(Li_{0.52}Na_{0.48})_2CO_3$ were also obtained by the four-probe DC method. The error of the conductivity measurement, which is probably caused by the disturbance of the molten carbonate phase, is around ±10%.

2.4. Model with the effective medium percolation theory (EMPT)

The EMPT is one of the most widely used models to predict the electrical conductivity of a multi-phase composite material

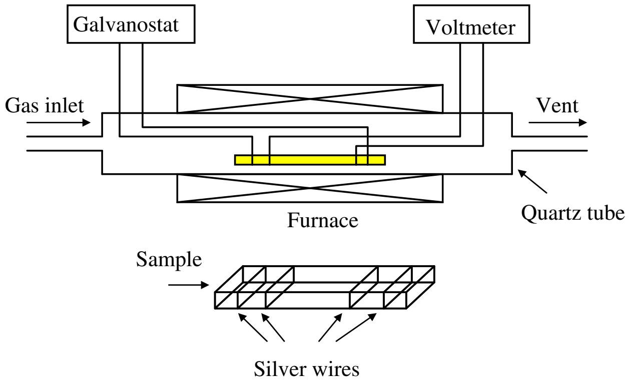

Fig. 1 – The schematic diagram of the four-probe measurement.

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