

Investigation of H⁺/O²⁻ conduction in doped ceria-carbonate composite electrolyte by four-probe method

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Solid oxide fuel cells (SOFCs) are potential substitutes for traditional power sources such as internal-combustion engines and coal plants. SOFCs using conventional electrolytes require high operating temperatures (800-1000 °C), which limits their commercialization (1). Consequently, much effort has been focused on reducing the operating temperature of SOFCs. In recent years, a series of oxide-salt composite electrolytes have been developed intensively. Among them, doped ceria (DCO)-carbonate is considered as the most promising one. It is widely believed that the simultaneous conduction of H⁺ and O²⁻ in the DCO-carbonate composite electrolyte brings excellent performances of corresponding single cells (2). The observation of water condensation in both of the anode and cathode chambers during the cell operation is the earliest evidence of this opinion. However, the mechanism of H⁺ and O²⁻ conduction in the composite electrolyte has not been revealed, and more accurate studies are still needed. In this work, the four probe DC method is employed to investigate H⁺ and O²⁻ conduction in the samarium doped ceria (Ce_{0.8}Sm_{0.2}O_{1.9}, SDC)-(Li_{0.52}Na_{0.48})₂CO₃ 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.

SDC powder was prepared by an oxalate coprecipitation technique (3). The SDC and eutectic salt of Li₂CO₃ and Na₂CO₃ (52 mol. %:48 mol. %) were mixed with various weight ratios, and then calcined at 650 °C in air for 1 h to get the composite electrolytes. The conductivities of the samples were measured using the four-probe DC method in the temperature range of 425-650 °C. 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 H₂ or pure O₂ atmospheres, respectively. A small constant direct current was applied on the sample through the two outer silver wires and the voltage drop between the two inner silver wires was measured.

Fig. 1 illustrates the comparison between the experimental results of O²⁻ conductivity in the composite electrolytes and the simulation values by EMPT. Above the melting point of the carbonate (about 500 °C), the conductivity of O²⁻ in pure carbonate is much higher than that in SDC, and both of the experimental data and the simulation results increase with the increase of carbonate content in the composite electrolytes. However, below this temperature, the O²⁻ conductivity in carbonate decreases rapidly to smaller than that in SDC, and O²⁻ conductivities in the composite electrolytes decrease with the increase of the content of carbonate. The differences between them are getting smaller with the increase of the carbonate content.

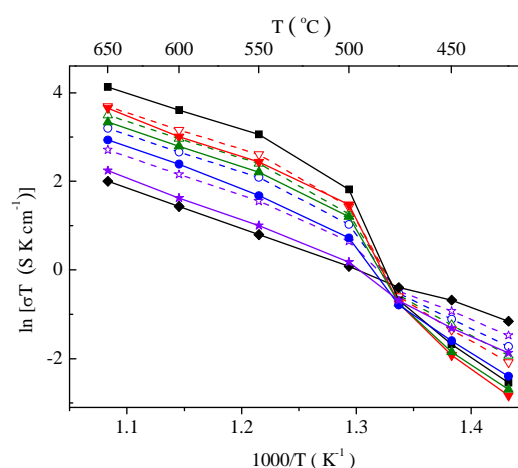


Fig. 1. Comparison of measured and simulated O²⁻ conductivities of samples with different carbonate content.

Solid line: Experimental results. Dash line: Simulated values. (◆) pure SDC; (★, ☆) SDC-10LN; (●, ○) SDC-20LN; (▲, △) SDC-30LN; (▼, ▽) SDC-40LN; (■) pure carbonate.

The experimental results and the simulated values of the H⁺ conductivity in composite electrolytes are presented in Fig. 2. The proton conductivity decreases quickly below the melting point of the carbonate, indicating a more difficult conduction of H⁺ in the solid carbonate phase than in the molten carbonate phase. With the increase of the carbonate content in the composite electrolyte, both of the experimental and simulated results enhance obviously, and the difference between these two values is reduced, implying that the EMPT model is suitable for proton conduction in SDC-carbonate composite materials with high carbonate content.

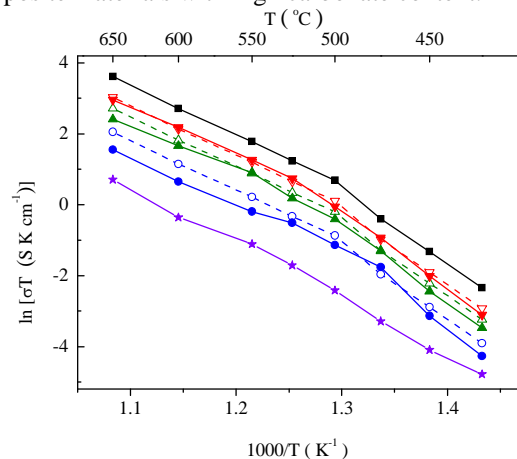


Fig. 2. Comparison of measured and simulated H⁺ conductivities of samples with different carbonate content.

Solid line: Experimental results. Dash line: Simulated values. (★) SDC-10LN; (●, ○) SDC-20LN; (▲, △) SDC-30LN; (▼, ▽) SDC-40LN; (■) pure carbonate.

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