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Electrical properties of ceria-carbonate composite electrolytes

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Abstract

Electrical conductivity and transport properties for composites consisting of samaria-doped ceria (SDC) and lithium–potassium carbonate were investigated at temperature of 450–550 °C. The conductivity at temperature above 500 °C as measured with ac impedance spectrum is 0.06–0.07 S cm^{-1}, which is about one magnitude higher than that of SDC. The conductivity increases with carbonate content and is boosted to several times when the volume fraction of carbonate reaches 30%. An abrupt change in the electrical conductivity at 500 °C infers that superionic phase transition possibly occurs in the interface between SDC and carbonate. Negligible electronic conduction, $\sim 10^{-4}$ S cm^{-1} at 500–550 °C, is observed with an ion-blocking cell. The dc transport numbers of carbonate ion and proton are determined by carbon dioxide and vapor concentration cells, respectively. Carbonate ionic transport number is about 0.67 above 500 °C whereas the protonic transport number is below 0.1. The oxygen ion transport number is calculated to be 0.23 at 550 °C and 0.31 at 500 °C.

Keywords: A. Oxides; A. Composites; C. Impedance spectroscopy; D. Electrical properties; D. Ionic conductivity

1. Instruction

Solid oxide fuel cells (SOFCs) have been developed rapidly in recent years due to their all-solid-state component, high efficiency with little pollution, and variety of fuel utilization. Although yttria stabilized zirconia (YSZ) is still the favored electrolyte for high-temperature SOFC stacks, some problems are difficult to solve such as interconnection materials and sealing. Therefore, alternative electrolyte materials that have much higher conductivity than YSZ at 500–800 °C had been developed to be applied in intermediate temperature fuel cells (ITFC). The use of ceria-based electrolytes such as $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) should in principle allow the cell-operating temperature to be lowered to around 500 °C. Doped $LaGaO_3$ (LSGM) is also attracting much attention for ITFCs that operated at temperatures around 600 °C, where the reduction of Ce^{4+} in GDC is becoming significant and the conductivity of YSZ is significantly low. Another electrolyte, ceria-salt composite, has been proved to show transport properties and fuel-cell performances that are enhanced when compared with those of single phase doped-ceria. For example, Huang et al. [1] reported a conductivity of 0.13 S cm^{-1} at 500 °C for a composite electrolyte consisted of samaria-doped ceria and Li_2CO_3–K_2CO_3. A maximum power density of 400 mW cm^{-2} was achieved at 500 °C for a single cell with the composite electrolyte. Another example is the work of Zhu et al., who reported very high current densities at intermediate temperatures for fuel cells built with such composites as electrolytes and electrodes [2–4]. Shown in

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Table 1
Ceria-salt composite electrolytes: the conductivities and maximum power densities for fuel cells that use the composite electrolytes

Composite	Conductivity (S cm^{-1})	Maximum power density (mW cm^{-2})	Reference
SDC-Li_2CO_3–K_2CO_3	0.13 (500 °C)	400 at 550 °C	[1]
SDC-Li_2CO_3–Na_2CO_3	0.02–0.9 (400–600 °C)	200–800 (400–600 °C)	[2]
GDC-alkaline earth carbonate	0.001–0.2 (400–600 °C)	200–600 (400–600 °C)	[3]
GDC-LiCl–$SrCl_2$	0.09–0.13 (500–650 °C)	260 at 550 °C, 510 at 625 °C	[5]
GDC-Li_2CO_3–K_2CO_3	–	300 at 530 °C	[6]

Table 1 is the conductivity and fuel-cell performance for some of ceria-salt composites reported in literatures. Due to the facts that water was observed at both anode and cathode sides and the open-circuit voltage was close to the theoretical value, the composite electrolyte was considered to be a mixed-conductor with both oxygen ions and proton as charge carriers [4]. The consideration is reasonable not only due to the experimental facts but also to that doped ceria is oxygen-ion conductor and oxysalt are believed to be proton conductor [7]. However, conducting mechanisms such as protonic transport number is not clear, especially the reason of conducting enhancement. In this work, the electrical conductivity of SDC-$Li_{0.62}K_{0.38}CO_3$ composite was measured with ac impedance spectra. And the dc transport numbers of proton, carbonate ions, electron were also measured to reveal the conducting mechanism in conditions similar to that of fuel cell operation.

2. Experimental

$Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) powder was prepared with an oxalate co-precipitation route using cerium–samarium nitrates as precursors [8]. Lithium–potassium carbonate, $Li_{0.62}K_{0.38}CO_3$, was formed by mixing Li_2CO_3 and K_2CO_3, and heating the mixture to 600 °C. The carbonate and SDC were then mixed with different volume ratio and ball-milled in ethanol for 24 h. After drying, it was heated to 680 °C for 40 min, quenched in air to the room temperature, and re-grounded. The grounded powder, SDC-carbonate composite, was dry pressed at 210 MPa to form 15-mm-diameter pellets, which was subsequently hardened at 600 °C for 1 h. A mixture consisting of equal amount of the SDC-carbonate composite and Ag_2O was applied to the pellets as electrodes. In order to understand the conductive mechanism of the SDC-carbonate composite, an oxide with neglectable conductivity, Sm_2O_3, was used to replace SDC. Sm_2O_3 was also prepared with the same route as SDC so that Sm_2O_3 had similar particle size with that of SDC.

The total conductivity was measured in air with impedance analysis using a Zahner IM6e electrochemical workstation. The measurements were carried out in the frequency range from 0.05 Hz to 1 MHz with a bias voltage of 10 mV. To examine ionic contribution to conduction, carbon dioxide and water vapor concentration cells were constructed. Their electromotive forces (EMFs) were measured using a Hewlett Packard 34401A multimeter. A gas consisted of 50% oxygen and 50% carbon dioxide was introduced to one side of the carbon-dioxide concentration cell, whereas a mixture gas consisted of 50% oxygen, 48.5% argon, and 1.5% carbon dioxide to the other side. In the measurement of the water vapor concentration cell, 1.9% and 6.9% vapor was carried with air to each side of the cell through a water-bubbling device. The partial pressure of the vapor was controlled by adjusting the bubbling temperature to 17.0 and 39.0 °C, respectively.

Electronic conductivities were measured by dc polarization using a Hebb-Wagner's ion-blocking cell [9] which is schematically shown in Fig. 1. The cell was tested in the ambient air so that the oxygen and carbon dioxide partial pressures were assumed to be constant. When a voltage was applied to the cell, the current decreased until the oxygen and carbon dioxide partial pressures inside the space decreased to a constant level. At this equilibrium state, the ion flow was blocked because of no electrochemical potential gradient of oxide and carbonate ion cross the sample. The measurements were performed with a potentiostat assembled to the Zahner IM6e electrochemical workstation.

3. Results and discussion

3.1. Conductive properties for SDC-carbonate composites

The electrical properties of a composite depend not only on the volume fraction of each continuous phase but also on the particular distribution of each phase. For a two-phase composite prepared by conventional ceramic processing,