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Electrical conductivity and related properties of molten carbonates coexisting with ceria-based oxide powder for hybrid electrolyte

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ABSTRACT

The electrical, thermal and structural properties of composite electrolyte containing $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) powder and $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ eutectics are investigated by AC impedance, differential thermal analysis and polarized Raman scattering spectroscopy. The system shows a dependence of the electrical conductivity upon the temperature. The transition point varies with the apparent average thickness of the liquid phase, while the activation energy, ΔE_a , remains constant at any distance from the solid phase. Higher electrical conductivity was obtained for the GDC/ $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ composite than that for $\alpha\text{-Al}_2\text{O}_3/(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$. Even in the N_2 or Air gas flow, the weight loss caused by decomposition of CO_3^{2-} ion based on Lux–Flood equilibrium was rarely observed. The symmetric stretching mode of the polarized Raman spectra shows that carbonate ion maintains its D_{3h} symmetry in the presence of ceria. A constant value of the depolarization ratio of the $\nu_1(A'_1)$ mode with regard to the apparent average thickness confirms that the symmetry of carbonate ions in the molten state is not altered by the presence of ceria powder. It was more stable than that for the system containing $\alpha\text{-Al}_2\text{O}_3$ as a reference sample. These findings contribute to the understanding of the properties of ceria-based carbonate electrolyte for intermediate temperature solid oxide fuel cells.

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1. Introduction

Molten salts permeated among highly dispersed inorganic particles are applied in various fields such as the synthesis of inorganic materials, batteries, fuel cells, crystal growth, or liquid-phase sintering process of ceramics. We have demonstrated in the past that the coexistence of molten salt electrolytes with inorganic materials, in some cases, leads to interactions between the two phases. Such interactions play a crucial role in the physical and chemical properties of the conductive ionic species [1–6]. For example in the

conventional MCFCs, insulating oxides such as $\gamma\text{-LiAlO}_2$ powder are utilized as the matrix of molten carbonate tile. Additionally, molten carbonate electrolytes find tangible applications in stationary power generation fuel cell systems such as molten carbonate fuel cells (MCFCs) [7,8], and direct carbon fuel cells (DCFCs) [9]. These molten-salts fuel cells operate at higher temperature, and still present major technical issues as well as economic challenges delaying their commercialization [10]. There is a great demand for alternative fuel cells operating at moderate temperatures. In such a system, the melting or eutectic points of carbonate

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decreases with an increase of the surface area of solid phase and the activation energy increases with the average thickness of the melt on the solid surface [3–6]. Therefore, a better understanding of the behavior of ionic species at the vicinity of the solid materials is appealing from the viewpoint of the development of advanced technologies.

$$[\text{Apparent average thickness}] = \frac{[\text{Total volume of the liquid phase (molten carbonate)}]}{[\text{Total surface area of solid phase}]} \quad (1)$$

Moreover, there is a great demand for alternative fuel cells operating at moderate temperatures. In this context, intermediate temperature (400–800 °C) fuel cells are very attractive since they combine the advantages of both high and low temperature fuel cells such as fast electrode kinetics, fuel flexibility and less degradation problems [11]. Furthermore, the tendency of lower temperatures makes the conventional ceramic fuel cells (mainly solid oxide fuel cells (SOFCs)) a leading candidate for application as stationary power plants but also the possibility to replace internal combustion engines in vehicles [12]. Ceramic fuel cells based on ceria-carbonate salt composite electrolytes have been intensively studied for the past decade due to their reliable ionic lattice conductivity and stability at intermediate temperature [13–18]. Although major challenges such as fabrication of thin electrolyte by conventional method and development of high-performance cathode materials have been addressed, less attention has been devoted to the interactions between molten salts and porous solid materials.

In this study, the electrical conductivity and related properties; such as thermal gravimetry, X-ray diffraction pattern, and Raman spectra, of composites containing ceria-based oxide (CeO_2 and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) and $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ eutectics are investigated. The ionic conductivity and the temperature dependence at the solid/melt interface in the various kinds of gas flow; such as CO_2 , N_2 , and air, are discussed. The activation energy of the electrical conductivity and the thermal behavior of the anionic species are compared with the systems containing alumina powders. The aim is to clarify the properties of molten carbonate electrolyte coexisting with ceria powder in intermediate temperature fuel cells.

2. Experimental

High purity CeO_2 powder (Nacalai Tesque, Inc.) with specific surface areas 1.5 and 6.0 m^2/g and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powder (Rhodia) with specific surface areas 6.5, 10.4 and 32.3 m^2/g were employed as the solid phase while a mixture of Li_2CO_3 and Na_2CO_3 (Nacalai Tesque, Inc.) in a ratio of 52:48 wt% was used as the liquid phase. As the reference sample, $\alpha\text{-Al}_2\text{O}_3$ (Showa Denko K. K.), and $\gamma\text{-LiAlO}_2$ (Wako pure Chemical Industries, Ltd.) powder having various kinds of specific surface area was used. The solid phase and each of the carbonate salts were annealed at 873 K for 2 h and 473 K for 48 h in N_2 gas flow, respectively prior to measurements. The dehydrated eutectic $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ was prepared by mixing

guaranteed reagents Li_2CO_3 and Na_2CO_3 at 873 K in CO_2 gas flow. A Li/Na binary carbonate and oxide powder were mixed in alumina agate mortar and molded into a tablet sample. The liquid content varied from 5–45 vol.%.

The apparent average thickness was calculated by the following equation [3–5]:

The apparent average thickness has a length dimension. If there is the anomalous phenomena near the solid/liquid interface, this number is changed in the region of the liquid phase having the certain average thickness of the liquid phase.

The measurement procedures of electrical conductivity and Raman spectra were the same as that in previous study [3–6].

AC impedance was measured under CO_2 , N_2 and air atmosphere with LCR precision meter HP 4284A using a platinum (Pt) electrode in a frequency range 20 Hz–1 MHz and the output voltage of 0.6 V. The temperature range was 673–823 K. The electrical conductivity was calculated from the Nyquist plots.

In order to check the stability of each samples, differential thermal analysis (DTA) measurements were carried out with Rigaku Thermo Plus under CO_2 and N_2 gas during all the measurements. 10 mg of ceria oxides/carbonate salts was loaded into an Au pan ($\phi = 5$ mm). The temperature range was 573–873 K and the scanning rate was 10 K/min in all cases. In order to decompose carbonates by the mixed acidic solid, a thermal gravimetry of the sample was carried out at a constant temperature above the eutectic point in N_2 gas flow for several hours.

X-ray diffraction pattern of the sample are measured before and after measurement of thermal treatment by X-ray diffractometer Rigaku TTR/S2 equipped with a scintillation detector, and a rotating Cu anode operating radiation at 50 kV and 300 mA. Using parallel beam optics formed by multilayered mirror (Rigaku, Cross Beam Optics attachment), $2\theta/\theta$ scans were carried out. A scan rate of 4° per minute was applied within the range of 20–90°.

Raman spectra were recorded with a Horiba Ramanor T-64000 spectrometer. Fig. 1 shows the optical alignment for polarized Raman spectroscopy using Horiba Ramanor T-64000 monochromator with AABSPEC #2000-A and detail schematic drawing of #2000-A. The excitation source was a 532 nm SHG of Nd:YVO₄ laser with a power of 20 mW at the sample point. The incident light was passed through a prism and perpendicularly focused onto the sample held within the high temperature cell. The scattered light was detected by Horiba CCD 2048 × 512-003 which has a resolution of 0.4 cm^{-1} . The wavenumber of monochromator was calibrated by silicon plate at 520 cm^{-1} . The back-scattered light was collected. For the polarization geometries Y(ZZ)Y (parallel position, $I_{//}$) and Y(ZX)Y (perpendicular position, I_{\perp}), a polarizer was rotated by exactly 90° in front of the slit, where X, Y, and Z are the directions of laser

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