Anomalous Properties of Molten Carbonates Coexisting with Porous Inorganic Powder

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Molten carbonates have been applied in various electrochemical applications such as molten carbonate fuel cells (MCFCs), CO2 sensors, etc. Especially, the binary eutectic molten carbonates have been utilized for MCFCs as a electrolyte in the reaction cells and have been studied for the conductivity of the molten salts and the corrosion of the materials for the electrodes and current collectors. On the other hand, the carbonates are utilized with the porous solid materials; for example, current collectors. On the other hand, the carbonates are used. Each powder was dried at 1273K for 1hour under N2 flow. For the liquid phase, several kinds of binary eutectic molten carbonates, LiKCO3 coexisting with several kinds of metal oxide powder was studied. The electrical conductivity was measured by ac impedance analysis and the activation energy was calculated. The transport phenomenon of the ionic species in molten salts are discussed. Raman spectra and the thermal analysis were also carried out in order to discuss the relationship between physicochemical properties and electrical conduction near the solid surface.

As the solid phase, α-Al2O3, ZrO2 and γ-LiAlO2 were used. Each powder was dried at 1273K for 1hour under N2 flow. For the liquid phase, several kinds of binary carbonates, LiKCO3 was used. The conductivity was calculated from ac impedance plots obtained by precision LCR meter. Activation energy of the conductivity was calculated from temperature dependence of the conductivity using Arrhenius equation. Raman spectra were obtained Horiba Ramanor T-64000 spectrometer equipped by 532 nm Nd:YAG laser. Temperature was controlled ceramic heater equipped with Rigaku Thermo Plus. These measurements were performed under CO2 gas flow.

Typical temperature dependence of the electrical conductivity for α-Al2O3/ LiKCO3 coexisting system is shown in Figure 1. Whereas the melting point is 777K, the abrupt change of the electrical conductivity was observed at ca. 730-770K. Since the Arrhenius-type temperature dependence is shown above the transition temperature, Tg, the carbonates are completely fused at the temperature range below the melting point. This tendency was emphasized for the system containing the powder with higher specific surface area. This anomalous behavior varied with the surface properties of the solid phase. Variation of activation energy with the species of solid phase is shown in Figure 2. The activation energy increased with the decrease of the apparent average thickness of the liquid phase, and the influence of the solid phase was intensive in the order of α-Al2O3 > γ-LiAlO2 > ZrO2 which is related to the surface acidity. CO3^2- stretching band (ν1) having D19 symmetry in Raman spectra was shifted toward lower wavenumber from 1056 cm^-1 to 1053 cm^-1 with the decrease of the liquid phase for the system containing ZrO2 powder and LiKCO3 melt at 780K, as shown in Figure 3. These results agree with the anomalous behaviors for other properties such as lowering of the transition point of conductivity, melting point and the decrease of the heat of fusion, i.e., the interaction between ionic species and the surface properties of solid phase.

References

Figure 1 Temperature dependence of the electrical conductivity of inorganic powder / LiKCO3 melt coexisting system.

Figure 2 Activation energy of the electrical conductivity for α-Al2O3/ LiKCO3 coexisting system.

Figure 3 Raman spectra of CO3^2- stretching band (ν1) in ZrO2 powder / LiKCO3 melt coexisting system at 780K.

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