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Anomalous Properties of Molten Carbonates Coexisting with Porous Inorganic Powder

Minoru Mizuhata, Shinsuke Suganuma, and Shigeito Deki
Department of Chemical Science and Engineering,
Faculty of Engineering, Kobe University
1-1 Rokkodai-cho, Nada, Kobe 657-8501, Japan

Molten carbonates have been applied in various electrochemical applications such as molten carbonate fuel cells (MCFCs), CO_2 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, several kinds of lithium aluminates in order to support and stabilize in the cells. In such systems, chemical and physical properties of carbonates are influenced by the interfacial interaction with the solid phase. We have been studying hetero-phase effect by the solid surface and the anomalous conduction and melting behaviors are reported for molten nitrates and carbonates.[1, 2] In this study, the electrical conductivity and melting behavior of binary molten carbonate, $LiKCO_3$ 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 and the transport phenomena 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-Al_2O_3, ZrO_2 and γ-$LiAlO_2$ were used. Each powder was dried at 1273K for 1hour under N_2 flow. For the liquid phase, several kinds of binary carbonates; $LiKCO_3$ 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 monochromator excited by 532 nm Nd:YAG laser. Temperature was controlled ceramic heater equipped AABSPEC #2000-A. Melting behaviors of carbonates in the coexisting system were observed by DTA measurement with Rigaku Thermo Plus. These measurements were performed under CO_2 gas flow.

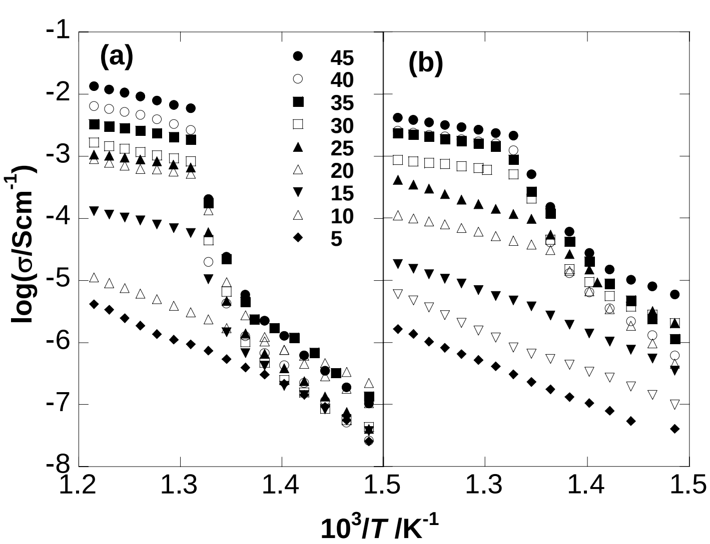

Figure 1 Temperature dependence of the electrical conductivity of α-Al_2O_3 powder /$LiKCO_3$ melt coexisting system. Specific surface area of powder: (a)5.1 m^2/g, (b)32.8 m^2/g

Typical temperature dependence of the electrical conductivity for α-Al_2O_3/ $LiKCO_3$ 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, T_t, 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-Al_2O_3 > γ-$LiAlO_2$ > ZrO_2 which is related to the surface acidity.

CO_3^{2-} stretching band (ν_1) having D_{3h} symmetry in Raman spectra was shifted toward lower wavenumber from 1056cm^{-1} to 1053cm^{-1} with the decrease of the liquid phase for the system containing ZrO_2 powder and $LiKCO_3$ melt at 780K, as shown in Figure 3. These results agree with the anormalous 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
1) A. B. Béléké, M. Mizuhata, A. Kajinami, and S. Deki, J. Colloid and Interface Sci. 268(2), 413 (2003).
2) M. Mizuhata, Y. Harada, G-J. Cha, A. B. Béléké, and S. Deki, *J. Electrochem. Soc.*, **151**, E179 (2004).

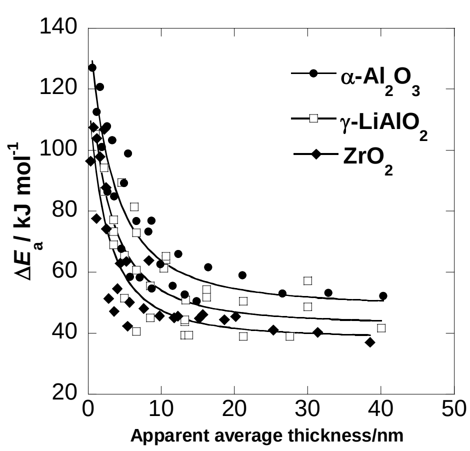

Figure 2 Activation energy of the electrical conductivity of inorganic powder / $LiKCO_3$ melt coexisting system.

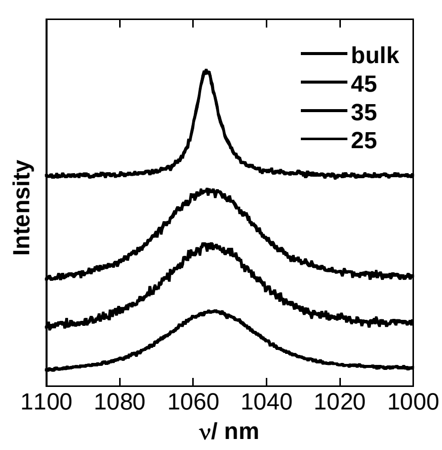

Figure 3 Raman spectra of CO_3^{2-}stretching band(ν_1) in ZrO_2 powder / $LiKCO_3$ melt coexisting system at 780K.