ELECTRICAL CONDUCTIVITY OF COEXISTING SYSTEM CONTAINING INORGANIC POWDER AND AMBIENT TEMPERATURE MOLTEN SALTS

Shigehito DEKI, Kazuo YASO, Minoru MIZUHATA,
and Akihiko KAJINAMI

Department of Chemical Science and Engineering,
Faculty of Engineering, Kobe University
1-1 Rokkodai-cho, Nada, Kobe 657-8501, JAPAN

Room-temperature molten salts (RTMS) have been studied in a viewpoint of the utilization as ionic conductors. Numerous studies have been carried out about the conductivity, stability, thermal property and its structure of various kinds of RTMS. For the utilization of the RTMS for electrochemical devices, it is necessary to be supported or stabilized in the porous solid materials or to be mixed into the solid materials. We have studied anomalous physicochemical properties of the several kinds of molten salts coexisting with the inorganic solid powder and discussed the influence of the solid phase.[1)]

In this study, the electrical conductivity was measured for the coexisting system containing the α-Al_2O_3 powder and RTMS, i. e. *n*-Propyltrimethylammonium bistrifluoromethanesulfonimide (TMPA-TFSI). The composition and temperature dependences are discussed. Also, the conductivity of the coexisting system containing the binary RTMS system HTFSI-TMPATFSI as the dissolving species was measured.

The RTMS; TMPA-TFSI was prepared by mixing the aqueous solutions of TMPAI and LiTFSI. The separated phase from aqueous LiI solution was refined by evaporation and heat-treatment.[2)] The α-Al_2O_3 powder was used as the porous solid phase. The specific surface area of the powder ranged from 1.18 – 32.8 m^2/g. These reagents were mixed in the range of the melt phase from 10-30 vol% and pressed into the alumina press. The electrical conductivity was measured by ac impedance analyzer (Frequency range; 20Hz-30MHz) at 20-50ºC. The activation energy is calculated from the ln σ -1/T plots. Also, the differential scanning calorimetry (DSC) was performed in order to observe the melting behavior of the RTMS. The binary molten salt was prepared by dissolving of HTMSI into TMPA-TFSI. Molar content of HTMSI ranged from 0-0.6. The electrical conductivity was measured at 30 vol% of the melt content.

The electrical conductivity increased exponentially as the melt content increased, and depended on the specific surface area of the powder. The conductivity showed the temperature dependence following the VTF (Vogel-Tammann-Fulcher) equation. The apparent activation energy, ΔE_a, was calculated from the differential coefficient of the ln σ -1/T plots at 30ºC. The activation energy increased with a decrease of the apparent average thickness of the melt phase (= [total volume of molten salt] / [total surface area of solid phase]) as shown in Figure 1. The increase of the value of ΔE_a was observed below ca. 30 nm of the thickness of the melt phase.

Whereas the melting point of bulk sample was observed at 25.8ºC, it decreased with the increase of the specific surface area of the solid phase as shown in Figure 2. The molar enthalpy of fusion also decreased. It is suggested that the phase transition behavior is influenced by the coexistence of the porous solid phase.

Normalized electrical conductivity calculated from the values of the conductivity of the binary systems divided by that of TMPA-TFSI is shown in Figure 3. Since HTFSI does not dissociate in the TMPATFSI and does not contribute to the conduction, the electrical conductivity decreased with the increase of the HTFSI content in the bulk system. However, in the coexisting system, the conductivity increased and the activation energy decreased with the HTFSI content up to ca 0.4. It is suggested that the HTFSI contributes the conduction near the solid phase.

A part of this study was supported by the CREST of Japan Science and Technology Corporation (JST).

References

1) S. Deki, et al., Proc. of 11th Intl. Symp. on Molten Salts, p.292 (1999).
2) H. Matsumoto, et al., *Chem. Lett.*, **2000(8)**,922.

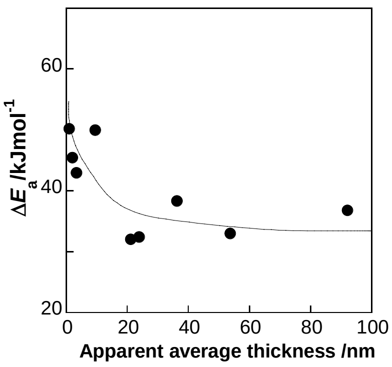

Fig.1. Variation of ΔE_a of the electrical conductivity with the apparent average thickness of the liquid phase for α-Al_2O_3 powder/ TMPA-TFSI coexisting system.

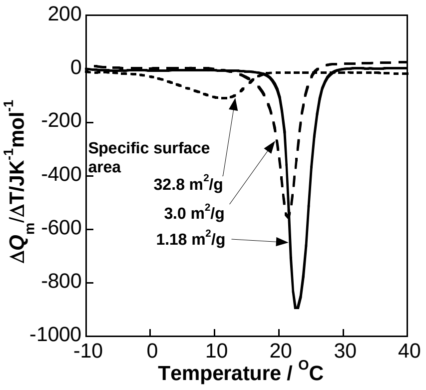

Fig.2. DSC spectra of α-Al_2O_3 powder/ TMPA-TFSI coexisting system. Melt content: 30vol%.

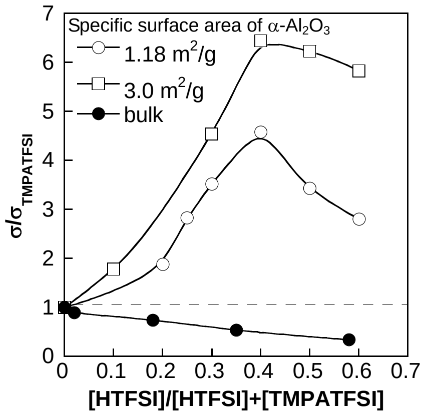

Fig.3. Variation of normalized electrical conductivity at 30°C and the value of ΔE_a with H^+ content for α-Al_2O_3 powder/ [TMPA-H]TFSI coexisting system.