ELECTRICAL CONDUCTIVITY AND MELTING BEHAVIOR OF INORGANIC POWDER / ALKALI-METAL CARBONATE CO-EXISTING SYSTEMS

Shigehito Deki, Yasuyuki Harada, Geumju Cha, 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

ABSTRACT

The electrical conductivity of the co-existing system containing inorganic powder, either γ-LiAlO₂ or MgO, and lithium carbonate was measured by the ac impedance method. The abrupt change in electrical conductivity caused by the melting of the carbonate was observed at the transition point, $T_t$. The value of $T_t$ decreased, as the melt content decreased in the co-existing system. The activation energy of the electrical conductivity, $\Delta E_a$, was calculated from the temperature dependence of the conductivity, i.e., Arrhenius plots. The value of $\Delta E_a$ increased with a decrease in the apparent average thickness of the liquid phase ($= [\text{total volume of the liquid phase}] / [\text{total surface area of the solid phase}]$) in the system. The melting behavior of Li$_2$CO$_3$ co-existing with inorganic powder was observed by means of differential thermal analysis (DTA). The endothermic peak of the fusion of Li$_2$CO$_3$ shifted toward lower temperature. The molar enthalpy of fusion, $\Delta H_m$, of the carbonate co-existing with the inorganic powder decreased, as the apparent average thickness of the liquid phase also decreased. The variations in the properties of the molten carbonate were caused by the co-existence of the inorganic powder. The influence of γ-LiAlO₂ powder was larger than that of MgO powder for both properties of conductivity and melting behavior.

INTRODUCTION

Molten carbonates have been applied in various electrochemical applications such as molten carbonate fuel cells (MCFCs), CO$_2$ sensors, etc (1). Generally, the carbonates are utilized with porous solid materials for easier handling and stabilizing. In such systems, the chemical and physical properties of carbonates are influenced by the interaction between the carbonate and the solid phase. However, there are few studies on the interaction between molten salts and porous solid materials.

In this study, the electrical conductivity and melting behavior of lithium carbonate (Li$_2$CO$_3$) co-existing with the inorganic powder, such as γ-LiAlO₂ and MgO, were measured. For the electrical conductivity, ac impedance measurements were performed for the co-existing system containing inorganic powder, γ-LiAlO₂ or MgO, and Li$_2$CO$_3$ melt
in the high content range of the solid phase. The composition dependence of the electrical conductivity, the activation energy of the conductivity calculated from the temperature dependence, and the electrical conductivity below the melting point were analyzed. The transport properties of the molten carbonates influenced by the solid phase are discussed. For the melting behavior, the thermal analysis was carried out for the lithium carbonate co-existing with the inorganic powder. The variations of the melting point and the heat of fusion of the carbonate were measured. Also, a relationship between the electrical conductivity and thermal analysis, and the effect of solid phase, are discussed.

**EXPERIMENTAL**

**Samples**

High-purity γ-LiAlO$_2$ powder and MgO powder are used as the solid phase. These reagents are annealed at 1273K for a few hours in a N$_2$ gas flow in order to remove the impurities, such as water. The particle size of the inorganic powder was measured with a transmission electron microscope (Hitachi H-7100TE). The physical properties of the powder are shown in Table 1.

A guaranteed reagent of Li$_2$CO$_3$ (Nacalai Tesque, Inc.) was used as the liquid phase. The carbonate sample was preheated at 473K for 48 hr in the air flow. The powder and carbonate were mixed thoroughly in an alumina mortar in a dry box. In order to confirm the stability of the powder during the measurement in the high temperature range, X-ray diffraction patterns of the co-existing systems consisting of the inorganic powder and carbonate were measured with a Rigaku RINT 2100 diffractometer, using CuKα radiation (40kV, 40mA) before and after the measurement of the electrical conductivity and thermal analysis. No difference between them was observed.

The content of Li$_2$CO$_3$ as the liquid phase ranged from 5 to 45 vol% in the inorganic powder/Li$_2$CO$_3$ co-existing systems. The sample for the measurement of the electrical conductivity was prepared by the molding into a tablet in an alumina press under 52 MPa for 30 min. The diameter of sample was 15 mm.

**Table 1.** Physical properties of inorganic powder.

| Samples  | Specific surface area $\text{m}^2\text{g}^{-1}$ | Average particle size $\mu$m | Roughness factor $\gamma$ |
|----------|---------------------------------|-----------------|-----------------|
| γ-LiAlO$_2$ |  |  |  |
| 1        | 3.2 | 0.5 | 1.44 |
| 2        | 9.3 | 0.2 | 1.24 |
| 3        | 19.4 | 0.1 | 1.19 |
| MgO | | | |
| 4        | 8.4 | 0.2* | - |
| 5        | 19.6 | 0.08* | - |

* Size distribution is broadened and roughness factor is not calculated.
Measurement of Electrical Conductivity

Since it is necessary to have the carbonate melt penetrate the powder sample homogeneously, the tablet sample was pre-heated to 1023 K in a CO₂ gas flow. The sample was placed in the thermostatted cell in the furnace as shown in Fig. 1. The molded sample was sandwiched between Au-Pd electrodes in the CO₂ gas flow. The ac impedance was measured over the frequency range 5 Hz - 13 MHz using a Hewlett Packard 4192A impedance analyzer. Measurements were performed in the temperature range 673-1133 K. The applied voltage between the electrodes was 0.6 V to avoid electrochemical reaction of the electrodes. The electrical conductivity was calculated from the Nyquest plots for each sample.

![Figure 1](image)

**Figure 1.** Schematic drawing of the apparatus for the electrical conductivity.

Thermal analysis

The melting behavior of the carbonates was measured by differential thermal analysis (DTA) with a Rigaku ThermoPlus thermometer. A sample was prepared by the same procedures for the conductivity measurement. The sample containing the inorganic powder and carbonate was put into a gold pan of diam. 5 mm. The temperature for the DTA measurement ranged from 773-1073 K. The scanning rate was 10 K min⁻¹. The
melting point of $\text{Li}_2\text{CO}_3$ was calculated by the method described in Ref. 2. The molar enthalpy of fusion, $\Delta H_m$, is calculated from the area of the endothermic peak assigned to the fusion of $\text{Li}_2\text{CO}_3$ in the obtained DTA curve. Prior to the calculation, a proportional relationship was confirmed between the sample weight and the area of the endothermic peak of the carbonate for $\text{Li}_2\text{CO}_3$ melt and $\gamma\text{-LiAlO}_2/\text{Li}_2\text{CO}_3$ co-existing system. This is because the value obtained is influenced by the distribution of flow of heat in the DTA measurement. It is confirmed that the proportional relationship was observed for the sample weight from 0 to 10 mg in the Au pan at 10 K min$^{-1}$ scan rate for DTA. The value of $\Delta H_m$ was obtained from Ref (3).

RESULTS AND DISCUSSION

Temperature Dependence of Electrical Conductivity

The temperature dependence of the electrical conductivity for $\gamma\text{-LiAlO}_2/\text{Li}_2\text{CO}_3$ co-existing system is shown in Fig. 2. The abrupt change in the electrical conductivity was observed near the melting point of $\text{Li}_2\text{CO}_3$ (997 K) for each system. The observed transition temperature was lower than that of the melting point of $\text{Li}_2\text{CO}_3$, and decreased as the liquid content decreased. If this phenomenon was caused by contamination from $\gamma\text{-LiAlO}_2$, which slightly dissolves into molten $\text{Li}_2\text{CO}_3$, the lowering of the melting point might well be observed (4). However, since the content of the solid phase is extremely high in these systems and the solubility of $\gamma\text{-LiAlO}_2$ is limited at each temperature, the concentration of $\gamma\text{-LiAlO}_2$ in the carbonate melt should be same (and very low, of course) in any case and the degree of lowering of the melting point should be the same; i.e., the

![Figure 2. Temperature dependence of the electrical conductivity of $\gamma\text{-LiAlO}_2$ powder/$\text{Li}_2\text{CO}_3$ melt co-existing system. Specific surface area of powder: 3.2 m$^2$g$^{-1}$.](image)

![Figure 3. Variations of $T_i$ with the apparent average thickness of the liquid phase for inorganic powders / $\text{Li}_2\text{CO}_3$ melt co-existing systems.](image)
observed transition temperature, $T_t$, should not depend on the liquid content or the specific surface area of the powder. Also, it is not a supercooling phenomenon because the conductivity measurement was carried out during heating process from room temperature. Therefore, it is considered that the lowering of the transition temperature was caused by interaction between the solid and liquid phases. In Fig. 3, the variations of the transition points of the electrical conductivities, $T_t$, with the “apparent average thickness” of the liquid phase for inorganic powder / Li$_2$CO$_3$ melt co-existing systems were shown. Here, the parameter “apparent average thickness” is regarded as the apparent thickness of the liquid layer on the surface of the solid phase. The value of the thickness was calculated from the following equation:

\[
\text{[Apparent average thickness]} = \frac{\text{[Total volume of liquid phase]}}{\text{[Total surface area of the solid phase]}}.
\]

The value of $T_t$ decreased with decrease in the apparent average thickness of the liquid phase. It was found that the effect of $\gamma$-LiAlO$_2$ is more marked than that of MgO.

Obviously, the melting of Li$_2$CO$_3$ in the system caused the abrupt change of the electrical conductivity at the transition point, because the ionic conduction in the coagulated carbonate was scarcely found. However, the electrical conductivity did not diminish even at temperatures below the melting point. Since the conductivity was much larger than that of pure $\gamma$-LiAlO$_2$ powder, as shown in Fig.2, it can be presumed that a part of the carbonate does not freeze and the conduction path is kept within the carbonate. Similar tendencies are observed in the case of the co-existing systems containing $\alpha$-Al$_2$O$_3$ powder and molten alkali-metal nitrates (5) and several kinds of hydrate melts (6, 7).

**Activation Energy of the Electrical Conductivity**

Since the measured conductivity showed the Arrhenius-type temperature dependence at temperatures above the transition point, $T_t$, the apparent activation energy of the electrical conductivity, $\Delta E_a$, was calculated by the Arrhenius equation. The variations of $\Delta E_a$ with apparent average thickness for the systems

![Figure 4. Variation of the activation energy of the electrical conductivity with the apparent average thickness of the liquid phase for inorganic powder / Li$_2$CO$_3$ co-existing system.](image-url)
systems containing the inorganic powder and Li₂CO₃ melt are shown in Fig.4.

The value of $\Delta E_\text{a}$ increased with decrease in the apparent average thickness of the liquid below 40 nm thickness. It is here suggested that the electrical conduction of the

![Figure 5. DTA curves for various kinds of $\gamma$-LiAlO₂ powder / Li₂CO₃ co-existing systems. Specific surface area of the powder: (a) 3.2 m²g⁻¹, (b) 9.3 m²g⁻¹, and (c) 19.4 m²g⁻¹.](image)

Electrochemical Society Proceedings Volume 99-41 297
carbonate was influenced by the solid phase. The decrease of the liquid phase and the increase of the specific surface area of the solid phase strengthen the influence of the solid phase. The increase of the $\Delta E_a$ value was observed at 10 nm of apparent average thickness for MgO powder /Li$_2$CO$_3$ system, whereas it is observed at ca. 40 nm for $\gamma$-LiAlO$_2$ powder /Li$_2$CO$_3$ system. It is suggested that the influence of the solid phase is caused not only by the specific surface area or porosity but also by chemical properties of the solid surface.

**Melting Behavior of Lithium Carbonate Co-existing with Inorganic Powder**

The DTA curves for the system containing $\gamma$-LiAlO$_2$ powder and Li$_2$CO$_3$ are shown in Fig. 5. The endothermic peak assigned the fusion of Li$_2$CO$_3$ was observed for each system. However, the temperature range of the peak shifted toward the lower temperature with an increase in the specific surface area of the inorganic powder as the solid phase. It is suggested that the melting point was lowered as the surface area of porous solid phase increased. In the case of the system containing the same powder, the endothermic peak increased in intensity with increase in the melt content. However, each endothermic peak followed the similar lines at the starting of melting. Also, the intensity of the endothermic peak is not completely proportional to the melt content. Typically, the endothermic peak did not appear for the system containing 5% of carbonate on the powder having large surface area, 19.4 m$^2$g$^{-1}$, as shown in Fig. 5(c). It is suggested that the melting behavior started from the nearest region on the solid phase and the heat of fusion decreased with a decrease of carbonate content in the co-existing system.

![Figure 6. Relationship between the transition point of the electrical conductivity, $T_i$, and the melting point of the carbonate, $T_m$, for the co-existing system containing inorganic powder and Li$_2$CO$_3$.](image)
A linear relationship between the transition point of the conductivity, $T_t$, and the melting point of Li$_2$CO$_3$, $T_m$, co-existing with the inorganic powder are observed, as shown in Fig.6. Changes in the values of $T_m$ and $T_t$ from those of bulk systems for the system containing γ-LiAlO$_2$ powder are larger than those for the system containing MgO powder. Although changes caused by the coexistence of the porous solid phase follow the similar relationship for the ionic conduction and melting behavior for both systems, the influence of the solid phase depends on their surface properties.

Molar Enthalpy of Fusion of Lithium Carbonate Co-existing with Inorganic Powder

The variation of the molar enthalpy of the fusion, $\Delta H_m$, for Li$_2$CO$_3$ co-existing with γ-LiAlO$_2$ powder is shown in Fig. 7. The value of $\Delta H_m$ decreases as the apparent average thickness decreases, even when two kinds of powder, having different specific surface areas, were used. These results support the existence of the non-frozen part in which the electrical conduction occurred in the melt phase. Typically, the value of the molar enthalpy, $\Delta H_m$, became 0 kJ mol$^{-1}$ for the co-existing system containing 10 vol% of the Li$_2$CO$_3$ and γ-LiAlO$_2$ powder of 19.4 m$^2$ g$^{-1}$. In this case, the electrical conductivity showed the Arrhenius type dependence and the transition point was barely observed. In this sample, the average thickness of the liquid phase was ca. 5 nm. It is suggested that the phase transition of the molten carbonate was influenced by the solid phase. The non-frozen part of the melt phase is stabilized and the conduction of the ionic species still remained in the vicinal liquid layer on the solid phase below the melting point.

![Figure 7. Variation of molar enthalpy of fusion of Li$_2$CO$_3$ co-existing with γ-LiAlO$_2$ powder with apparent average thickness.](image-url)
CONCLUSIONS

The electrical conductivity and melting behavior of systems containing inorganic powder and lithium carbonate was discussed. The melting point, $T_m$, of Li$_2$CO$_3$ lowered, due to the coexistence of the solid phase. The transition point of the electrical conductivity was also lowered and corresponded with the melting point. Above the melting point, the activation energy of the electrical conductivity, $\Delta E_a$, increased with a decrease in the apparent average thickness of the liquid phase. The molar enthalpy of fusion, $\Delta H_m$, decreased with a decrease in the apparent average thickness of the liquid phase. In such cases, the electrical conductivity does not diminish, even at temperatures below the melting point. It is suggested that the non-frozen part of the melt phase is stabilized and the conduction of the ionic species still remained in the vicinal liquid layer on the solid phase below the melting point. Consequently, the anomalous phase of the molten salts is observed near the solid surface. It is expected that molten salts are applied as the ionic conductor by the coexistence with the porous solid materials as the quasi-, or semi-solid materials in the temperature range below the melting point.

ACKNOWLEDGMENTS

Part of this study was supported by the Proposal-Based New Industry Creative Type Technology R&D Promotion Program from NEDO of Japan, Grant-in Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan. MM is supported by Kao Foundation for Art and Sciences, and Kinki Invention Center for this study.

REFERENCES

1. F. Salam, W. Weppner, P. Birke., *Electrochem. Solid State Lett.*, 2, 201(1999).
2. K. Kambe, “Netsu Bunseki (Thermal Analysis)” (in Japanese), p. 72, Kodansha Scientific, Tokyo (1975).
3. G. J. Janz, *J. Phys. Chem. Ref. Data*, 17, Suppl. 2, 159 (1988).
4. H. Sotouchi, Y. Watanabe, T. Kobayashi, and M. Murai, *J. Electrochem. Soc.*, 139, 1127 (1992).
5. S. Deki, T. Utsumi, M. Taira, M. Mizuhata, and A. Kajinami, *Molten Salts Forum*, 5-6, 175 (1998).
6. S. Deki, M. Mizuhata, A. Kajinami, and Y. Kanaji, *J. Chem. Soc. Faraday Trans.*, 89, 3805 (1993).
7. S. Deki, M. Mizuhata, and A. Kajinami, in *Molten Salts/1998*, P. Trulove, H. DeLong, G. R. Stafford, and S. Deki, Editors, PV 98-11, p. 513, The Electrochemical Society Proceedings Series, Pennington, NJ (1998).