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LETTERS

Infrared Spectroscopy of Molten LiCl−KCl under Hydrogen Gas Atmosphere

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Infrared spectroscopy of molten LiCl−KCl eutectic melt under several hydrogen pressures at 673 K provided an absorption band in the wavenumber region of 1300−1600 cm^{-1}. This absorption band is ascribed to the vibration of a Li−H interaction in the melt. On the other hand, the absorption bands ascribed to a K−H interaction and H−Cl interaction were not observed. The existence of the Li−H interaction shows a strong attractive force between dissolved hydrogen atoms and Li$^+$ ions in the melt.

1. Introduction

The state of the dissolved hydrogen in molten salts is interesting from scientific points of view. In particular, the interactions between the dissolved hydrogen and the other ions in molten salts are interesting because the interactions affect the thermodynamic and transport properties of the dissolved hydrogen in the melts.[1] The interactions also affect the rate of the hydrogen electrode reactions since the solvation reorganization at the electrode surface influences the charge-transfer rate.[2] The state of dissolved hydrogen is also worth studying from engineering points of view. An example is a molten carbonate system since such interactions affect the gas diffusion anodes for molten carbonate fuel cells. Another example is a molten LiF−KF−NaF system since tritium behavior in the melts is important to develop the molten salt breeder reactor and molten salt blankets for the nuclear fusion reactor.[3]

In this article, we focus on dissolution of hydrogen in a molten LiCl−KCl system for the following reason. The hydride ion (H$^-$) has been reported to exist in molten alkali metal halides containing alkali metal hydrides, such as a molten LiCl−KCl−LiH system.[4,5] In these systems, the following hydrogen electrode reaction involving H$^-$ ion exists:

$$\frac{1}{2}H_2 + e^- \rightleftharpoons H^- \tag{A}$$

There are promising applications that use the hydrogen electrode reaction involving the H$^-$ ion, e.g., the Li−H$_2$ thermally regenerative fuel cell[4,6] and SiH$_4$ production in molten alkali halides.[7−9] The interactions between the dissolved hydrogen and the other ions possibly affect the reaction. However, there has been no study on the interactions in molten LiCl−KCl systems. To investigate such interactions, infrared spectroscopy is appropriate.

Hence, the purpose of this article is to clarify the interactions between the dissolved hydrogen and other ions such as Li$^+$, K$^+$, and Cl$^-$ ions in molten LiCl−KCl using infrared spectroscopy.

2. Experimental Section

All chemicals were anhydrous reagent grade. LiCl and KCl (99% each, Wako Pure Chemical Co., Ltd.) were well-mixed into eutectic composition (LiCl/KCl = 0.585:0.415/mole fraction) in a high purity alumina crucible (SSA-S, 99.5%, Al$_2$O$_3$, Nikkato Co., Ltd.) and dried in a furnace under vacuum at 473

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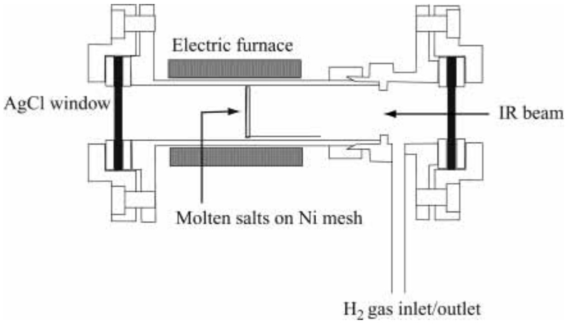

Figure 1. Schematic diagram of a high-temperature IR cell.

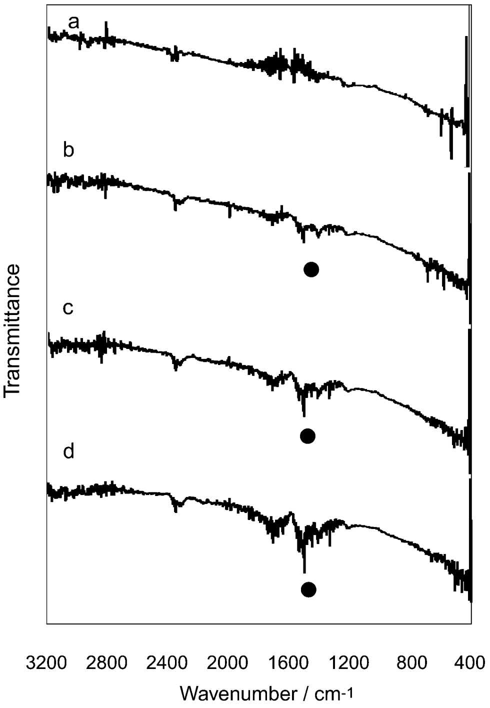

Figure 2. FT-IR spectra of molten LiCl−KCl under H_2 gas atmosphere when H_2 pressure was increased. (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0 atm at 673 K.

K for at least 24 h. After that, it was melted at 673 K. A high-temperature IR cell is shown in Figure 1. The IR cell consists of a SUS-316 body with a pair of AgCl windows. Ni mesh (99%, 10 mm × 20 mm, 20 mesh, Nilaco Corp.) was used to hold the molten salts. The molten salt was attached to the Ni mesh by immersing it into the melt in the crucible, and then the Ni mesh was installed in the IR cell. The preparation of the melt, immersion, and installing of the Ni mesh were performed in an argon glovebox with gas circulating purifier, where H_2O and O_2 contaminations were both less than 1 ppm. The cell was evacuated to 0.02 Torr, and then H_2 gas was introduced to control hydrogen pressure by increasing and decreasing the total pressure inside the cell. The body of the cell was maintained at 673 K. A chromel−alumel thermocouple was used for the temperature measurement. The IR spectra were recorded at 4 cm^{-1} resolution by BIO-RAD FTS-155. The background was measured for the Ni mesh without molten salt in the evacuated IR cell at 673 K.

3. Results and Discussion

IR Spectra. Figure 2 shows IR spectra of molten LiCl−KCl under hydrogen gas atmosphere when the pressure was increased. Figure 3 shows IR spectra of molten LiCl−KCl under hydrogen gas atmosphere when the pressure was decreased. The absorption band around 500 cm^{-1} is ascribed to the vibration of a short-lived Li−Cl interaction.[10] In Figure 2, intense absorption bands were observed at 1300−1600 cm^{-1} for molten LiCl−KCl under hydrogen gas atmosphere (spectra b−d) in contrast to molten LiCl−KCl under vacuum (spectrum a). In Figure 3, the similar behavior was observed except that a weak band was observed in the melt under vacuum (spectrum a). Dissolved hydrogen described later seems to remain in this case. Sharp peaks observed at 1400−1900 cm^{-1} for all spectra resulted from atmospheric water in the IR beam path between the IR cell and spectrometer.

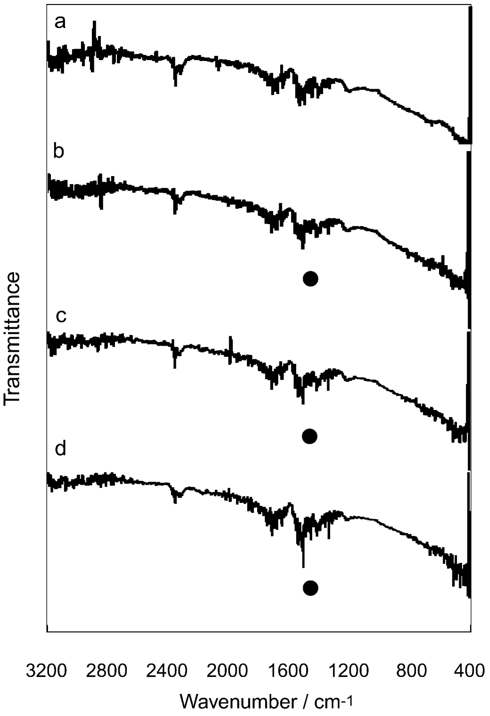

Figure 3. FT-IR spectra of molten LiCl−KCl under H_2 gas atmosphere when H_2 pressure was decreased. (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0 atm at 673 K.

The Absorption Bands of a Li−H Interaction. Comparison of the spectra under hydrogen gas atmosphere with that under vacuum shows that the absorption bands at 1300−1600 cm^{-1} originate from the dissolved hydrogen in the melts. The decrease of the transmittance according to the increase of hydrogen gas pressure supports the correlation between the bands and dissolved hydrogen. The increase in the transmittance with the decrease of hydrogen gas pressure also supports this correlation. The existence of the bands shows the interaction between the dissolved hydrogen and ions such as Li^+ ion, K^+ ion, and Cl^- ion in the melt since a hydrogen molecule is IR inactive in itself. The band in 1300−1600 cm^{-1} overlaps the reported region of the vibrational modes of a LiH molecule in the gas phase.[11] The band is not ascribed to the vibration of a K−H interaction, which is expected between 400 and 800 cm^{-1}.[10] The band is also not ascribed to the vibration of a H−Cl interaction since a vibrational mode of H−Cl interaction in liquid phase was reported to exist around 2800 cm^{-1}.[12] Here, the band is not associated with an oxide ion from impurities such as H_2O and O_2 since the absorption bands of Li−O[13−15] and K−O[16,17] have not been reported in this region. The band in 1300−1600 cm^{-1} is therefore ascribed to the vibration of a Li−H interaction. This interaction is reasonable since the vibrational mode of Li−H interaction in a molten LiCl−KCl−LiH system was reported in 1400−1500 cm^{-1}.[10] The existence of the Li−H interaction shows a strong attractive force between the hydrogen atom and the Li^+ ion. The strong electrostatic field around the Li^+ ion due to its small ionic radii may easily induce a negative charge in hydrogen atoms and then attract. Such effects were reported for Ar and CO_2 in alkali metal halides.[18,19] The absences of the K−H and H−Cl interactions may result from the weak electrostatic field around the K^+ ion and Cl^- ion due to their large ionic radii. According to the strong attractive force between hydrogen atom and Li^+ ion, hydrogen gas is likely to dissolve chemically into the melt.

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