

Chemical Reaction Complex Processes Research Section

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1. Introduction

In this research section, we study electrochemistry and materials science. We also apply them to the development of new material production methods, new metal plating processes, and new rechargeable batteries.

In this fiscal year, we have researched a new water electrolysis method using hydrate melts, a titanium film plating process using molten salts, and dual-carbon batteries using ionic liquids.

2. Development of New Water Electrolysis Method Using Hydrate Melts

Alkaline water electrolysis (AWE) is currently one of the primary commercial methods for water electrolysis. At the commercial scale, AWE typically uses an electrolyte consisting of a 20–40 wt% KOH aqueous solution and operates at temperatures ranging from 70 to 90 °C under pressures below 30 atm. Here, conducting AWE at higher temperatures is believed to offer numerous advantages. Operating AWE at high temperatures offers several advantages, including a reduction in the theoretical decomposition voltage due to thermodynamic effects, a reduction in overvoltage at the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) due to kinetic effects, and a decrease in ohmic losses in the electrolyte. Despite these anticipated benefits, there are very few research reports on AWE at temperatures above 150°C. This is because the vapor pressure of conventional KOH aqueous solutions becomes too high at high temperatures.

To improve the efficiency of AWE, this study focused on molten NaOH–KOH hydrates (NaOH : KOH : H₂O = 9 : 61 : 30 mol%) in the temperature range of 100–200 °C [1]. We investigated the behavior of the HER and OER on a Ni electrode under atmospheric pressure. Fig.1 shows the obtained liner sweep voltammograms for (a) HER and (b) OER at 100, 120, 150, 180, and 200 °C. For comparison, the results obtained in 30 wt% KOH aqueous solution at 80 °C are also plotted. As can be seen, both HER and OER exhibit a significant decrease in overpotential as the temperature rises. The total overpotential for HER and OER was compared to the value of 1133 mV obtained in a 30 wt% KOH aqueous solution at 80 °C and 500 mA cm⁻². The total overpotentials of the NaOH–KOH hydrate melt at 200 °C and current densities of 500

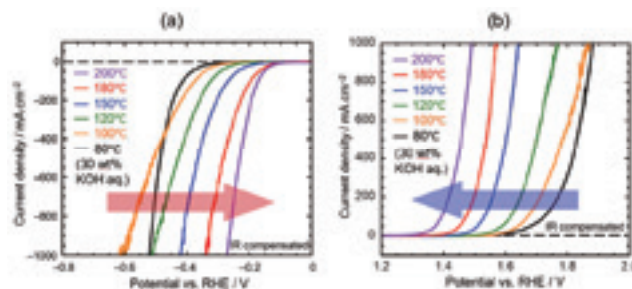


Fig. 1. Linear sweep voltammograms for (a) HER and (b) OER on a Ni electrode in the NaOH–KOH hydrate melt at 100, 120, 150, 180, and 200 °C, and in 30 wt% KOH aqueous solution at 80 °C. Scan rate: 10 mV s⁻¹.

and 1000 mA cm⁻² were 545 and 619 mV, respectively. Thus, the reduction rates in overpotential were calculated to be 52% and 45%, respectively. In conclusion, water electrolysis using NaOH–KOH hydrate melt shows promising potential for significantly improving energy efficiency even at higher current densities compared to conventional AWE.

3. Effect of F⁻ Ion Concentration on Electrodeposition of Ti Films in LiCl–LiF Molten Salt

Titanium (Ti) possesses excellent specific strength, corrosion resistance, and heat resistance, but its broader application is hindered by high production costs and processing difficulties. To overcome these challenges, we aimed to electrodeposit Ti films onto easily processable metal substrates. While chloride- and fluoride-based molten salts are typically used for Ti electrodeposition, fluoride-containing baths generally yield smoother films. Although it is known that increasing the molar ratio of F⁻ to Ti²⁺ results in smaller particle sizes in electroplated Ti, the specific role of F⁻ ions in the formation of smooth films remains unclear [2]. Therefore, in this study, we investigated the effect of F⁻ concentration on Ti film electrodeposition by varying the amount of LiF added to a LiCl–TiCl₂ molten salt at 923 K.

In an Ar glove box, TiCl₂ (1.0 mol%) and Ti powder (1.0 mol%) were added to molten LiCl at 923 K. Electrodeposition was conducted by galvanostatic electrolysis using a Ni electrode. LiF was added to the molten salt to achieve LiCl:LiF molar ratios of 80:20 and 60:40. Fig. 2

shows the optical, surface, and cross-sectional SEM images of the electrodeposited samples. Deposits with a metallic luster were obtained at all concentrations, but their appearance varied depending on the amount of LiF added. While black deposits were observed at a LiCl:LiF ratio of 100:0, gray deposits were observed at ratios of 80:20 and 60:40. Surface SEM observations revealed that granular deposits were present up to a LiCl:LiF ratio of 80:20, but at a ratio of 60:40, no granular deposits were observed; instead, Only large crystals that had grown in a film-like form were observed. Cross-sectional SEM observation confirmed the formation of a Ti film under all conditions; however, a particularly dense and thick film was obtained at LiCl:LiF = 60:40, achieving a film thickness close to the theoretical value (26.4 μm). This result demonstrates that the addition of F⁻ ions suppress the granular deposition of Ti and promotes film-like deposition.

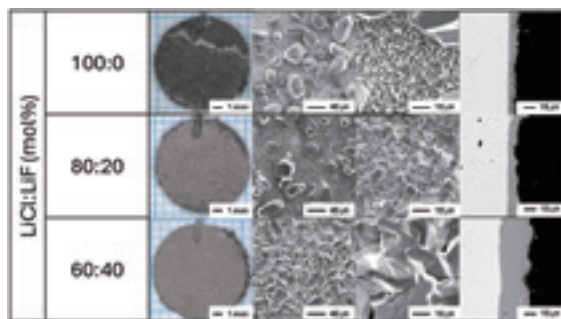


Fig. 2 Optical, surface, and cross-sectional SEM images of the samples prepared in molten LiCl–LiF–TiCl₂ (+ Ti powder) in various LiCl:LiF molar ratios at 923 K.

4. Development of Dual-Carbon Batteries Using Ionic Liquid Electrolytes

Lithium-ion batteries (LIBs) have been widely spread for portable devices such as mobile phones and laptops, and are being installed in large-scale applications including electric vehicles and stationary use. However, uneven distribution of cobalt and nickel resources used in the positive electrodes poses a potential risk of supply instability in the future. From these backgrounds, we have focused on dual-carbon batteries (DCBs), in which carbon-based materials are used for both positive and negative electrodes [3,4]. Unlike rocking-chair batteries such as LIBs, charge carriers are preserved in electrolytes before DCB operation. Ionic liquids (ILs) are promising electrolytes for DCBs because they are composed of only ions without any neutral solvents. In this fiscal year, anion intercalation behavior into graphite positive electrode was investigated by using in-situ Raman spectroscopy.

Fig. 3 shows in-situ Raman spectra of graphite positive electrode in Na[FSA]–[C₃C₁pyrr][FSA] IL electrolytes (FSA = bis(fluorosulfonyl)amide, C₃C₁pyrr = *N*-methyl-*N*-propylpyrrolidinium). Before test (pristine), a characteristic G band is observed at approximately 1580

cm⁻¹, which is known as E_{2g}(i) band originating from graphene layers without contacting to anions. After charging to the state (1), a new band appears above 1600 cm⁻¹, which is called E_{2g}(b) band, indicating the formation of graphite intercalation compounds (GICs). At a distinct potential plateau around 4.8 V, E_{2g}(b) band shifts to 1625 cm⁻¹ and E_{2g}(i) band disappears, which suggests the formation stage-2 GIC. Finally, at fully charged state (3), an additional band appears at 1640 cm⁻¹, which is assignable to stage-1 GIC. In conclusion, in-situ Raman spectroscopy is a powerful tool to clarify anion intercalation behavior into graphite positive electrode.

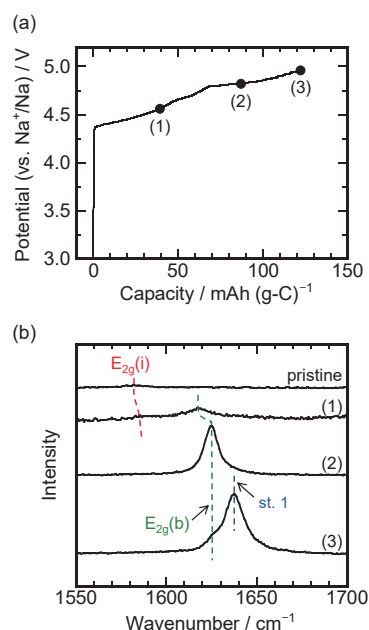


Fig. 3. (a) Initial charge curve and (b) in-situ Raman spectra of graphite positive electrodes in Na[FSA]–[C₃C₁pyrr][FSA] IL electrolyte at 298 K.

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Collaboration Works

(該当なし)

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