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 water electrolysis, new metal plating processes, and new rechargeable batteries.

In this fiscal year, we have researched a highly efficient water electrolysis using hydrate melt, a tungsten film plating process using molten salts, and dual carbon batteries using ionic liquids.

2. Development of Highly Efficient Water Electrolysis Using Hydrate Melt

Hydrogen production by water electrolysis using electricity from renewable energy sources is attracting attention. However, one of the challenges in conventional water electrolysis, including alkaline water electrolysis (AWE), is the improvement of energy efficiency. Recently, we reported that water electrolysis using an 85 wt% KOH hydrate melt (KOH:H_2O = 65:35 mol%) at 150°C significantly reduced the overpotential for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) compared to a conventional 30 wt% KOH aqueous solution (KOH:H_2O = 12:88 mol%) at 80°C [1].

In this fiscal year, we focused on a NaOH–KOH hydrate melt (NaOH:KOH:H_2O = 9:61:30 mol%), which has a lower melting point (88°C) than the KOH hydrate melt (101°C), and investigated HER and OER behavior at a Ni electrode.

Fig. 1 shows a comprehensive summary of the overpotentials for HER and OER at 200°C in the NaOH–KOH hydrate melt. This summary includes data for each current density, highlighting the total overpotential and the corresponding reduction in comparison with the KOH aqueous solution at 500 mA cm^{-2} and 80°C (total overpotential: 1133 mV). At a current density of 500 mA cm^{-2}, the total overpotential of 545 mV is 588 mV (52%) lower than that of the KOH aqueous solution at 80 °C. At an increased current density of 1000 mA cm^{-2}, the total overpotential of 619 mV is 514 mV (45%) lower. Even at 2000 mA cm^{-2}, the total overpotential of 714 mV is 419 mV (37%) lower. Water electrolysis utilizing the NaOH–KOH hydrate melt shows promising potential for significantly enhancing the energy efficiency, even at higher current densities relative to conventional AWE.

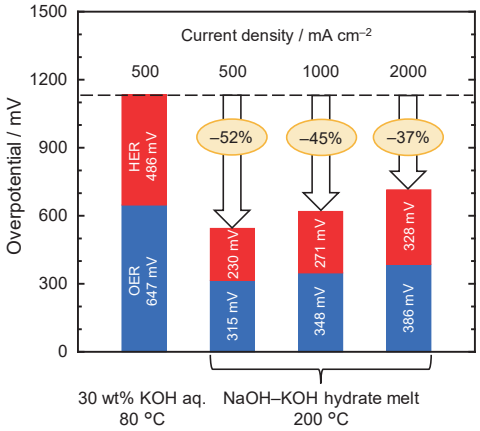

Fig. 1. Comparison of overpotential on a Ni electrode in 30 wt% KOH aqueous solution at 80°C and the NaOH–KOH hydrate melt at 200°C.

3. Development of W film Plating Process Using Molten Salt Electrolyte: Effect of O^{2-} Ion Concentration on the Crystal Structure of W Films

Tungsten (W) is a metal with superior properties, such as heat resistance, high strength, and low thermal expansion. However, its hardness and brittleness make it difficult to process into complex shapes and conventional tungsten processing methods are costly. Thus, the electrodeposition in molten salts was explored as an alternative processing method [2]. Typically, α-W was electrodeposited from molten salts. However, we have electrodeposited β-W, metastable phase of W, from CsF-CsCl-WO_3 melt at 773 K [3,4]. We predicted that oxygen content in W films, which is affected by O^{2-} ion concentration in molten salt, has an influence on the crystal structure. To investigate the effect of O^{2-} ion concentration, W electrodeposition was performed in molten CsF–CsCl at 773 K with different W sources and Li_2O concentration.

W was electrodeposited in molten CsF–CsCl–WCl_6 at −200 mA cm^{-2} for 360 C cm^{-2} and in molten CsF–CsCl–WO_3 with various added amounts of Li_2O at −4 mA cm^{-2} for 90 C cm^{-2}. Phase identification of the samples was conducted by X-ray diffraction (XRD). As shown in Fig. 2, the pre-dominant α-W formation was observed in molten CsF–CsCl–WCl_6, while only β-W formation was confirmed in molten CsF–CsCl–WO_3. Furthermore, the addition of Li_2O increased the orientation of β-W crystal

to the 111 plane. The structure of W(IV) complex ions might depend on O^{2-} ion concentration, resulting in different crystal structures of electrodeposited W and crystal orientation.

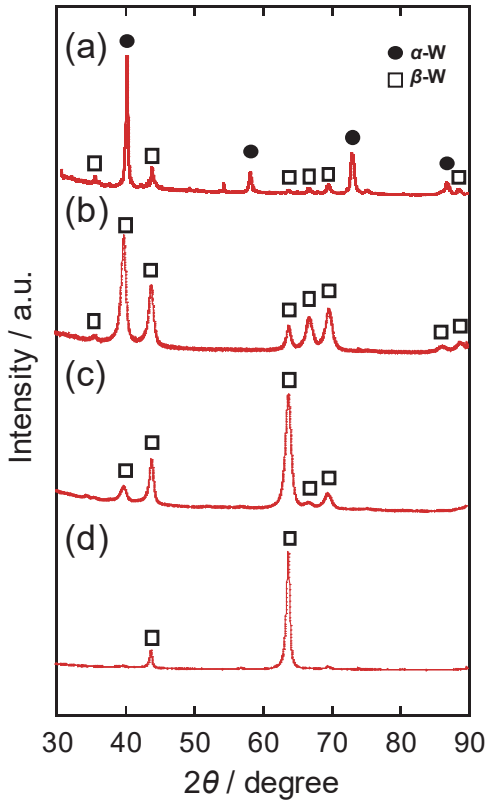

Fig. 2. XRD patterns of W films electrodeposited in molten CsF–CsCl with (a) WCl_6 (1.0 mol%), (b) WO_3 (2.0 mol%), (c) WO_3 (2.0 mol%)–Li_2O (1.0 mol%), and (d) WO_3 (2.0 mol%)–Li_2O (2.0mol%) at 773 K.

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

The large-scale electrochemical energy storage (EES) devices are indispensable for the establishment of energy supply system with intermittent renewable energy resources such as solar photovoltaic and wind power. Current lithium-ion batteries (LIBs), which are being used for portable electronic devices, have been the candidates of the EES system. However, the geological scarcity and uneven distribution of lithium and cobalt resources cannot fulfill the increasing demands of large-scale EES devices, evoking the necessity of other viable options. To address these issues, we have developed LIB alternatives such as sodium and potassium secondary batteries because sodium and potassium resources are abundant in the Earth's crust and seawater [5].

Furthermore, we recently investigated the feasibility of dual-carbon batteries (DCBs) [6,7]. Since carbon-based materials are used for both positive and negative electrodes in DCBs, the conventional metal oxide-based positive electrodes containing scarce metals like cobalt and nickel are no longer necessary. Also, we adopted ionic liquids (ILs) as promising electrolytes because DCBs are categorized in reserve-type batteries that require a large amount of charge carriers in electrolytes at the initial state. Fig. 3 shows the discharge capacities of graphite/graphite full cell with K[FTA]–[C_4C_1pyrr][FTA] IL electrolyte (FTA = (fluorosulfonyl)(trifluoromethylsulfonyl)amide, C_4C_1pyrr = *N*-butyl-*N*-methylpyrroridinium) at 298 K. In the initial 10 cycles, the discharge capacity gradually decreases from 84.0 (1st) to 69.5 (10th) mAh g^{-1}. Thereafter, the full cell shows the stable cycling performance and retains the reversible capacity of 62.5 mAh g^{-1} at 100th cycle, which indicates the feasibility of DCBs utilizing IL electrolytes.

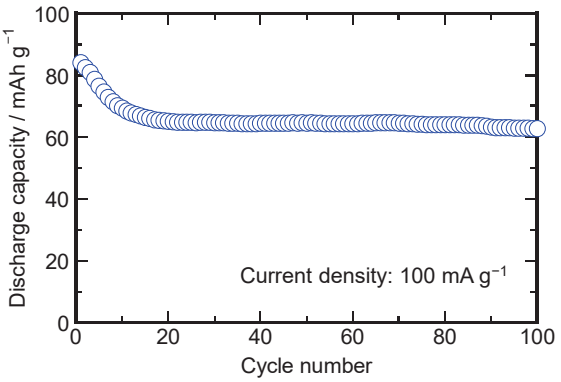

Fig. 3. Discharge capacities of graphite/graphite full cell at 298 K. Electrolyte: K[FTA]–[C_4C_1pyrr][FTA] (molar fraction: x(K[FTA]) = 0.20). Capacity and current density are expressed per the active material weight in the positive electrode.

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