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 recycling processes, new metal plating processes, and new rechargeable batteries.

In this fiscal year, we have researched a new recycling process for rare earth elements from magnet scraps using molten salt electrolysis and alloy diaphragm. We have also studied a silicon film plating process using molten salts, and dual carbon batteries using ionic liquids.

2. Development of New Recycling Process for Rare Earth Elements from Magnet Scraps Using Molten Salt Electrochemical Process and Alloy Diaphragm

Dy-doped Nd–Fe–B magnets are utilized in many important applications such as high-performance motors for electric vehicles. However, heavy rare earth (RE) elements such as Dy are difficult to supply stably. Thus, it is necessary to develop an efficient recycling process for RE elements. We have proposed a new recycling process for RE elements from magnet scraps using a molten salt electrochemical process and an alloy diaphragm [1]. Our previous studies have mainly used solid alloys as diaphragms, whereas in recent years we have focused on liquid alloys, which are expected to diffuse RE much faster than solids [2]. In this fiscal year, we investigated the electrochemical RE (RE = Nd and Dy) –alloying behaviors of Fe in molten LiF–CaF_2–NdF_3–DyF_3 systems at 1123 K.

To confirm the formation of liquid alloys, we performed potentiostatic electrolysis of the Fe plate electrode at 0.10 V vs. Li^+/Li for 1 hour. After electrolysis, the cross-section of the sample had a metallic luster and swelled into a drop-like shape, confirming the formation of liquid alloys. Fig. 1a shows the cross-sectional SEM image of the sample after potentiostatic electrolysis at 0.10 V for 5 minutes. A Nd-rich composition is confirmed. Fig. 1b shows the cross-sectional SEM image of the sample after potentiostatic electrolysis at 0.10 V for 5 minutes (1st-step), followed by changing the potential to +0.215 V for 30 minutes (2nd-step). The composition of the alloy is Dy-rich. From these results, we expect that controlling the RE dissolution potential from the liquid alloy diaphragm will enable its application as a selective permeation diaphragm for Nd.

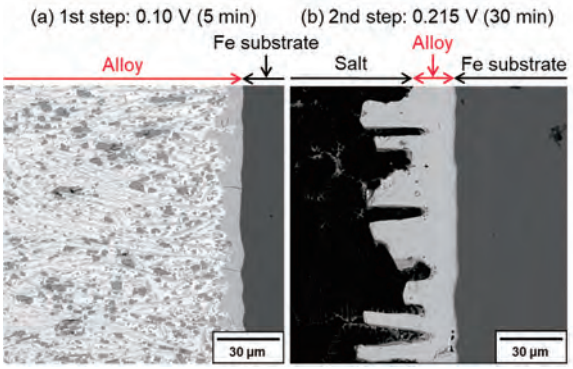

Fig. 1. Cross-sectional SEM images of the samples after potentiostatic electrolysis in molten LiF–CaF_2–NdF_3 (0.5 mol%)–DyF_3 (0.5 mol%) at 1123 K.

3. Development of Si film Plating Process Using Molten Salt Electrolyte: Fabrication of p-n Junction Si

To manufacture solar cells with fewer steps, plating n- and p-type Si directly on the substrate is a promising method. We have already proposed a new electrodeposition process of Si utilizing molten KF–KCl as an electrolyte and $SiCl_4$ as a Si ion source [3]. So far, we have reported the electrodeposition of dense and smooth Si films in KF–KCl at 923–1073 K [4,5]. Further, we have reported n-type Si electrodeposition in KF–KCl–K_2SiF_6 [6] In this fiscal year, we investigated the fabrication of p–n junction Si films by two-step electrodeposition. Furthermore, we measured the solar cells characteristics of the obtained p–n junction Si film.

We electrodeposited a p-type Si film as the first layer on a graphite substrate in KF–KCl–K_2SiF_6 with 5 mol ppm of KBF_4 at 1023 K. Subsequently, an n-type Si film was electrodeposited as the second layer in KF–KCl–K_2SiF_6 at 1023 K. Fig. 2 shows the cross-sectional SEM image of electrodeposited p-n junction Si film. A dense Si film with a thickness of around 40 μm was obtained. There was no clear boundary between p-type and n-type Si, indicating good interface formation. Fig. 3 shows the current–voltage characteristic of the electrodeposited p–n junction Si film under light illumination. A high short circuit current density (J_{sc}) of 21.1 mA cm^{-2} flowed. On the other hand, V_{oc} was much smaller than the desired

value, which might be caused by impurities in Si films. Therefore, further improvement of the electrodeposition method is needed.

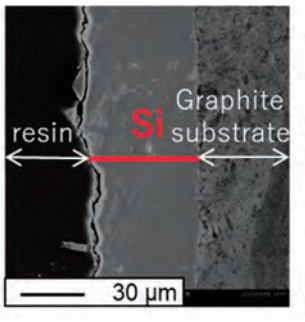

Fig. 2. Cross-sectional SEM image of the electrodeposited p-n junction Si film in KF–KCl molten salt at 1023 K.

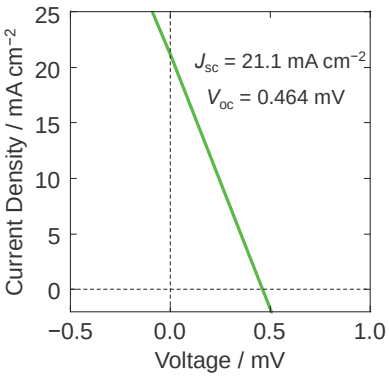

Fig. 3. A current–voltage characteristic of the electrodeposited p-n junction Si film under light illumination.

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

The establishment of carbon neutral society is one of our urgent matters, and large-scaled energy storage devices are required toward the wide spread use of renewable energy. Although current lithium-ion batteries (LIBs) are the candidates owing to their high energy densities, the usage of scarce lithium and cobalt resources and flammable organic solvents are potential barriers to further distribution as large-scaled batteries. Thus, our group has focused on novel rechargeable batteries utilizing abundant sodium and potassium resources as charge carriers and ionic liquids (ILs) as safe electrolytes [7].

We explored the feasibility of dual-carbon batteries, which is composed of carbon-based materials as both positive and negative electrodes [8]. In general, cations and anions are involved with electrode reactions at negative and positive electrodes, respectively. In the case of conventional organic solvent-based electrolytes, several issues remain unsolved such as aluminum corrosion and solvent co-intercalation. In contrast, ILs are composed of only ions, which suppress the depletion of charge carriers and side reactions at the electrode/electrolyte interface.

In this fiscal year, we investigated the anion intercalation/deintercalation behavior of graphite positive electrodes in amide-based ILs containing FSA^- or FTA^- anion (FSA = bis(fluorosulfonyl)amide, FTA = (fluorosulfonyl)(trifluoromethylsulfonyl)amide). As the results of charge–discharge tests of M/graphite (M = Li, Na, K) half-cells using various ILs, K[FTA]–[C_4C_1pyrr][FTA] was found to be a promising electrolyte. Fig. 4 shows charge–discharge curves of graphite positive electrodes in K[FTA]–[C_4C_1pyrr][FTA] IL electrolyte at 298 K. Initial charge and discharge capacities are 115 and 87.6 mAh g^{-1}, respectively, with a coulombic efficiency of 76%. Multistep voltage plateaus are observed, suggesting FTA^- intercalation between graphene layers to form graphite intercalation compounds (GICs). According to X-ray diffraction analysis, stage 1 FTA-GIC was detected at the full-charged state. After the 2nd cycle, the discharge capacities of ca. 90 mAh g^{-1} are maintained up to 50th cycle.

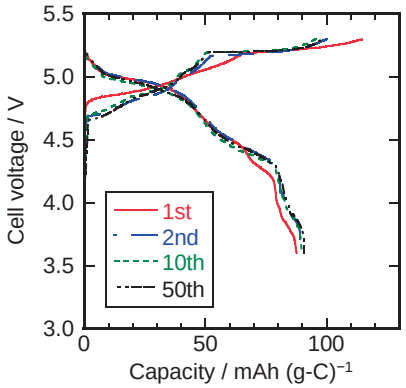

Fig. 4. Charge–discharge curves of K/graphite half-cells in K[FTA]–[C_4C_1pyrr][FTA] IL electrolyte at 20 mA g^{-1} at 298 K.

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