Advanced Energy Utilization Division

Chemical Reaction Complex Processes Research Section

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1. Introduction

In this research section, we study on electrochemistry, materials science, genetic engineering and protein engineering. We also apply them to the developments of efficient metal plating processes, new secondary batteries and efficient bioethanol production processes.

In this fiscal year, we have researched an electrodeposition processes of titanium, a potassium secondary battery using ionic liquids, and an efficient bioethanol production process using ionic liquids.

2. Development of New Plating Processes of Titanium Using Molten Salt Electrolytes

Titanium metal has excellent properties such as high specific strength, high corrosion resistance, and biocompatibility. In addition to these properties, the amount of titanium present in the earth's crust is more than 40 times greater than the commonly used copper and nickel. However, titanium is not widely used due to two problems: high cost and poor workability. Therefore, there is a need for new smelting and processing methods. One way to solve these problems is to plate titanium metal on an inexpensive substrate. Electrodeposition of titanium is a promising plating method in terms of cost and flexibility of substrate shape. Therefore, electrodeposition of titanium metal using molten salt at high temperature has been studied for a long time [1-3].

We have already reported the electrodeposition of compact, smooth and well adherent titanium films using molten salts of KF–KCl and LiF–LiCl containing Ti(III) ions at 923 K [4,5]. However, as the titanium film thickness increases, the crystal grains become larger and the surface becomes rougher. It is expected that the titanium film has a smoother surface at lower electrodeposition temperature. In the present study, we investigated the effect of temperature on the morphology and smoothness of titanium films electrodeposited in LiF–LiCl eutectic melt at 823-973 K.

Galvanostatic electrolysis was carried out at 823, 873, 923 and 973 K. The cathode current density was 100 mA cm^{-2} and the electrolysis time was 10 min. Figure 1 shows the optical and surface SEM images of the samples. All the samples have metallic luster; the 823K sample has the highest brightness and metallic luster. SEM observation of the surface shows that the grain size increases with increasing temperature. This trend can be reasonably explained by previous studies on temperature-dependent grain growth of Ti [6]; the value of Arithmetic mean height (*S*a) also increases with increasing temperature. These results conclude that at lower temperatures, smoother surface Ti films can be electrodeposited by suppressing the grain growth of Ti.

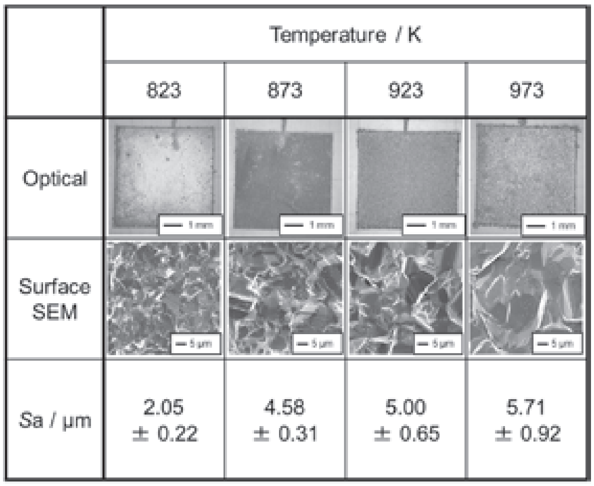

Fig. 1. Optical and surface SEM images of the samples obtained by galvanostatic electrolysis of Ni plates in molten LiF–LiCl after the addition of Li_2TiF_6 (2.0 mol%) and Ti sponge (1.3 mol%) at 823, 873, 923, and 973 K. Cathodic current density and time: 100 mA cm^{-2} and 10 min. Arithmetic mean heights (*S*a) are also listed.

3. Development of Potassium Secondary Batteries Using Ionic Liquid Electrolytes

Widespread installation of large-scaled energy storage devices is essentially required to establish the sustainable society based on renewable energy resources such as solar and wind power. Lithium-ion batteries (LIBs), which has been applied for portable electronic devices, could be candidates of large-scaled energy storage devices. However, scarce lithium resources and flammable organic solvents are used as main components of LIBs, which might be a major barrier to the further distribution. Our group has focused on potassium secondary batteries using ionic liquid electrolytes because potassium resources are abundant in the Earth's crust and ionic liquids possess high safety such as negligible volatility and nonflammability [7].

In this fiscal year, we developed several ionic liquid electrolytes for potassium secondary batteries. K[FSA]–[C_2C_1im][FSA] ionic liquid (FSA = bis(fluorosulfonul)amide, C_2C_1im = 1-ethyl-3-methylimidazolium; K[FSA] molar fraction: x(K[FSA]) = 0.20) exhibited an ionic conductivity of 10.1 mS cm^{-1} at 298 K, which was twice as high as that of K[FSA]–[C_3C_1pyrr][FSA] counterpart (C_3C_1pyrr = *N*-methyl-*N*-propylpyrrolidinium) [7]. We also explored new ionic liquids with an asymmetric anion, FTA^- (FTA = (fluorosulfonyl)(trifluoromethylsulfonyl)amide). K[FTA]–[C_4C_1pyrr][FTA] ionic liquid (C_4C_1pyrr = *N*-butyl-*N*-methylpyrrolidinium; x(K[FTA]) = 0.20) showed a moderate ionic conductivity of 2.2 mS cm^{-1} at 298 K. Lastly, charge–discharge behaviors of graphite negative electrodes were investigated using the K[FTA]–[C_4C_1pyrr][FTA] ionic liquid at 313 K. As shown in Fig. 2, the graphite electrode exhibited reversible capacities of ca. 230 mAh $(g\text{-}C)^{-1}$, corresponding to 80–85% of the theoretical capacity (279 mAh $(g\text{-}C)^{-1}$).

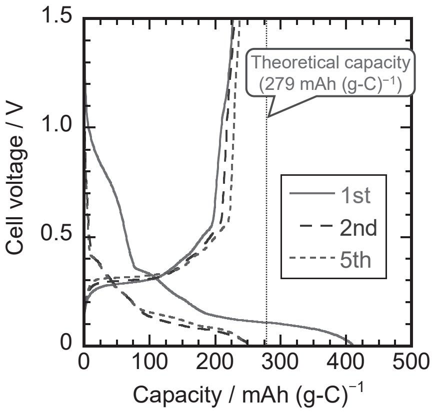

Fig. 2. Charge–discharge curves of a K/graphite cell using K[FTA]–[C_4C_1pyrr][FTA] electrolyte at 313 K. Current density: 27.9 mA $(g\text{-}C)^{-1}$.

4. Efficient Bioethanol Production from Lignocellulosic Biomass Using Ionic Liquid

Recently, pretreatment with ionic liquid was found to be improved yields of sugars from lignocellulosic biomass. On the other hand, ionic liquid was deleterious for growth of microorganisms including yeast.

In this fiscal year, several mutant strains of a recombinant xylose fermenting yeast with increased tolerance to ionic liquid were isolated in order to improve fermentation efficiency in the presence of ionic liquid. Ionic liquid tolerant yeast strains were selected by culturing in the presence of 150 mM of a ionic liquid, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) after UV irradiation mutation. As shown in Fig. 3, a representative mutant strain was grown even in the presence of 300 mM [Bmim]Cl. Furthermore, this strain metabolized both glucose and xylose, and fermented ethanol efficiently in the presence of 300 mM [Bmim]Cl (Fig. 4).

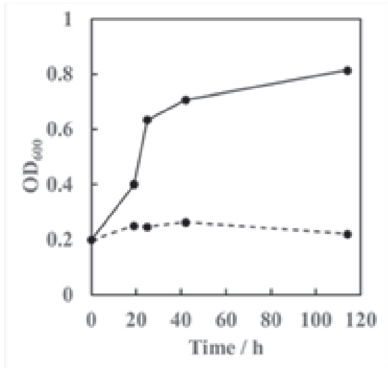

Fig. 3. Growth in the presence of 300 mM [Bmim]Cl. ionic liquid tolerant strain: solid line, wild type strain: dashed line.

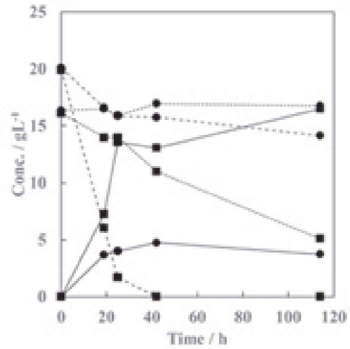

Fig. 4. Glucose and xylose consumption and ethanol fermentation in the presence of 300 mM [Bmim]Cl. ionic liquid tolerant strain: square, wild type strain: circle, ethanol: solid line, glucose: dashed line, xylose: dotted line.

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Collaboration Works

大垣英明，森井孝，片平正人，野平俊之，モンゴル国立大学，インドネシア大学，フィリピン大学ディリマン校，ベトナム国家大学ハノイ校，ラオス国立大学，王立プノンペン大学，アジア新興国産天然資源を由来とする機能性物質創生のための高度分析研究拠点の形成

Financial Support

1. Grant-in-Aid for Scientific Research

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法川勇太郎，特別研究員奨励費，金属チタンのより広範な利用を目的とした新規電解めっき法に関する研究

華航，特別研究員奨励費，溶融フッ化物電解と合金隔膜を用いた希土類金属の高精度・高速分離プロセスの構築

2. Others

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