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 process of tungsten, sodium and potassium secondary batteries using ionic liquids, and an efficient bioethanol production process using ionic liquids.

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

Tungsten is a metal with excellent properties such as high heat resistance, high strength, and low thermal expansion. Therefore, it is used in a variety of applications, including carbide tools, heat sinks, and divertors in nuclear fusion reactors. However, due to its hardness and brittleness, tungsten is difficult to process into complex shapes and thin films. If tungsten can be plated on substrates with good processability, the range of applications will be greatly expanded. Thus, electrodeposition of tungsten in high-temperature molten salts has been investigated as one of the promising plating methods [1–3].

We have already reported the electrodeposition of α-W films in molten $KF–KCl–WO_3$ at 923 K and mixed phase films of α-W and β-W in molten $CsF–CsCl–WO_3$ at 873 K [4]. We also reported that β-W films with mirror-like surface were electrodeposited in molten $CsF–CsCl–WO_3$ at 773 K [5]. As continuing research, in this fiscal year, we investigated the effect of bath temperature on the smoothness and crystal structure of W films electrodeposited from molten $CsF–CsCl–WO_3$.

Fig. 1 shows the samples obtained at 6–25 mA cm^{-2} and 773–923 K. At 25 mA cm^{-2} and 773 K, no W deposits were obtained due to co-deposition of Cs metal fog because the potential during electrolysis was close to 0 V with respect to Cs^+/Cs potential. Under other conditions, gray or silver-colored deposits were obtained. The results of XRD analysis showed that all electrodeposits were metallic W. Interestingly, only β-W was detected below 823 K, both α-W and β-W were detected at 873 K, and only α-W was detected at 923 K. This indicates that the crystal structure of W electrodeposited varies with bath temperature. At 6 mA cm^{-2} and 773 K, a mirror-like surface was obtained, indicating that the surface of the electrodeposited W film was highly smooth. The reason for the smoother surface at lower bath temperatures is speculated to be due to the crystal structure of β-W and the suppression of crystal growth.

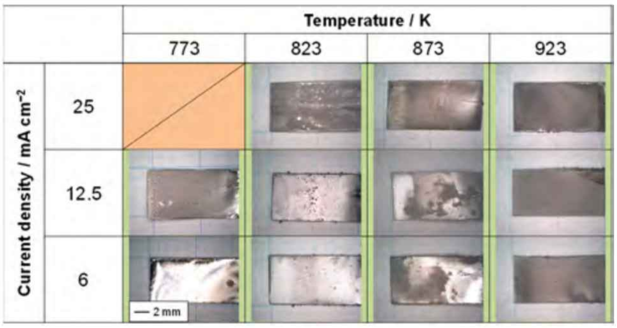

Fig. 1. Optical images of the samples obtained by galvanostatic electrolysis of Cu plate electrodes at various current densities and temperatures in molten $CsF–CsCl–WO_3$ (1.0 mol%). Charge density: 90 C cm^{-2}.

3. Development of Sodium and Potassium Secondary Batteries Using Ionic Liquid Electrolytes

The establishment of zero-carbon society requires the popularization of renewable energy and large-scaled energy storage devices. Although current lithium-ion batteries (LIBs) have been considered to the candidates because of their high energy densities, scarce lithium resources and flammable organic solvents are used, possibly leading to a major barrier to further distribution as large-scaled batteries. Our group has focused on sodium and potassium secondary batteries using ionic liquid electrolytes because sodium and potassium resources are abundant in the earth's crust and ionic liquids possess high safety such as negligible volatility and non-flammability [6,7].

In this fiscal year, we investigated charge–discharge performance of Hard carbon/$NaCrO_2$ full cell using Na[FSA]–[C_3C_1pyrr][FSA] ionic liquid electrolytes (FSA = bis(fluorosulfonyl)amide, C_3C_1pyrr = *N*-methyl-*N*-propylpyrrolidinium) with various Na^+ concentrations ($C(Na^+)$ = 1.0–2.2 mol dm^{-3}). As reported in our previous study [6], the highly concentrated electrolytes conferred the superior rate capability. Then, *in-situ* Raman spectroscopy was attempted, revealing that the Na^+ ion shortage hardly occurred at the electrode/electrolyte interface for the highly concentrated electrolytes. We also tried to improve the performance of graphite negative electrode in K[FTA]–[C_4C_1pyrr][FTA] ionic liquid (FTA = (fluorosulfonyl)(trifluoromethylsulfonyl)amide, C_4C_1pyrr = *N*-butyl-*N*-methylpyrrolidinium). By changing the binder material from PVdF to CMC (PVdF = Polyvinylidene difluoride, CMC = Sodium carboxymethyl cellulose), initial reversible capacity and coulombic efficiency increased from 227 to 267 mAh g^{-1} and 55 to 85%, respectively. As shown in Fig. 2, stable cycle performance was obtained for 30 cycles with negligible capacity decline.

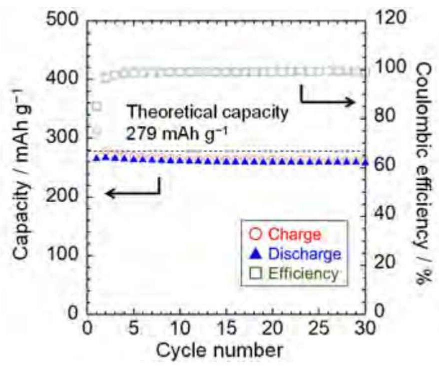

Fig. 2. Cycling properties of a K/graphite cell using K[FTA]–[C_4C_1pyrr][FTA] electrolyte and 313 K. Current rate: 0.1C rate (= 27.9 mA g^{-1}). Binder: CMC.

4. Efficient Bioethanol Production from Lignocellulosic Biomass Using Ionic Liquid

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

We have recently isolated several mutant strains of yeast with enhanced tolerance to an ionic liquid, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) in order to improve fermentation efficiency in the presence of ionic liquid by means of "adaptive laboratory evolution" [8] and conventional UV irradiation.

In this fiscal year, we first performed whole genome analysis of mutant strains obtained by conventional UV irradiation to identify genetic mutations. ATP synthase genes (*ATP1* and *ATP2*) were identified as candidates for mutations to improve ionic liquid tolerance, in addition to genes already known to confer ionic liquid tolerance, *PTK2* and *SKY1*. *ATP1* and *SKY1* or *ATP2* and *PTK2* mutations were introduced into the recombinant xylose fermenting yeast (SK-N1). These strains showed ionic liquid tolerance to growth (Fig. 3) and ethanol fermentation (Fig.4), conforming that *ATP1* or *ATP2* mutations, along with *SKY1* or *PTK2* mutations, emphasized ionic liquid tolerance.

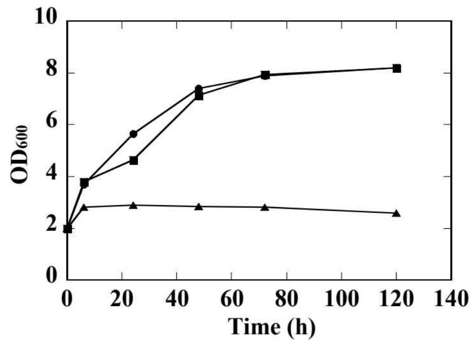

Fig. 3. Growth in the presence of 300 mM [Bmim]Cl. *ATP1* and *SKY1* mutated strain: square, *ATP2* and *PTK2* mutated strain: circle, SK-N1: triangle.

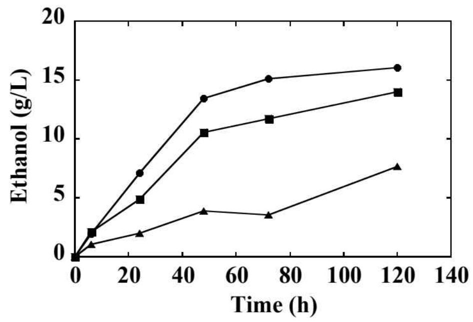

Fig. 4. Ethanol fermentation from glucose and xylose containing medium in the presence of 300 mM [Bmim]Cl. *ATP1* and *SKY1* mutated strain: square, *ATP2* and *PTK2* mutated strain: circle, SK-N1: triangle.

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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

野平俊之，基盤研究(A)，液体亜鉛陰極を利用した太陽電池用シリコンの新製造法

野平俊之，挑戦的研究（萌芽），二酸化炭素を原料とした革新的常圧ダイヤモンド電解合成法の開発

山本貴之，若手研究，反応電位に立脚したデュアルカーボン電池の構築

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

野平俊之，新エネルギー・産業技術総合開発機構，高効率な資源循環システムを構築するためのリサイクル技術の研究開発事業

野平俊之，国際協力機構，JICA 研修員受入

小瀧努，科学技術振興機構，サトウキビ収穫廃棄物の統合バイオリファイナリー

山本貴之，（公財）高橋産業経済研究財団，汎用元素を用いた高安全性を有する大容量二次電池の開発

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