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Short Communication

Electrodeposition of zirconium in an amide-type hydrophobic ionic liquid containing zirconium tetrachloride

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ABSTRACT

Electrochemical behavior of zirconium tetrachloride ($ZrCl_4$) was investigated in an amide-type hydrophobic ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) amide (BMPTFSA). $ZrCl_4$ was found to be soluble in BMPTFSA with or without addition of 1-butyl-1-methylpyrrolidinium chloride (BMPCl) as a Lewis base. Cyclic voltammograms recorded at a glassy carbon (GC) electrode showed two noticeable reduction peaks at about –1.9 V and –2.3 V for the $ZrCl_4$ in ionic liquid without addition of BMPCl at room temperature, while no reduction peak was noticed for the $ZrCl_4$ in ionic liquid in the presence of BMPCl at room temperature. The absence of any cathodic current peak corresponding to the reduction of Zr(IV) in ionic liquid with BMPCl at room temperature is presumably ascribed to the formation of a stable anion, $[ZrCl_6]^{2-}$ by addition of excess chloride ion to the electrolyte. Electrodeposition of Zr from $ZrCl_4$ on a GC electrode substrate in BMPTFSA ionic liquid with or without addition of BMPCl at elevated temperature or room temperature was observed. Scanning electron microscopy, energy dispersive X-ray and X-ray photoelectron spectroscopy results confirmed the presence of Zr in the deposits obtained by electrolysis of $ZrCl_4$ in BMPTFSA.

KEYWORDS: electrodeposition, zirconium, zirconium tetrachloride, ionic liquid, cyclic voltammetry.

INTRODUCTION

Zirconium (Zr) has been widely used in industries due to its high resistance to corrosion, tolerance to temperature, and small neutron cross section. Zr and Zr alloys are important in chemical industry, aviation industry and nuclear reactors [1]. Electrodeposition of Zr has been attempted in high temperature molten salt media [2-4]. Generally, electrolysis or electroreduction of Zr in molten salt is conducted at several hundred degrees centigrade. Contrary to that ionic liquids are expected to be useful in obtaining deposits of less noble metals at lower temperature. Aprotic hydrophobic ionic liquids have been considered as promising electrolytes for metal deposition due to their high thermal and chemical stability, less volatility and wide electrochemical potential window [5].

In 2004, Tsuda *et al.* reported electrodeposition of Zr-Al alloy in 1-ethyl-3-methylimidazolium chloride-aluminum chloride ionic liquid [6]. The structure of the deposits was found to be dependent on the Zr content. The reaction bath containing high Zr content led to the formation of Zr-Al alloy. Later in 2012, Fu and coworkers investigated the electrochemical behavior of $ZrCl_4$ in an amide-type TFSA-based BMPTFSA ionic

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liquid employing a platinum working electrode [7]. The chronoamperometric test revealed the reduction of Zr(IV) to Zr(III) in the ionic liquid. Recently, Krishna and colleagues reported the electroreduction of $ZrCl_4$ in another TFSA-based ionic liquid composed of 1-butyl-3-methylimidazolium using cyclic voltammetry, chronopotentiometry and chronoamperometry [8]. Authors confirmed that the presence of two cathodic peaks were due to the reduction of Zr(IV) to Zr(0) and Zr(II) to Zr(0) at 0.2 V and –1.3 V (vs. Pd), respectively. According to previous studies, cathodic reduction of Zr(IV) to metallic Zr might occur *via* a two-step, two-electron transfer reduction reaction. Although, there are a few reports on the electrochemistry of $ZrCl_4$ in molten salts and ionic liquids, the detailed electrochemical behavior and deposition mechanism of $ZrCl_4$ in ionic liquids have not been investigated till now probably due to formation of various Zr species and complex reaction mechanism. Moreover, volatility, water sensitivity and rapid electrolysis of $ZrCl_4$ made it difficult to conduct electrochemical analysis of $ZrCl_4$ in ionic liquid.

Previously, we have reported that addition of excess BMPCl and BMPBr to BMPTFSA containing $SeCl_4$ and $TiBr_4$, respectively, led to the formation of $[SeCl_6]^{2-}$ and $[TiBr_6]^{2-}$, respectively [9, 10]. Herein we report the electrodeposition of Zr in BMPTFSA containing $ZrCl_4$ with or without the addition of BMPCl. In this work we focused our attention to investigate the electrochemical behavior of $ZrCl_4$ in an amide-type hydrophobic ionic liquid, BMPTFSA in the presence or absence of excess chloride ion e.g. BMPCl. We also aimed to understand the effect of BMPCl on the morphology and microstructure of the Zr deposits obtained by electrochemical reduction of $ZrCl_4$ in the ionic liquid.

MATERIALS AND METHODS

BMPTFSA (99.5%) ionic liquid was received from Kanto Chemical and used without further purification. The water content of BMPTFSA was found to be less than 30 ppm by Karl Fischer titration (Metrohm, 831 KF). BMPCl was synthesized from 1-methylpyrrolidine (Tokyo Chemical Industry, >98%) in combination with butyl chloride (Wako Pure Chemical Industries, >98%) in acetonitrile (Kanto Chemical, 99.5%). The mixture was stirred for 24 hours and then recrystallized. The as-prepared BMPCl was dried under vacuum for 24 hours at 100 ºC. All the hygroscopic chemicals were stored and handled in an argon-filled glove box with a continuous gas purification system (Miwa MFG, DBO-1K-SH). The H_2O and O_2 concentrations inside the glove box were kept below 0.8 and 1 ppm, respectively.

Cyclic voltammetric data were recorded in a potentio/galvanostat (HABF 5001, Hokuto Denko, or HSV-110) connected to a three electrode cell system assembled inside the glove box. The working electrode was a glassy carbon (GC, GC-20SS, Tokai Carbon) disk electrode (7.06×10^{-2} cm^2). A silver wire (Sanwa Kinzoku) immersed in 0.1 M $AgCF_3SO_3$/BMPTFSA was employed as the reference electrode. A porous glass (Vycor) was used to separate the inner electrolyte of the reference electrode from the bulk electrolyte. The potential of the as-constructed reference electrode was estimated to be +0.43 V vs. ferrocene/ferrocenium redox couple [11]. The counter electrode was a platinum wire (Sanwa Kinzoku). Electrodeposition of Zr was performed with a two-compartment cell using a GC plate (1.54 cm^2) as the substrate. The counter electrode was placed in the compartment separated from the bulk electrolyte by a porous PTFE membrane (Millipore®, JGWP02500 Omnipore™ PTFE Membrane Filter). Electrodeposits were analyzed using scanning electron microscope (SEM, Keyence VE-9800), energy dispersive X-ray (EDX) spectrometer (Oxford Instruments, IncaPentalFETx3) and X-ray photoelectron spectrometer (XPS, JEOL, JPS-9010TR) after washing them with dehydrated acetonitrile.

RESULTS AND DISCUSSION

Cyclic voltammetry of $ZrCl_4$ in neat BMPTFSA

$ZrCl_4$ was found to dissolve in neat BMPTFSA at room temperature irrespective of the addition of BMPCl. The cyclic voltammogram of 10 mM $ZrCl_4$ in BMPTFSA was recorded at a GC electrode at room temperature and shown in Figure 1.

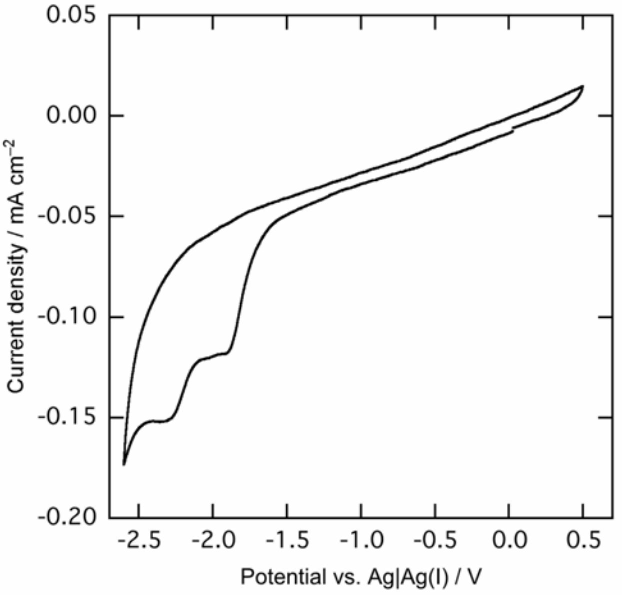

Figure 1. Cyclic voltammogram of a GC electrode in BMPTFSA containing 10 mM $ZrCl_4$ at room temperature. Scan rate: 50 mV s^{-1}.

The cathodic current below –2.5 V was ascribed to the reduction of BMP^+. During negative scan of the cyclic voltammetry two cathodic current peaks were noticed at ca. –1.9 and –2.3 V, while no anodic current was observed during the positive scan within the examined potential region. A previous study showed that Zr(III) was formed by electroreduction of Zr(IV) in BMPTFSA, and no further reduction of Zr(III) was observed in the BMPTFSA [7]. Meanwhile, Chen *et al.* [3] proposed the electroreduction mechanism of Zr(IV) assuming two reduction steps namely, Zr(IV) to Zr(II) and finally Zr(II) to Zr(0) in LiCl–KCl molten salt. Cathodic reduction of Zr(IV) has been reported to be complicated as various species of Zr with different oxidation states, such as 0, +1, +2, and +4, could coexist in LiCl-KCl eutectic [12]. Formation of Zr(II) by cathodic reduction of Zr(IV) was also reported by Tsuda *et al.* [6] in an acidic chloroaluminate ionic liquid. Moreover, Vacca's group obtained Zr on boron-doped diamond electrode by electrochemical reduction in BMPTFSA *via* a two-step, two-electron transfer pathway i.e. Zr(IV) ⇒ Zr(II) ⇒ Zr [13]. Since Zr has multiple oxidation states in ionic liquid, the cathodic currents noticed in the cyclic voltammogram (Figure 1) in the present study are considered corresponding to reduction of some Zr species according to the previous reports.

Electrodeposition of Zr from $ZrCl_4$ in neat BMPTFSA

The cathodic reduction of 10 mM $ZrCl_4$ in BMPTFSA at –2.3 V on the GC electrode gave electrodeposits on the GC substrate. The SEM image of the electrodeposit is displayed in Figure 2a. EDX showed that the electrodeposit contained Zr, oxygen (O) and chlorine (Cl) (Figure 2b). However, XRD of the electrodeposit gave no diffraction pattern corresponding to Zr, indicating that the electrodeposit might not be metallic Zr but some compounds composed of Zr, O and Cl. On the other hand, the small grain size of the Zr electrodeposit and/or the lesser thickness of deposited Zr layer might also result in the absence of characteristic diffraction peak for Zr in the XRD pattern.

Electrochemical behavior of $ZrCl_4$ in BMPTFSA with BMPCl

Figure 3 represents the cyclic voltammogram of 10 mM $ZrCl_4$ with addition of 20 mM BMPCl in BMPTFSA recorded on a GC electrode at room temperature and 100 ºC. Although no cathodic current was noticed in the presence of excess

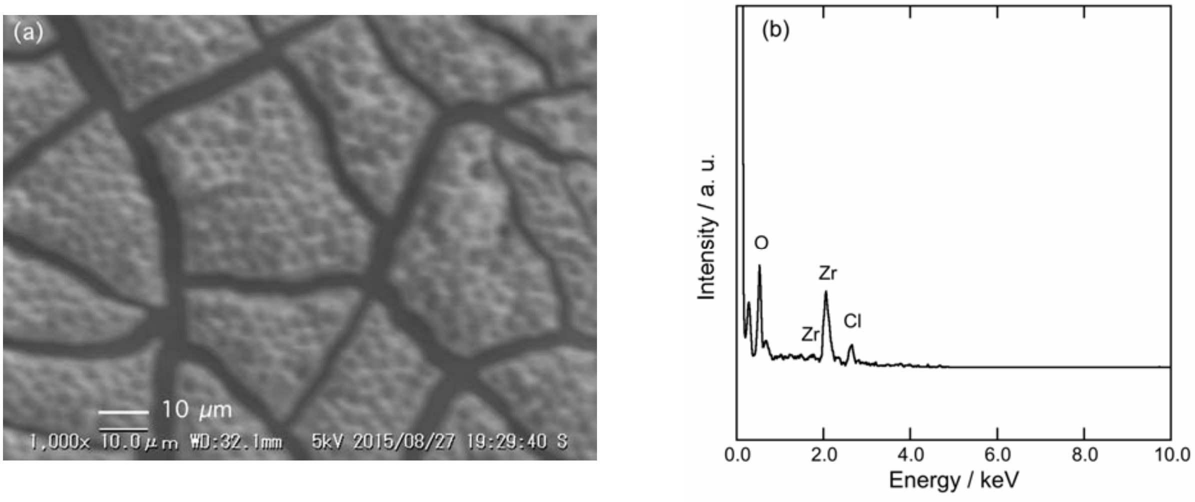

Figure 2. (a) SEM image and (b) EDX spectrum of the electrodeposits obtained on the GC substrate after electrolysis in BMPTFSA containing 10 mM $ZrCl_4$ at –2.3 V at room temperature.

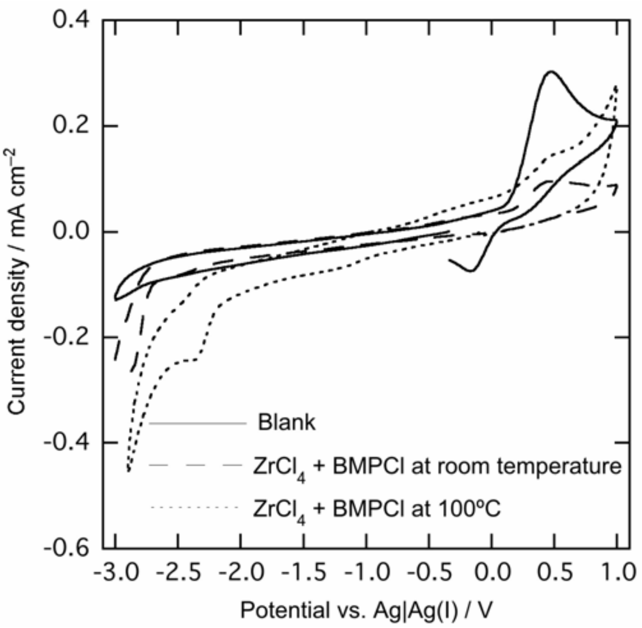

Figure 3. Cyclic voltammograms of a GC electrode in BMPTFSA containing 10 mM $ZrCl_4$ with and without 20 mM BMPCl at room temperature and 100 ºC. Scan rate: 50 mV $s^{-1.}$

BMPCl at room temperature, a single cathodic current peak appeared around –2.35 V at 100 ºC. It is expected that the addition of BMPCl to $ZrCl_4$ results in the formation of a Zr complex, $[ZrCl_6]^{2-}$, in BMPTFSA [14]. Reduction of Zr(IV) was not observed at room temperature probably due to the formation of a stable anion complex. We have already reported on the formation of $[TiBr_6]^{2-}$ in BMPTFSA containing BMPBr [10]. The anodic current peak at a potential of ca. +0.5 V was attributed to the oxidation of chloride [9, 15].

Figure 4 displays the SEM image and XPS spectrum of the deposits obtained on the GC electrode surface by electroreduction of 10 mM

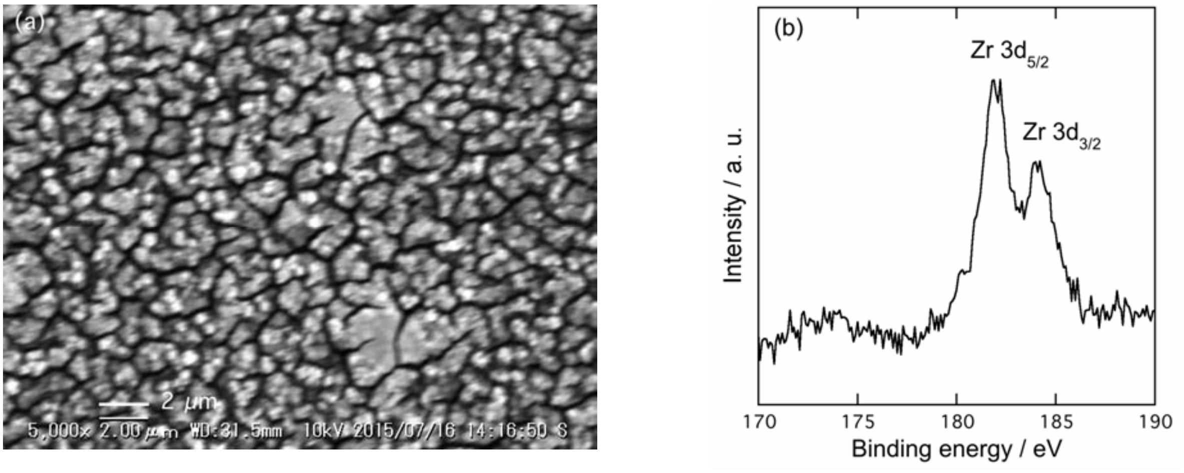

Figure 4. (a) SEM image and (b) XPS spectrum of the electrodeposits obtained on the GC substrate after electrolysis in BMPTFSA containing 10 mM $ZrCl_4$ in the presence of 20 mM BMPCl at –2.35 V. Temperature: 100 ºC.

$ZrCl_4$ with 20 mM BMPCl in BMPTFSA at a constant potential, –2.35 V at 100 ºC. EDX (data not shown) and XPS spectra confirmed that the electrodeposit contains Zr. From XPS, the electrodeposit was found to consist of ZrO_2 since the binding energies were assignable to those of ZrO_2 [16, 17]. A previous study reported that reduction of Zr(IV) led to the formation of metallic Zr by electrolysis in BMITFSA containing $ZrCl_4$ at –1.7 V (vs. Pd) [8]. Formation of ZrO_2 in this study can be attributed to the oxidation of the reduced products by oxygen in the air since the sample had to be exposed to air before XPS analysis.

CONCLUSIONS

$ZrCl_4$ was found to be reduced cathodically in BMPTFSA with or without addition of excess BMPCl. The observed cathodic currents correspond to reduction of Zr(IV): presumably Zr(IV) to Zr(II) and Zr(II) to metallic Zr. At 100 ºC, potentiostatic electrolysis in BMPTFSA containing $ZrCl_4$ with and without addition of BMPCl gave deposits containing Zr. This shows that hydrophobic amide-type ionic liquids could be advantageous for electrodeposition of Zr with desirable morphology and microstructure for diverse technological applications.

CONFLICT OF INTEREST STATEMENT

Authors declare no conflicts of interest associated with this study.

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