Electrochemical formation of a cesium–tin alloy in an amide-type ionic liquid

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ABSTRACT

Electrochemical formation of cesium–tin alloys in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) containing 0.5 M CsTFSA has been studied. Cathodic decomposition of BMPTFSA on a platinum electrode was suppressed by addition of CsTFSA, suggesting that Cs^+ accumulated on the electrode surface and hindered the reduction of BMPTFSA. Multiple cathodic current peaks were observed on a tin electrode in the ionic liquid. Energy-dispersive X-ray analysis and X-ray diffraction results suggested formation of cesium–tin alloys after potentiostatic cathodic reduction on the tin electrode at room temperature.

1. Introduction

Radioactive cesium isotopes, [135]Cs and ^{137}Cs, are found in the spent nuclear fuel of light water reactors. [135]Cs in particular is a long-lived fission product with an extremely long half-life, 2.3×10^6 years, requiring controlled waste storage over several million years. About 450 g of [135]Cs is produced per metric ton of uranium from the spent nuclear fuel with the burn-up of 45 GWd t^{-1} in a light water reactor [1]. Although the half-life of ^{137}Cs is only 30.1 years, its high radioactivity results in strong radiation and decay heat from the nuclear waste. Cs is a highly reactive metal with a low melting point (28.4 °C). Electrolytic recovery of Cs has been investigated using aprotic ionic liquids, which can be used as both electrolytes and solvents for extraction [2]. Electrodeposition of Cs as an amalgam was reported using a mercury electrode in tributylmethylammonium bis(trifluoromethylsulfonyl)amide (TBMATFSA) [3,4]. Although the electrode potential of Cs(I)|Cs on a nickel electrode in BMPTFSA (BMP^+ = 1-butyl-1-methylpyrrolidinium) has been reported [5], electrodeposition of metallic Cs has not been confirmed in these ionic liquids. On the other hand, lithium has been known to form alloys with tin at room temperature [6]. Thus, it may be possible to recover Cs as an alloy with Sn instead of Hg. Several Cs–Sn alloy phases with different compositions have been reported [7]. However, there is no report of the electrochemical formation of Cs–Sn alloys in ionic liquids. In the present study, the electrochemical formation of Cs–Sn has been studied in BMPTFSA containing CsTFSA at room temperature.

2. Experimental

BMPTFSA was purchased from Kanto Chemical and used as received. The water content of the BMPTFSA was confirmed to be below 30 ppm by Karl Fischer titration (Metrohm, 831KF). CsTFSA was prepared by reacting anhydrous Cs_2CO_3 (Wako Pure Chemical Industries) and HTFSA (Kanto Chemical) in dehydrated ethanol (Wako Pure Chemical Industries), followed by evaporation and vacuum drying at 100 °C for 24 h [8]. All the hygroscopic reagents were handled and stored in a glovebox filled with dry Ar (Miwa MFG, DBO-1KP-K03). Pt (Kojima Chemicals) and Sn (Nilaco) were used as the working electrodes (3 mmϕ, 7.07×10^{-2} cm²). The counter electrode was Pt wire (Sanwa kinzoku). The reference electrode, represented as Ag|Ag(I), was composed of Ag wire (Sanwa kinzoku) dipped in 0.1 M $AgCF_3SO_3$ (Aldrich)/BMPTFSA, which was isolated from the test electrolyte by a porous glass (Vycor). The potential of the ferrocenium|ferrocene couple is -0.43 V vs. Ag|Ag(I) [9]. Electrochemical measurements were conducted using an air-tight three-electrode cell with a potentio/galvanostat (Hokuto denko, HABF501 or HSV-110). The electrolyte volume was approximately 2.3 mL. Electrochemical formation of Cs–Sn alloys was performed with an air-tight two-compartment cell with a membrane filter as diaphragm. An Sn plate (14 mmϕ, 1.54 cm², Nilaco) was used as the substrate. The electrolyte volume in each compartment
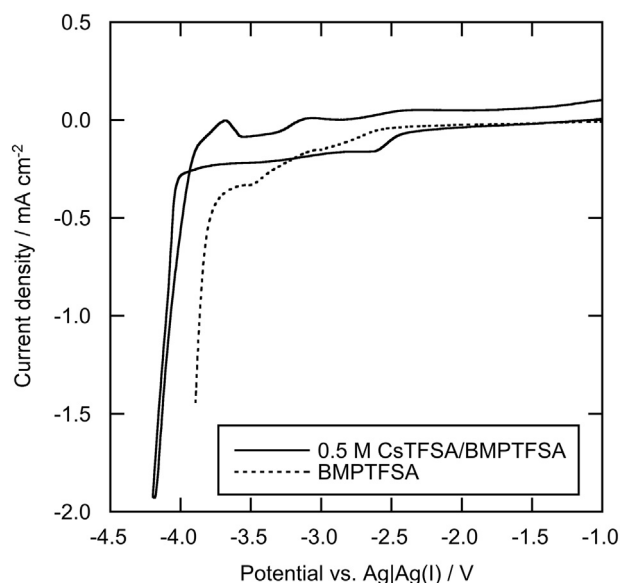

Fig. 1. Cyclic and linear sweep voltammograms of a Pt electrode in BMPTFSA with and without CsTFSA (0.5 M) at 50 mV s^{-1}. Temperature: 25 °C.
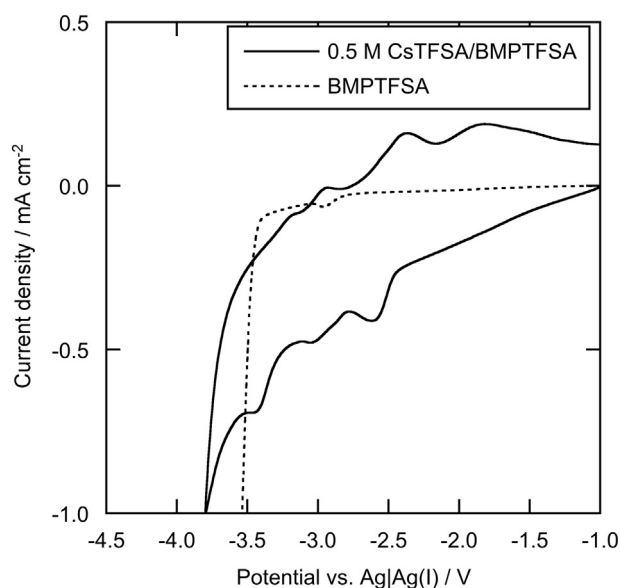

Fig. 2. Cyclic and linear sweep voltammograms of an Sn electrode in BMPTFSA with and without CsTFSA (0.5 M) at 50 mV s^{-1}. Temperature: 25 °C.

was approximately 2.3 mL. After potentiostatic cathodic reduction the substrate was washed with dehydrated 1,2-dimethoxyethane (DME) and characterized (without exposure to air) by X-ray diffraction (XRD, Rigaku, MiniFlex 600), scanning electron microscopy (SEM, secondary electron image, Keyence, VE-9800) and energy-dispersive X-ray analysis (EDS, Oxford, INCA-E250X3K).

3. Results and discussion

CsTFSA was soluble in BMPTFSA, resulting in a colorless ionic liquid. The viscosity of 0.5 M CsTFSA/BMPTFSA at 25 °C was 116 mPa s, which is greater than that of BMPTFSA (71 mPa s). Fig. 1 shows the cyclic and linear sweep voltammograms of a Pt electrode in BMPTFSA with and without 0.5 M CsTFSA. A cathodic current corresponding to the decomposition of BMPTFSA was seen at potentials more negative than − 2.5 V without CsTFSA [10]. However, the cathodic current was

suppressed in the presence of CsTFSA and a steep cathodic current assignable to reduction of Cs$^+$ [5] was observed at potentials more negative than − 4 V, suggesting that the reductive decomposition of BMPTFSA was hindered by accumulation of Cs$^+$ at the negatively polarized electrode surface. Cs(I) has been reported to exist as [Cs(TFSA)$_4$]$^{3-}$ by Raman spectroscopy [11]. However, Cs$^+$ seems to be liberated from TFSA$^-$ and adsorbed on the electrode surface, probably due to the lower charge density of Cs$^+$ compared with Li$^+$, which forms a stable anionic complex [Li(TFSA)$_2$]$^-$ [11]. On the other hand, a small anodic current peak observed during the anodic potential sweep may be attributed to the reoxidation of Cs deposited on the Pt electrode, suggesting instability of metallic Cs in the ionic liquid. Fig. 2 shows the cyclic and linear sweep voltammograms of an Sn electrode in BMPTFSA with and without 0.5 M CsTFSA at 25 °C. Although little current was observed at the potentials more positive than − 3.5 V without CsTFSA, a cathodic current with three peaks was observed in the presence of CsTFSA, suggesting the formation of Cs–Sn alloys with different compositions, for example Cs$_8$Sn$_{46}$, CsSn$_2$, Cs$_2$Sn$_3$ and CsSn [7].

Potentiostatic cathodic reduction was carried out on an Sn plate electrode in 0.5 M CsTFSA/BMPTFSA at − 3.5 V at 25 °C. Fig. 3 shows the SEM image, EDS spectrum and XRD pattern of the surface of the Sn electrode after electrolysis with an electric charge of 3.6 C cm^{-2}. The surface of the Sn electrode was roughened after the electrolysis, as shown in Fig. 3a. The EDS spectrum (Fig. 3b) shows the existence of Cs on the Sn electrode. The signals corresponding to fluorine, sulfur and oxygen are thought to be due to the ionic liquid trapped in the pores of the samples, although the sample had been washed with DME. The XRD pattern of the Sn electrode exhibits several peaks in addition to those assignable to Sn metal, as shown in Fig. 3c. Some of these peaks correspond to those reported for Cs$_8$Sn$_8$ [12] while other peaks have not been assigned to the XRD patterns of Cs–Sn alloys in the literature. In the cross-sectional view of the Sn electrode (Fig. 4), there is a surface layer which appears to be clearly different to the inner part. The EDS analysis along the line A–B showed that Cs was detected in the layer in addition to Sn, indicating that Cs–Sn alloys formed and grew into the Sn electrode. These results strongly suggest that Cs–Sn alloys were obtained electrochemically on the Sn electrode in the ionic liquid. The mass gain of the Sn electrode after the electrolysis was 4.9 mg cm^{-2}, which is close to the theoretical value of 5.0 mg cm^{-2}, assuming the current efficiency to be 100%. However, the thickness of the layer was about 180 μm, which is much thicker than expected for dense Cs$_8$Sn$_8$ (~ 21 μm), suggesting that the layer was composed of multiple Cs–Sn alloy phases. Consequently, it is suggested that highly efficient recovery of Cs may be possible by electrolysis using an Sn electrode in BMPTFSA containing CsTFSA.

4. Conclusions

Electrochemical formation of Cs–Sn alloys in 0.5 M CsTFSA/BMPTFSA was considered possible. Although all of the alloy phases present have not been identified yet, formation of Cs$_8$Sn$_8$ was suggested by the X-ray diffraction results. It is interesting that the mass of Cs per cubic centimeter in Cs$_8$Sn$_8$ is calculated to be 2.34 g cm^{-3}, which is larger than the density of Cs metal (1.87 g cm^{-3}). In addition, the incongruent melting temperature of Cs$_8$Sn$_8$ is 630 °C, which is much higher than the melting point of Cs metal. Thus, recovery of Cs as Cs$_8$Sn$_8$ is considered superior to recovery in the form of Cs metal or Cs–Hg amalgam. Further investigation is under way.