Selenium is an important element due to its many-fold applications including electrocatalysis,1 X-ray imaging,2 glass deoxidizing, grain refining,3,4 and so on. Especially, Se is an essential constituent of the materials for photovoltaic and photo-conductive properties of Se. Furthermore, such compound semiconductors containing selenium, as CdSe, ZnSe or CuInSe2 (CIS),5–7 have also been studied widely for various optoelectronic applications. Various approaches including photodeposition,8 chemical bath deposition,9 and chemical vapor deposition10 have been developed for preparation of selenium thin film. Electrodeposition is expected to be an alternative technique for preparation of Se thin films at lower cost as compared with other techniques. The electrodeposition of selenium has been studied intensively in aqueous systems.11–15 However, the deposition process of Se has been known to be complicated due to several interrelated factors, such as under potential deposition (UPD), formation of compounds with electrode materials, formation of H2Se, coupled chemical reactions, and requirement of extreme pH conditions. Furthermore, the electrodeposition of selenium in aqueous solutions at room temperature often leads to formation of amorphous Se. Crystalline Se is able to be obtained at elevated temperature, where volatility of water becomes a serious issue from a practical point of view. Therefore, aprotic room-temperature ionic liquids (RTILs) can be used for electrodeposition of selenium due to their advantageous properties, including wide electrochemical potential window, acceptable conductivity compared to non-aqueous electrolytes and negligible vapor pressure (up to 300 °C).20–22 Several groups have investigated electrodeposition of both amorphous and crystalline selenium using different ionic liquids and selenium species. Grey crystalline Se was obtained from 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide containing SeCl4 above 100 °C, whereas red amorphous Se was found at room-temperature.5 Electrodeposition of the polycrystalline Se film was successfully performed in 1-ethyl-3-methylimidazolium chloride-tetrafluoroborate at 30 °C.23 The electrochemical behavior, morphology and structure of Se deposits have been reported to be influenced by Se(IV) species in 1-ethyl-3-methylimidazolium tetrafluoroborate/chloride and zinc chloride-1-ethyl-3-methylimidazolium chloride ionic liquid.8 Recently, selenium electrodeposition has been studied in 1-butyl-1-methylpyrrolidinium and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate containing H2SeO3 with H2O as a co-solvent (5 mol%) in open air conditions at various temperatures.24,25 In situ UV-Vis spectroelectrochemistry of diethyl selenite in 1-propyl-1-methylpyperidinium bis(trifluoromethylsulfonyl)amine revealed deposition of amorphous selenium consisting of Se rings and polymeric Se chains.26 The previous studies indicate that electrodeposition of Se is quite complicated and that the morphology and structure of Se deposits are affected by Se species, ionic liquids and temperature.

Among hydrophobic RTILs, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) has received much attention because of its low melting point, acceptable conductivity and high cathodic stability.28,29 Endres’s group has already reported the electrodeposition of Se using SeCl4 as selenium ion source from this IL.9 However, the electrochemistry of selenium in BMPTFSA has not been explored in depth due to the possibility of existence of different selenium species. SeCl4 may form stable chloro-complex in the presence of excess chloride in BMPTFSA. Besides, addition of excess chloride is expected to be a promising way of increasing the solubility of SeCl4 in IL systems.

In the present study, the electrodeposition of selenium was investigated in BMPTFSA in the presence of excess chloride. The coordination environment of the dissolved Se(IV) species in BMPTFSA containing excess chloride was also studied using Raman spectroscopy.

**Experimental**

BMPTFSA (Kanto Chemical, 99.5%) was used as supplied. The water content in BMPTFSA was found to be below 30 ppm by Karl Fischer titration (Metrohm, 831KF). Anhydrous SeCl4 powder (Alfa Aesar, 99%) was used as received. BMPCl was prepared by the reaction of 1-methylpyrrolidine (Tokyo Chemical Industry, >98%) and butyl chloride (Wako Pure Chemical Industries, >98%) in acetonitrile (Kanto Chemical, 99.5%) at 75 °C for 24 hours, then purified by recrystallization and finally dried under vacuum at 100 °C for 24 hours.30,31 The solubility of SeCl4 in BMPTFSA in the absence and presence of BMPCl was estimated using inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent Technologies, 5100).

All the electrochemical measurements and electrodeposition experiments were conducted with an air-tight three-electrode cell using potentiostat/galvanostat (Hokuto Denko, HABF-501 and HSV-110). A single-compartment three-electrode cell was used for the electrochemical measurements. A glassy carbon (GC, Tokai Carbon, GC-20SS) disk electrode (7.07 × 10⁻² cm²) was employed as a working electrode after mirror polishing. A platinum wire was used as a counter electrode. A silver wire immersed in BMPTFSA containing 0.1 M AgF2SO3 (Aldrich, >99.0%) was used as a reference electrode, of which the inner electrolyte was separated from the main electrolyte by porous glass (Vycor). The potential of ferrocenium/ferrocene (Fc⁺/Fc) was −0.43 V versus this reference electrode.32 All the potentials in this paper were referred to this Ag/Ag(I) electrode. Electrodeposition experiments were conducted with a two-compartment three-electrode cell. A glassy carbon (1.54 cm²) plate under mirror polishing was used as a substrate. The counter and reference electrode were the same as described above. The counter electrode was placed in the compartment containing excess chloride.
separated from the electrolyte with a membrane filter made of polytetrafluoroethylene (PTFE). Handling of all the hygroscopic reagents were performed in an argon-filled glove box with a continuous gas purification apparatus (Miwa MFG, DBO-1K-SH). The concentrations of H₂O and O₂ in the gas were kept under 0.8 and 1 ppm, respectively. The electrodeposit was washed with dehydrated acetonitrile, dried in the air and characterized by a scanning electron microscope (SEM, Keyence, VE-9800), energy dispersive X-ray analyzer (EDX, Oxford Instruments, INCA-E250×3K), X-ray diffractometer (XRD, Rigaku, Miniflex600) and X-ray photoelectron spectrometer (XPS, JEOL, JPS-9010TR). Raman spectra of BMPTFSA with and without SeCl₄ and BMPCl were obtained using a Raman spectrometer (Renishaw, InVia Raman Microscope) equipped with Nd:YAG laser operating at 532 nm. The same Raman instrument was used for the characterization of the selenium deposits. Since potentiostatic bulk electrolysis at the peak potential of C1 resulted in deposition of elemental Se (data not shown), the peak C1 is considered ascribed to reduction of [SeCl₃]⁻ with liberation of Cl⁻ in acetonitrile. On the other hand, the peak potential of C2 is close to that for reduction of [SeCl₆]²⁻ to Se⁰, as described below. Therefore, dissolution of SeCl₄ in BMPTFSA without Cl⁻ is considered explained by the following reaction.

$$3\text{SeCl}_4 \rightarrow 2[\text{SeCl}_3]^{1+} + [\text{SeCl}_6]^{2-}$$  \[1\]

Since potentiostatic bulk electrolysis at the peak potential of C1 resulted in deposition of elemental Se (data not shown), the peak C1 is considered ascribed to reduction of [SeCl₃]⁻ to Se⁰. The peak C3 was able to be assigned to further electroreduction of Se, as described below. Thus, it was suggested that the complexity of electrode reactions of SeCl₄ in BMPTFSA without excess Cl⁻ is due to co-existence of different Se(IV) species.

Results and Discussion

**Linear sweep voltammogram of Se(IV) in BMPTFSA.**—The solubility of SeCl₄ in BMPTFSA at room temperature was estimated to be 23 mM by ICP-OES measurement and that in BMPCl with 150 mM BMPCl was estimated to be 40 ± 2 mM. Figure 1 shows the linear sweep voltammogram (LSV) of a GC electrode in BMPTFSA containing 10 mM SeCl₄ at 25°C. The potential was swept in the negative direction from the open circuit potential at the scan rate of 50 mV s⁻¹. The LSV shows three reduction peaks C1, C2 and C3. Since [3] 

$3\text{SeCl}_4 + 2\text{Cl}^- \rightarrow [\text{SeCl}_3]^{1+} + [\text{SeCl}_6]^{2-}$  \[2\]

**Dissolved species of Se(IV) in BMPCl/BMPTFSA system.**—The coordination chemistry is an important factor for the electrochemical behavior of metal ions in ILs. Figure 2 shows the Raman spectra of neat BMPTFSA and BMPTFSA containing 40 mM SeCl₄ and 150 mM BMPCl. Raman spectrum of BMPTFSA containing 40 mM SeCl₄ and 150 mM BMPCl shows Raman bands at 151, 237 and 288 cm⁻¹. The Raman bands for an octahedrally coordinated chlorocomplex of Se(IV), [SeCl₆]²⁻, in solid and liquid states are listed in the Table I. Since the observed Raman peaks in BMPTFSA containing 40 mM SeCl₄ and 150 mM BMPCl were consistent with those of [SeCl₆]²⁻ as listed in Table I, the dissolved species of Se(IV) in BMPTFSA containing SeCl₄ with excess chloride was identified as [SeCl₆]²⁻, which forms according to the Eq. 2. The small difference in the observed Raman band positions compared to those listed in Table I may arise due to the interaction of the octahedral complex with the IL.

$$\text{SeCl}_4 + 2\text{Cl}^- \rightarrow [\text{SeCl}_6]^{2-}$$  \[2\]
The cathodic current peak C1 was assigned to reduction of \([\text{SeCl}_6^{2-}]\) to Se(0) since the deposit obtained by the potentiostatic electrolysis at C1 was confirmed as metallic Se by various techniques, as described below. Thus, the cathodic reaction for the peak C1 is represented by the following four-electron transfer reaction.

\[
\text{Se}^{2+} + 4e^- \rightarrow \text{Se} + 6\text{Cl}^-
\]

Se is known to be further reduced to Se(−II)\(^{8,25}\). However, Se(−II) is expected to react with \([\text{SeCl}_6^{2-}]\) present in the IL. In order to examine the redox reaction between Se(0) and Se(−II), cyclic voltammetry of Se deposited on a GC electrode in the IL was conducted in BMPTFSA with and without 150 mM BMPCI, as shown in Fig. 3. Although no cathodic and anodic current peaks were observed in the potential range from −2.0 to −1.0 V on a GC electrode in BMPTFSA and BMPTFSA containing 150 mM BMPCI, as shown in Figs. 3a and 3b, respectively, a cathodic current peak was observed at about −1.8 V, which was close to the peak potential of C3 in Fig. 3c, for Se deposited on a GC electrode in both ILs without \([\text{SeCl}_6^{2-}]\). Thus, the cathodic current peak at about −1.8 V was ascribed to reduction of Se(0) to Se(−II), as represented follows.

\[
\text{Se} (0) + 2e^- \rightarrow \text{Se} (\text{−II})
\]

The anodic current peak A\(^{∗}\) at about −1.2 V was able to be attributed to anodic oxidation of Se(−II) to Se(0). Little difference in the potentials of the cathodic and anodic current peaks suggested little influence of free Cl\(^{−}\) on the dissolved species of Se(−II). On the other hand, the anodic peak A\(^{∗}\) was not found in the presence of \([\text{SeCl}_6^{2-}]\) as can be seen in Fig. 3c, probably due to proportionation reaction of Se(−II) and \([\text{SeCl}_6^{2-}]\), as represented by the following reaction.\(^{19,25}\)

\[
2\text{Se} (\text{−II}) + \text{[SeCl}_6^{2-}] \rightarrow 3\text{Se} (0) + 6\text{Cl}^-
\]

Therefore, the cathodic current peak C3 at about −1.8 V in Fig. 3c was ascribed to reduction of deposited Se(0) to Se(−II), which reduces \([\text{SeCl}_6^{2-}]\) in the IL to form Se(0) according to Eq. 5. The overall reaction is identical to Eq. 3. On the other hand, it was difficult to identify the reaction for the cathodic current peak C2 at about −1.6 V, which may be related to reduction of some oxychloro species of Se because of the high reactivity of SeCl\(_6^−\) with moisture.\(^{8}\) The similar cathodic current peak was also observed in 1-ethyl-3-methylimidazolium triﬂuoromethylsulphonate containing SeCl\(_6^−\).\(^{26}\)

Considering previous report regarding oxidation of Cl\(^{−}\) in IL,\(^{35}\) the anodic current peak A2 at about 0.6 V was assigned to oxidation of Cl\(^{−}\) to Cl\(_3^−\) since the similar anodic current peak was observed in BMPTFSA containing BMPCI, as shown in Fig. 3b. The anodic current peaks A1 and A3 at about 0.2 and 1.0 V, respectively, were considered to be related to anodic oxidation of Se. The anodic current peak A1 was observed in the presence of free Cl\(^{−}\), as seen in Fig. 3c and Fig. 4a, while the anodic current peak A3 was observed regardless of the presence of free Cl\(^{−}\), as seen in Fig. 3c and Fig. 4a. Thus, the anodic current peak A1 was considered to be assigned to oxidation of Se to \([\text{SeCl}_6^{2-}]\). On the other hand, the anodic current peak A3 might be due to oxidation of Se to some Se species other than \([\text{SeCl}_6^{2-}]\) since the local concentration of free Cl\(^{−}\) at the electrode surface was expected to be low during the cyclic voltammetry at the peak potential of A3 due to consumption of free Cl\(^{−}\) by the preceding anodic reactions represented by A1 and A2. However, further study is necessary to clarify the anodic reactions of Se in this system. Figure 5 shows the linear sweep voltammograms of a GC electrode in BMPTFSA containing 40 mM SeCl\(_4\) and 150 mM BMPCI at various scan rates. The peak potential of the cathodic wave C1 was shifted to the more negative side with an increase in the scan rate, suggesting the irreversible nature of the electrode reaction between \([\text{SeCl}_6^{2-}]\) and Se(0). However, the quantitative analysis of the cyclic voltammograms was avoided because of ohmic drop due to low conductivity of the IL and the possibility of existence of other Se(IV) species, as described above. The irreversibility of the electrode reaction is also demonstrated by the large separation of the potentials between cathodic and anodic peaks, as seen in Fig. 3c.

**Electrodeposition of Se.**—Electrodeposition of selenium was performed on a GC substrate in BMPTFSA containing 40 mM SeCl\(_4\) and 150 mM BMPCI at −1.4 V. The deposit obtained at 25°C was reddish metallic grey while that at 50°C was metallic grey. Figure 6a shows the EDX spectra of the deposits. The signal attributed to Se was clearly observed in the deposits obtained at 25 and 50°C in addition to that attributed to carbon derived from the GC substrate. Figure 6b shows the XRD patterns of the deposits obtained at 25 and 50°C. Two peaks at 23.5° and 29.6° in the deposit obtained at 50°C were assigned...
Figure 5. Linear sweep voltammograms of a GC electrode in BMPTFSA containing 40 mM SeCl4 and 150 mM BmPCI at various scan rates. Temperature: 25°C.

to (100) and (101) diffractions of hexagonal phase of Se (JCPDS-06-0362). An additional peak at 20.7° in addition to the peaks attributed to hexagonal phase of Se was observed in the deposit obtained at 25°C. The peak was assignable to (112) diffraction of monoclinic phase of Se (JCPDS 24–1202) since deposition of polymorphic Se has been reported at room-temperature.23,25,26 Figure 7 shows the SEM images of the deposits obtained at 25 and 50°C. Small particles and needles were observed in the deposit obtained at 25°C, while more compact and leaf or flower-like particles were observed in the deposit obtained at 50°C. The difference in the crystal phases and morphology of Se deposits at different temperature may be related to the rate of crystal growth and/or electric conductivity of Se. Se is a semi-conductor with a low electronic conductivity at room-temperature.36 However, the electronic conductivity of Se increases with elevating temperature above 40°C, resulting in facile crystal growth and formation of coarser particles by cathodic reduction of [SeCl6]2− on the deposited Se. In addition, the steady-state current density during the potentiostatic electrodeposition at 50°C was higher than that at 25°C, reflecting the difference in the electronic conductivity of Se in addition to a decrease in the viscosity of the IL. Figure 8 shows the Raman spectra of the deposits. Two Raman bands at 144 and 236 cm−1 observed in the deposits obtained at 25 and 50°C were consistent with the peaks observed for hexagonal (trigonal) Se, 143(E), 233(E) and 237(A1) cm−1.27,28 Since the Raman band typical to amorphous Se at 250 cm−1 (Se8, A1, E2) was not observed, the deposits were considered mainly composed of crystalline Se. Figure 9 shows the XPS spectra of the 3d region of Se for the deposits obtained at 25 and 50°C. These XPS spectra were taken after Ar+ etching for 15 sec. The distorted peak was deconvoluted to two components corresponding to Se 3d5/2 and Se 3d3/2 orbitals of metallic Se, by the least-square fitting.27 It is worth mentioning there was no additional peak assignable to selenium oxide, suggesting high purity of the deposited selenium.
The solubility of SeCl$_4$ in BMPTFSA with excess Cl$^-$ was higher than that in BMPTFSA. SeCl$_4$ was found to be dissolved in the IL with excess Cl$^-$ by forming [SeCl$_6$]$^{2-}$. Electrochemical reduction of [SeCl$_6$]$^{2-}$ was possible in the IL, resulting in deposition of metallic Se. Electrodeposition of crystalline selenium was confirmed at 25$^\circ$C with excess Cl$^-$ by forming [SeCl$_6$]$^{2-}$. Electrochemical reduction of Se(II) was confirmed at the potential more negative than the reduction of Se at 30$^\circ$C, where the electronic conductivity of C, where the electronic conductivity of C, was 1.4 V in BMPTFSA containing 40 mM SeCl$_4$ and 150 mM BMPCl at 25 and 50$^\circ$C. SeCl$_4$ and 150 mM BMPCl at 25 and 50$^\circ$C led to deposition of Se.

Conclusions

Figure 8. Raman spectra of the electrodeposits obtained by potentiostatic electrolysis on a GC electrode at $-1.4$ V in BMPTFSA containing 40 mM SeCl$_4$ and 150 mM BMPCl at 25 and 50$^\circ$C. Electric charge: 2 C.

The solubility of SeCl$_4$ in BMPTFSA with excess Cl$^-$ was higher than that in BMPTFSA. SeCl$_4$ was found to be dissolved in the IL with excess Cl$^-$ by forming [SeCl$_6$]$^{2-}$. Electrochemical reduction of [SeCl$_6$]$^{2-}$ was possible in the IL, resulting in deposition of metallic Se. Electrodeposition of crystalline selenium was confirmed at 25$^\circ$C. Compact and granular deposits were able to be obtained by elevating temperature at 50$^\circ$C, where the electronic conductivity of Se increased compared with room-temperature. Reduction of Se to Se(–II) was confirmed at the potential more negative than the reduction of [SeCl$_6$]$^{2-}$. However, proportionation reaction of Se(–II) and [SeCl$_6$]$^{2-}$ led to deposition of Se.

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Figure 9. XPS spectra of the Se deposits (3d region) obtained by potentiostatic electrolysis on a GC electrode at $-1.4$ V in BMPTFSA containing 40 mM SeCl$_4$ and 150 mM BMPCl at (a) 25 and (b) 50$^\circ$C. Electric charge: 2 C.
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