ELECTROCHEMICAL STUDIES ON SELENIUM SPECIES IN A BASIC AlCl$_3$-NaCl MELT

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ABSTRACT

The electrochemistry of selenium species in a basic AlCl$_3$-NaCl melt has been studied by cyclic, differential pulse, sampling voltammetries as well as emf measurements of a Na/SeCl$_4$ battery. The reaction of selenium tetrachloride with elemental selenium forms the low oxidation states of selenium compounds even in the basic melt. The oxidation of selenium proceeds from elemental selenium to tetravalent selenium through four electrochemical steps and involves intermediates Se$_8^{2+}$, Se$_4^{2+}$ and Se(II). From the results of emf measurements, it is possible that Se(I) participates in the reaction mechanism.

INTRODUCTION

In recent years we have been interested in developing a sodium/selenium(IV) molten salt battery for load leveling and electric vehicle applications (1-5). The chemistry and electrochemistry of selenium species in AlCl$_3$-NaCl melts were studied by the electrochemical and spectroscopic analyses (6-10), which suggested the existence of tetravalent selenium and several low oxidation states of selenium. The mechanism for the reduction of tetravalent selenium was proposed as follows,

\[ 2 \text{SeCl}_n^{(n-4)^-} + 8 \text{e}^- \rightarrow \text{Se}_2 + 2n \text{Cl}^- \]  

[1]

where \( n \) is 5 in an acidic melt and 6 in a basic melt (7). Potentiometric and spectroscopic studies, however, suggested that the reactions in acidic melts were more complex, because of the existence of low oxidation states such as Se$_{16}^{2+}$, Se$_{12}^{2+}$, Se$_8^{2+}$, Se$_4^{2+}$ and Se$_2^{2+}$ (8-10). While the electrochemical reactions of selenium species in acidic melts have been widely studied, there was few reports on the detailed discussion in basic melts. Previous studies on the performance of the
Na/SeCl₄ battery utilizing a basic AlCl₃–NaCl melt by us (4, 5) indicated that the reaction mechanism between Se(0) and Se(IV) is quite complex and the low oxidation state species are stable even in NaCl–saturated melts. In this paper we have demonstrated the reaction mechanism of selenium species in the basic melt.

**EXPERIMENTAL**

Melt preparation and several other experimental procedures have been described previously (3–5). 99.999% pure selenium and 99.9% pure selenium tetrachloride were used as received.

The electrochemical cells made of Pyrex glass were equipped with vitreous carbon (Tokai Carbon, GC-20SS) and tungsten working electrodes, a coiled tungsten wire counter electrode and a tungsten quasi-reference electrode. The reference electrode (99.999% pure aluminum wire in a NaCl–saturated melt) was separated from the main compartment by a thin glass membrane. The electrochemical reactions of selenium were studied for the solutions of several formal oxidation states (FOXS) of selenium. The FOXS was changed by adding known amounts of either SeCl₄ or Se to the basic melt. Commercially available electrochemical instrumentation (Hokuto Denko Models HA-501G, HB-105, and Yanako P-1100) was used for all voltammetric (cyclic, sampling, and differential pulse) studies.

Na/SeCl₄ cells for emf measurements were composed of a Pyrex compartment filled with the mixture of a basic melt and elemental selenium which was separated from a sodium electrode by means of a β’–alumina tube (NGK Spark Plug, 13mm ID, 15mm OD, 100mm length). The FOXS was changed by either charging or discharging with coiled tungsten wire electrodes in the negative and positive compartments. The positive compartment was also equipped with a tungsten microelectrode for potentiometric measurements. The melt composition was kept basic even at a fully charged state.

**RESULTS AND DISCUSSION**

Figure 1 shows the dependence of emf of a Na/SeCl₄ battery on the FOXS of selenium. It can be seen in Fig. 1 that there are several points of inflection at the FOXS close to +1/4, +1/2, +1 and +2. Because the activity of chloride ion is constant in a basic AlCl₃–NaCl melt (11), the emf in Fig. 1 depends on only the activity of selenium compounds, even if those are chlorocomplexes as previously proposed (7). The results on the emf suggest that the electrochemical reactions of selenium species in the basic melt are quite complex and involve several intermediates.
No well-defined voltammetric wave was observed, when the elemental selenium was dissolved in a NaCl-saturated melt. The reason seems to be that the solubility of elemental selenium in NaCl-saturated melts is quite low (7,9). While the basic melt containing selenium is colorless, SeCl₄ dissolves in this melt to give a light orange solution. The dissolved SeCl₄ reacts slowly with elemental selenium and the color of the solution changes to be dark violet, when the FOXS is 0.23. Figure 2 depicts the typical cyclic voltammogram obtained with the vitreous carbon electrode at 473 K in the basic melt, in which the FOXS of selenium is 0.23. Similar cyclic voltammograms were obtained at a tungsten electrode. Four oxidation waves (A, B, C, H) and four reduction waves (D, E, F, G) are present in Fig. 2. Comparing the voltammograms in the different ranges of potential, the shape of voltammetric curves indicates that the waves A–F, B–E, C–D and H–G each correspond to a different redox couple. These results support the complex reaction mechanism of selenium indicated from the emf curve.

Some additional quantitative information about the waves A–F have been obtained by differential pulse voltammetry and sampling voltammetry. Figures 3a and 3b show the typical differential polarogram and the voltammogram constructed from current–time curves at 1 sec. Four individual waves for the oxidation and reduction of selenium species can be observed in Fig. 3a. The peak potential for the wave A is 1856±3 mV and the width of this peak at half height is 74 mV. This peak width agrees well with the theoretical value for a reversible two-electron process (72 mV at 473 K). In order to deduce the stoichiometry involved in this electrochemical step, the wave A in Fig. 3b was analyzed. The potential vs. log \( \{i^2/(i_d - i)\} \) is linear with the slope of 42.4 mV, which is close to the theoretical value for the two-electron transfer (46.9 mV at 473 K). Considering that the wave A corresponds to the first oxidation step of selenium species with the FOXS near +1/4, a possible over-all reaction for the wave A–F is,

\[
2 \text{Se}^{2+} + 2 e^- \rightarrow \text{Se}^8^{2+}. \tag{2}
\]

Equation [2] is also supported by the emf curve, which shows the points of inflection at the FOXS of +1/4 and +1/2. Similar analysis for the voltammetric results for the melt with the FOXS of 0.23 gives no stoichiometric conclusions for other three steps. Further electrochemical study for the selenium solutions with different FOXS, for example +1/2, +1 and +2, is now in progress.

The reaction mechanism for the waves B–E and C–D have been discussed from Nernst plots constructed from the emf data. While the voltammetric results suggested that the oxidation of \( \text{Se}_4^{2+} \) to Se(IV) may consist of two clear steps, the emf curve
indicated more complex reaction sequence between the FOXS of +1/2 and +4. We, therefore, have discussed the final oxidation step, a redox couple C–D, at first. If the following reaction is assumed for the waves C–D,

$$\text{Se}^{4+} + 2e^- \rightarrow \text{Se}^{2+},$$  \[3\]

the emf vs. log ($m(\text{Se}^{4+}) / m(\text{Se}^{2+})$) should show the linear relation between the FOXS of +2 and +4 with the slope of 46.9 mV at 473 K. The plot constructed from the emf values was successfully linear with the slope of 44.5 mV. In addition, the emf values are in good agreement with the Nernst equation for the reaction [3] as shown in Fig. 4, as the half wave potential is estimated from the peak potential of the wave C in the differential pulse voltammogram.

Based on the above discussion, it may be reasonable to consider that Se$_4^{2+}$ and Se$_2^{2+}$ participate in the reaction of the waves B–E. The relation between the emf and log ($m^4(\text{Se}^{2+}) / m(\text{Se}^{42+})$), however, was not linear in the whole range between the FOXS of +1/2 and +2. The linearity is obtained only within the FOXS of +1 to +2 with the slope of 14.2 mV. Considering that the theoretical value is 15.6 mV for the six-electron step at 473 K, the following reaction may correspond to the waves B–E,

$$4 \text{Se}^{2+} + 6e^- \rightarrow \text{Se}_4^{2+}.$$ \[4\]

The deviation from the linearity in the FOXS range between +1/2 and +1 may be caused by the slow chemical reaction following the electrochemical reaction, although we have obtained no clear evidence for the EC mechanism by voltammetric studies. If Se$_2^{2+}$ forms slowly by chemical reaction of Se$_4^{2+}$ with Se$_2^{2+}$ and is stable even in basic melts, the Nernst plot will show a break at the FOXS of +1. In order to prove this assumption and to demonstrate the total reaction mechanism of selenium species, the spectroscopic study will be necessary as well as further electrochemical analysis.

**CONCLUSION**

The electrochemical reactions of selenium species in basic AlCl$_3$–NaCl melts have been investigated by voltammetric techniques and emf measurements of Na/SeCl$_4$ batteries. The reaction mechanism during the oxidation and reduction between Se(0) and Se(IV) is quite complex and involves intermediates as Se$_8^{2+}$, Se$_4^{2+}$ and S(II). S(I) may participate in the selenium reactions.
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REFERENCES

1. M. Matsunaga, K. Kitagawa, and K. Hosokawa, *Denki Kagaku*, 51, 847 (1983).
2. M. Matsunaga and K. Hosokawa, *Yoyuen (Molten Salts)*, 30, 83 (1987).
3. M. Matsunaga, T. Gouda, R. Otogawa, and K. Hosokawa, *Nippon Kagaku Kaishi*, 8, 1466 (1988).
4. M. Matsunaga, M. Morimitsu, and K. Hosokawa, in "Proceedings of International Symposium on Molten Salt," C. L. Hussey, J. S. Wilkes, S. N. Flengas, and Y. Ito, Editors, PV 90–17, pp. 753–760, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1990).
5. M. Morimitsu, M. Matsunaga, and K. Hosokawa, in "Proceedings of International Symposium on Molten Salt Chemistry and Technology 1993," M.-L. Saboungi and H. Kojima, Editors, PV 93–9, pp. 403–412, The Electrochemical Society Soft–bound Proceedings Series, Pennington, NJ (1993).
6. R. Marassi, G. Mamantov, and J. Q. Chambers, *Inorg. Nucl. Chem. Lett.*, 11, 245 (1975).
7. J. Robinson and R. A. Osteryoung, *J. Electrochem. Soc.*, 125, 1454 (1978).
8. D. J. Prince, J. D. Corbett, and B. Garbisch, *Inorg. Chem.*, 9, 2731 (1970).
9. R. Fehrmann, N. J. Bjerrum, and H. A. Andreasen, *ibid.*, 14, 2259 (1975).
10. R. Fehrmann and N. J. Bjerrum, *ibid.*, 16, 2089 (1977).
11. D. E. Bartak and R. A. Osteryoung, *J. Electrochem. Soc.*, 122, 600 (1975).
Fig. 1 Electromotive force of a Na/SeCl₄ battery with various FOXS at 473 K.

Fig. 2 Cyclic voltammogram for the selenium species in a AlCl₃-NaCl melt at 473 K. VC electrode area: 0.07 cm². Scan rate: 0.1 V/s. FOXS of Se: 0.23.

Fig. 3(a) Differential pulse voltammogram (scan rate: 0.5 mV/s, pulse width: 50 ms, modulation amplitude: 5 mV) and (b) voltammogram constructed from current-time curve at 1 sec. VC electrode area: 0.07 cm². FOXS of Se: 0.23. Temperature 473 K.

Fig. 4 Experimental (O, ●) and theoretical (—) emf of a Na/SeCl₄ battery between the FOXS of +2 and +4.