Measurement And Thermodynamic Analysis Of Reference Electrode Potentials In A Few Fluoride Melts Containing HF

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A reference electrode used in electrochemical measurements needs to have structural simplicity and stability, reversibility and thermodynamic meaning of its potential. New types of reference electrodes were prepared and their potentials were determined in molten KF-HF, NH_4F-HF, and NH_4F-KF-HF systems. The time dependences of their potentials *vs.* hydrogen evolution potential on Pt electrode were investigated by cyclic voltammetry with a slow sweep rate.

Figure 1 shows the time dependence of copper reference electrode immersed in a KF·2HF melt at 100℃. The value of its potential was unstable for first 30 days, and then it became stable to be 0.396 ± 0.003 V. Figure 2 shows SEM image of the surface of reference electrode after electrolysis. It was clearly found that the surface was covered with a dense film. XPS spectra of Cu 2p, F 1s, and O 1s levels on the surface of the immersed reference electrode are shown in Figure 3. XPS analysis indicated that the film on the Cu reference electrode was composed of CuF_2.

The copper reference electrodes treated with anodic oxidation and thermally fluorination with NF_3 at 300ºC were covered with CuF_2. Figure 4 shows the time dependence of thermally fluorinated copper reference electrode in a molten KF·2HF at 100℃. The value of its potentials became stable for the shorter time and its was 0.402 ± 0.003 V. Since the potential of Cu/CuF_2 electrode calculated from the thermodynamic data is 0.388 V, it has a little difference from the observed value of it. Figure 5 shows the anodic polarization curve obtained by cyclic voltammetry with a sweep rate of 100mV/s. Two peaks due to anodic dissolution were obserbed and these peaks corresponded to the Reactions (1) and (2), respectively.

$$Cu + 2HF \leftrightarrows CuF_2 \qquad E^0 = 0.295\ V\ vs.\ H_2 \qquad (1)$$

$$Cu + HF \leftrightarrows CuF \qquad E^0 = 0.403\ V\ vs.\ H_2 \qquad (2)$$

Although the difference seems to be within an error, it may be caused by coexistence of CuF_2 and CuF. From the potentiostatic polarization measurement, it was also found that the potential observed on the thermally fluorinated copper reference electrode was reversible.

In the mixed melts of NH_4F·2HF and KF·2HF, the more ratio of NH_4F·2HF, the lower potential of copper reference electrode became, because the vapor pressure of HF on the melts increased with increasing the ratio of NH_4F·2HF in the mixed melts. The value of a thermally fluorinated copper reference electrode in a molten NH_4F·2HF was 0.357 ± 0.003 V. Also, the temperature dependence of potential of the copper reference electrode was investigated and its potential decreased monotonously with elevating temperature of the electrolyte, because of increasing the vapor pressure of HF on the melts.

The potential of nickel reference electrode was also determined in a molten KF·2HF at 100ºC and the stationary value was 0.096 ± 0.010 V. Its value determined in a molten NH_4F·2HF at 100℃ was 0.072 ± 0.009 V. On the other hand, the potential of the Ni/NiF_2 reference electrode calculated from thermodynamical data was –0.248 V and the observed potential of nickel reference electrode was different from the calculated potential of Ni/NiF_2 electrode.

From these results, it is concluded that a new type of copper reference electrode is useful as a reference electrode in all the KF-HF, the NH_4F-HF, and the NH_4F-KF-HF systems.

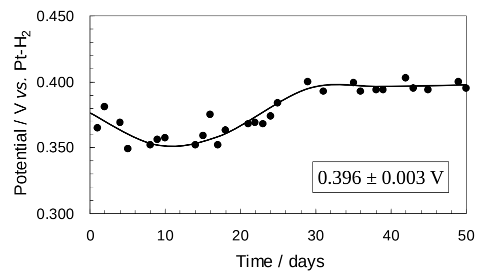

Figure 1 Change of potential of a copper reference electrode in a KF・2HF melt at 100°C as a function of time.

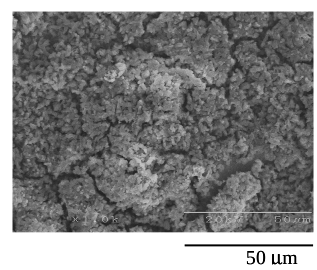

Figure 2 SEM image of the surface of a copper rod after immersion in a KF・2HF melt at 100°C for 50 days.

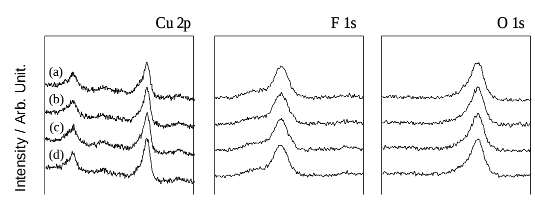

Figure 3 Cu 2p, F 1s, and O 1s XPS spectra obtained for a copper rod after immersion in a KF・2HF melt at 100°C for 50 days.
(a) Outmost surface, (b) Exposed to Ar^+ beam for 1 minute*, (c) Exposed to Ar^+ beam for 2 minutes*, (d) Exposed to Ar^+ beam for 3 minutes*.
*Beam current = 20 mA at 4.49 kV

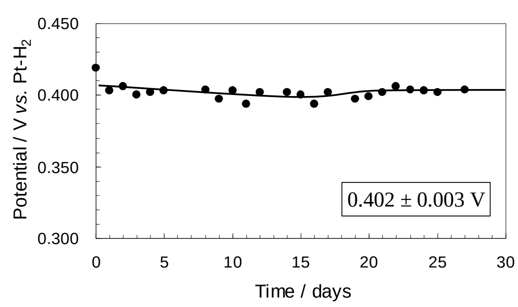

Figure 4 Change of potential of the thermally fluorinated copper reference electrode in a KF・2HF melt at 100°C as a function of time.

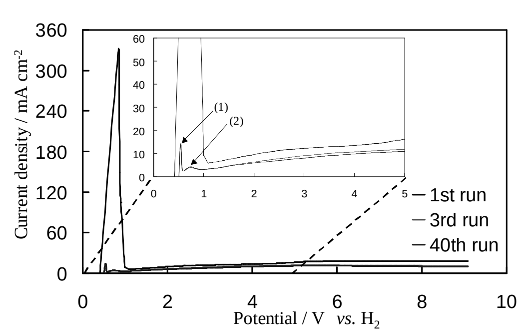

Figure 5 Anodic polarization curves of the Cu electrode in a NH_4F·2HF melt at 100°C by potential sweep method with a sweep rate of 100mV s^{-1}.