ELECTROCHEMICAL BEHAVIOR OF GLASSY CARBON AND SOME METALS IN A ZnCl₂–NaCl MELT

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Stability and reactivity of glassy carbon, nickel, platinum, and tungsten in ZnCl₂–NaCl (60–40 mol%) melt at 450°C were investigated by cyclic voltammetry and constant-potential electrolysis. Glassy carbon was stable in the potential range of 0.23–1.8 V vs. Zn in ZnCl₂–NaCl(saturated). Nickel was oxidized and partially passivated around 0.8–0.9 V. X-ray diffraction analysis revealed the formation of β₁–NiZn alloy at 0.3–0.35 V and γ–NiZn alloy at 0.2–0.25 V. Platinum was oxidized and partially passivated around 1.7–1.8 V, formed δ–PtZn alloy at 0.35–0.4 V, γ₁–PtZn alloy at 0.4 V, and γ–PtZn alloy at 0.2–0.25 V. Voltammograms from a rotating tungsten disk electrode suggested the formation of a poorly soluble compound in an anodic process.

INTRODUCTION

Stability and reactivity of metals in molten salts are important in considering their use in electrolytic processes. We have been interested in ZnCl₂–NaCl and ZnBr₂–NaBr melts which have characteristics such as low melting point and low halide activity (1, 2). In previous papers (3, 4) we reported that the electrodeposition of tungsten occurred on nickel and glassy carbon substrates in these melts. Voltammetric studies of some tungsten compounds were performed on platinum and glassy carbon electrodes (5, 6). For interpreting the obtained results, it is necessary to know the electrochemical behavior of these electrode materials. Furthermore, the dissolution of tungsten anode is important in an electroplating cell. With these objectives in mind, a voltammetric study and constant-potential electrolysis were performed on glassy carbon, nickel, platinum, and tungsten in a ZnCl₂–NaCl (60–40 mol %) melt at 450°C.

EXPERIMENTAL

Voltammetric experiments were carried out in a Pyrex cell. Platinum (0.5 mm in diameter), nickel (0.5 mm in diameter), and tungsten wires (0.8 mm in diameter) and a glassy carbon rod (Tokai Carbon, GC–20, 3 mm in diameter) were used as the working electrode. The effective area of the glassy carbon electrode was a circular section (0.071 cm²) of the rod sealed in a Pyrex tube. For constant-potential electrolysis, nickel and platinum plates (0.5 mm in thickness) were used. A rotating tungsten disk electrode was made of a tungsten rod (3 mm in diameter) and a Pyrex tube. The counter electrode was
a glassy carbon rod, which was separated from the main compartment by a glass frit. The reference electrode (RE) was molten zinc in ZnCl₂-NaCl(saturated) which was separated from the bulk electrolyte by a small piece of sodium β-alumina. Potential values were expressed in V vs. RE.

Zinc chloride (Wako) was dried at 250°C under vacuum, and then sublimed at 450°C. Sodium chloride (Wako) was dried at 350°C under vacuum. ZnCl₂-NaCl (60-40 mol%) melt was prepared at 350°C in a Pyrex tube and then cooled and pulverized. The cell was loaded with appropriate materials under a nitrogen atmosphere in a Mecaplex Model GB80 glove box equipped with a Vacuum/Atmospheres HE-493 purifier. The moisture level in the box was monitored with a Shaw Model OEM-2 dew point meter; it was typically below 4 ppm. The cell was heated and maintained at 450°C in an electric furnace which had a window for visual observation. The inside of the cell was kept under a nitrogen atmosphere at slightly positive pressure in order to avoid atmospheric oxygen and moisture. Nitrogen gas was occasionally bubbled through the melt for stirring.

Cyclic voltammetry was performed by using a Hokuto Denko Model HA–501 potentiostat and Model HB–104 function generator. X-ray diffraction was performed with a JEOL Model JDX–8F diffractometer using CuKα radiation.

RESULTS AND DISCUSSION

Glassy Carbon

Cyclic voltammetry was performed to examine the stability of glassy carbon as the working electrode in ZnCl₂-NaCl (60–40 mol%) melt at 450°C. Voltammograms shown in Fig. 1 was very reproducible. Cathodic (Cl) and anodic (A1) currents occurring around 0.23 V can be ascribed to the deposition and dissolution of metallic zinc (liquid), since a separate experiment showed that the potential of zinc in an identical melt was 0.23 V at open circuit. An anodic current (A2) was observed above 1.8 V and gas bubbles were generated at 1.9 V. The corresponding cathodic current was not observed, indicating that the reaction at A1 was irreversible. Lantratov and Alabyshev (7) measured the electromotive force (EMF) of the cell Zn/ZnCl₂-NaCl/Cl₂(l atm)/graphite and reported the value of 1.63 V for the melt composition of 60 mol% ZnCl₂ at 450°C. Assuming that the equilibrium potential of Zn/Zn²⁺ in ZnCl₂-NaCl (60–40 mol%) melt is 0.23 V vs. RE, the equilibrium potential of Cl⁻/Cl₂(1 atm) is calculated to be 1.63 + 0.23 = 1.86 V vs. RE. Therefore the sharp rise of anodic current (A2) is due to the reaction

\[ \text{Cl}^- \rightarrow (1/2)\text{Cl}_2 + \text{e}^- \]

Glassy carbon is a good electrode material within the potential window of 0.23–1.8 V.

Nickel

Figure 2 shows cyclic voltammograms obtained for a nickel electrode in different modes of potential scanning. Anodic (A1) and cathodic (C1) peaks on curves a and d seem to represent the oxidation of nickel and the reverse reaction (reduction) of the product, which is presumably solid NiCl₂ (see below). The anodic peak A1 exhibits the characteristics of passivation which is also suggested by the fact that the anodic current due to the evolution of Cl₂ did not occur at potentials as high as 1.86 V.

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Chemical potential data at 723 K, which are calculated from the literature (8) and listed in Table I, give the Gibbs energy change $\Delta G^\circ = -195.8$ kJ/mol for the reaction

$$\text{Ni(s)} + \text{Cl}_2(g) = \text{NiCl}_2(s)$$

at 723 K. Therefore, the EMF of the cell Ni(s)/NiCl$_2$(s)/Cl$_2$(g) is $-\Delta G^\circ/2F = 1.014$ V. Since the equilibrium potential of Cl$_2$(g)/Cl$^-$ in ZnCl$_2$–NaCl(60–40 mol%) is 1.86 V vs. RE, the potential of Ni(s)/NiCl$_2$(s)/ZnCl$_2$–NaCl(60–40 mol%) is calculated to be $1.86 - 1.014 = 0.85$ V vs. RE, which is in the middle of the peaks A1 and C1. Therefore the following reaction can be assigned:

$$A1 \quad \text{Ni(s)} + 2\text{Cl}^- \rightleftharpoons \text{NiCl}_2 + 2e^-$$

Comparison of voltammetric curves a, b, and c suggests that the anodic peaks A2 and A3 are coupled with the cathodic peaks C2 and C3, respectively. Since it was considered that the formation of nickel–zinc alloys (9, 10) might occur, constant–potential electrolysis was carried out with a nickel electrode, and X-ray diffraction analysis of the deposit was performed. Published data of X-ray powder diffraction (11) were used for identification. As shown in Table II, different types of Ni–Zn alloys were formed depending upon the potential. Figure 3 shows X-ray diffraction patterns obtained for different duration of electrolysis at 0.250 V. It can be seen that the diffraction due to the nickel substrate decreases in the course of electrolysis, whereas the diffraction due to the $\gamma$–NiZn alloy increases. The results of Table II suggest that the currents C2 and C3 represent the formation of $\beta_1$–NiZn and $\gamma$–NiZn alloys, respectively. Although the increase of cathodic current (C4) below 0.23 V might be associated with the deposition of pure zinc, the corresponding anodic current was not observed, and only $\gamma$–NiZn alloy was found in constant–potential electrolysis at 0.200 V. It seems that the deposited zinc (liquid) quickly reacted with the nickel substrate to yield $\gamma$–NiZn alloy.

In order to interpret the voltammetric results, thermodynamic activity data of Ni–Zn alloys obtained from vapor pressure measurements (12) were used. Table III shows the Zn activity $a_{\text{Zn}}$ at 450°C, in mole fraction scale, which was calculated from experimentally obtained activity parameters (12). Table III includes the corresponding equilibrium potentials referred to Zn/Zn$^{2+}$ in ZnCl$_2$–NaCl(60–40 mol%) and to RE:

$$E [\text{V vs. Zn/Zn}^{2+} \text{ in ZnCl}_2–\text{NaCl(60–40 mol%)}] = -(RT/2F)\ln a_{\text{Zn}}$$

$$E [\text{V vs. RE}] = -(RT/2F)\ln a_{\text{Zn}} + 0.23$$

It can be seen, for example, that $\gamma$–NiZn alloy is thermodynamically stable in the potential range 0.235–0.299 V vs. RE. Figure 4 shows the relationship between the alloy composition and the equilibrium potential, together with the relevant voltammograms (reproduced from Fig. 2). The vertical broken lines are the boundaries which separate the regions of thermodynamically stable phases ($\alpha$, $\beta_1$, etc). Figure 4 confirms that the anodic current C2 and C3 represent the formation of $\beta_1$– and $\gamma$–NiZn alloys, respectively. The anodic current A2 and A3 correspond to the oxidation of zinc in $\beta_1$– and $\gamma$–NiZn alloys, respectively, to Zn$^{2+}$. The anodic current A5 may represent the dissolution of zinc in $\alpha$–NiZn alloy.
**Platinum**

Similar experiments were performed for a platinum electrode. Figure 5 shows cyclic voltammograms obtained in different modes of potential scanning. The anodic peak A1 on curve a seems to represent the oxidation of platinum. In the reverse scan, current oscillation occurred (A1'), which indicates the alternation of passivation and reactivation, that is, the repeated formation and dissolution of a passive film. The cathodic current C1 may be due to the reduction of the oxidation product, which is presumably solid PtCl₂. Thus, chemical potential data (8), shown in Table I, give the Gibbs energy change \( \Delta G^0 = -16.3 \text{ kJ/mol} \) for the reaction

\[
\text{Pt}(s) + \text{Cl}_2(g) \rightarrow \text{PtCl}_2(s)
\]

at 723 K. Therefore, EMF of the cell \( \text{Pt}(s)/\text{PtCl}_2(s)/\text{Cl}_2(g) \) is \( -\Delta G^0/2F = 0.084 \text{ V} \). The potential of \( \text{Pt}(s)/\text{PtCl}_2(s)/\text{ZnCl}_2-\text{NaCl}(60-40 \text{ mol%}) \) is calculated to be \( 1.86 - 0.084 = 1.776 \text{ V} \) vs. RE, which is in the middle of the peaks A1 and C1. Therefore the following reaction can be assigned:

\[
\text{A1} \quad \text{Pt}(s) + 2\text{Cl}^- \rightarrow \text{PtCl}_2 + 2\text{e}^-
\]

Comparison of voltammetric curves b, d and e suggest that the anodic currents A2 and A3 are coupled with the cathodic currents C2 and C3, respectively. In order to investigate the formation of platinum–zinc alloys, constant-potential electrolysis was carried out with a platinum electrode, and X-ray diffraction analysis was performed. As shown in Table IV, different types of Pt–Zn alloys (10, 13) were formed depending upon the potential. The results of Table IV suggest that the current C2 represents the formation of \( \delta_1 \)-PtZn alloy. \( \gamma \)- and \( \gamma_1 \)-PtZn alloys are formed by the cathodic current C3. Thermodynamic activity data on Pt–Zn alloys (14) are not sufficient for detailed discussion.

**Tungsten**

Figure 6 shows cyclic voltammograms obtained for a tungsten wire electrode. Cathodic and anodic currents due to the deposition and dissolution of metallic zinc were observed at 0.23 V. Anodic current occurred above 0.7 V with no indication of passivation. Evolution of gas bubbles was seen at 1.2 V. Since the equilibrium potential of \( \text{Cl}_2(1 \text{ atm})/\text{Cl}^- \) has been estimated to be 1.86 V, the gas may not be chlorine but volatile chloride of tungsten. Chemical potential data (Table I) yield the following values of equilibrium potentials (V vs. RE):

\[
\begin{align*}
\text{WCl}_2(s) + 2\text{e}^- &= \text{W} + 2\text{Cl}^- \quad 0.958 \text{ V} \\
\text{WCl}_4(s) + 4\text{e}^- &= \text{W} + 4\text{Cl}^- \quad 1.215 \text{ V} \\
\text{WCl}_5(g) + 5\text{e}^- &= \text{W} + 5\text{Cl}^- \quad 1.277 \text{ V} \\
\text{WCl}_6(g) + 6\text{e}^- &= \text{W} + 6\text{Cl}^- \quad 1.353 \text{ V} \\
\text{WCl}_3(g) + 3\text{e}^- &= \text{WCl}_2(s) + 3\text{Cl}^- \quad 1.489 \text{ V} \\
\text{WCl}_6(g) + 4\text{e}^- &= \text{WCl}_2(s) + 4\text{Cl}^- \quad 1.551 \text{ V}
\end{align*}
\]

It is probable that WCl₅ and WCl₆ are formed at higher potentials.

In order to investigate the anodic behavior more closely, a rotating tungsten disk electrode was used. The obtained voltammograms (Fig. 7) show complex phenomena...
occurring at potentials 1.1–1.4 V. Thus, anodic current decreased as the potential increased, and that to greater extent at higher rotation rates. Such observations suggest that poorly soluble product was formed which was facilitated by the forced convection in the melt. Although the situation is not clear yet, anodic behavior of tungsten seems important in designing a tungsten electroplating cell.

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| Table I. Chemical potential at 723K |
|-------------------------------------|
| Substance | Phase | $\mu^0$(kJ/mol) at 723K |
| Cl$_2$ | gas | -168.9 |
| Ni | solid | -27.9 |
| NiCl$_2$ | solid | -392.6 |
| Pt | solid | -35.9 |
| PtCl$_2$ | solid | -221.1 |
| W | solid | -29.1 |
| WCl$_2$ | solid | -372.1 |
| WCl$_4$ | solid | -616.0 |
| WCl$_5$ | gas | -732.9 |
| WCl$_6$ | gas | -829.2 |
Table II. Deposits on Ni substrate in constant-potential electrolysis

| Potential | Deposit       | Crystal structure         | Atomic percent Zn* |
|-----------|---------------|---------------------------|--------------------|
| 0.200 V   | $\gamma$-NiZn alloy | Body-centered cubic        | 73-85 %            |
| 0.250 V   | $\gamma$-NiZn alloy | Body-centered cubic        | 73-85 %            |
| 0.300 V   | $\beta_1$-NiZn alloy | Tetragonal, CuAu type     | 45-52 %            |
| 0.350 V   | $\beta_1$-NiZn alloy | Tetragonal, CuAu type     | 45-52 %            |
| 0.500 V   | No deposits    |                           |                    |

*Estimated from the phase diagram in Ref. 10

Table III. Logarithm of activity of zinc $a_{Zn}$ in Ni–Zn alloys and the corresponding equilibrium potential $E$ in the ZnCl$_2$–NaCl (60–40 mol %) melt at 450°C

| $X_{Zn}$* | Phase | $\log_{10} a_{Zn}$** | $E$(V)** |
|-----------|-------|-----------------------|----------|
| 0.0507    | $a$   | -10.125               | 0.545    |
| 0.1005    | $a$   | -9.125                | 0.514    |
| 0.1502    | $a$   | -8.612                | 0.498    |
| 0.2493    | $\beta$ | -7.332               | 0.458    |
| 0.2890    | $\beta$ | -6.787               | 0.441    |
| 0.4575    | $\beta$ | -6.787               | 0.441    |
| 0.4750    | $\beta$ | -6.197               | 0.423    |
| 0.4900    | $\beta$ | -5.452               | 0.400    |
| 0.5000    | $\beta$ | -3.978               | 0.354    |
| 0.5190    | $\beta$ | -2.201               | 0.299    |
| 0.7390    | $\gamma$ | -2.201               | 0.299    |
| 0.8020    | $\gamma$ | -1.534               | 0.278    |
| 0.8260    | $\gamma$ | -0.963               | 0.260    |
| 0.8380    | $\gamma$ | -0.786               | 0.254    |
| 0.8500    | $\gamma$ | -0.155               | 0.235    |
| 1         | pure Zn | 0.000              | 0.230    |

*Mole fraction of zinc in alloy

**Obtained from vapor pressure measurements (12)

***Referred to the potential of zinc in ZnCl$_2$–NaCl$_{sat}$

Table IV. Deposits on Pt substrate in constant-potential electrolysis

| Potential | Deposit       | Crystal structure         | Atomic percent Zn* |
|-----------|---------------|---------------------------|--------------------|
| 0.200 V   | $\gamma$-PtZn alloy | Cubic                    | 77-81 %            |
| 0.250 V   | $\gamma$-PtZn alloy | Cubic                    | 77-81 %            |
| 0.300 V   | $\delta$-PtZn alloy | Cubic                    | 74-76 %            |
| 0.350 V   | $\delta$-PtZn alloy | Tetragonal, CuAu type    | 32-50 %            |
| 0.400 V   | $\delta$-PtZn alloy | Tetragonal, CuAu type    | 32-50 %            |

*Estimated from the phase diagram in Ref. 10
Fig. 1 Cyclic voltammogram of a glassy carbon electrode in a ZnCl$_2$-NaCl (60–40 mol %) melt. Temperature, 450°C; scan rate, 0.05 V/s.

Fig. 2 Cyclic voltammograms of a nickel electrode in a ZnCl$_2$-NaCl (60–40 mol %) melt. Temperature, 450°C; scan rate, (a) 0.2, (b) 0.05, (c) 0.05, (d) 0.2 V/s.
Fig. 3  X-ray diffraction patterns of deposits obtained in constant-potential electrolysis on nickel substrates. Potential, 0.250 V vs. RE; amount of electricity, (a) 10, (b) 25, (c) 50 C/cm². ○, Ni; other peaks, 7–NiZn.

Fig. 4  Alloy composition–potential relationship and cyclic voltammograms of the nickel electrode in a ZnCl₂–NaCl (60–40 mol %) melt. Temperature, 450°C.
Fig. 5  Cyclic voltammograms of a platinum electrode in a ZnCl$_2$–NaCl (60–40 mol %) melt. Temperature, 450°C; scan rate, 0.05 V/s.

Fig. 6  Cyclic voltammograms of a W electrode in a ZnCl$_2$–NaCl (60–40 mol %) melt. Temperature, 450°C; scan rate, 0.05 V/s.
Fig. 7 Cyclic voltammograms of a rotating tungsten disk electrode in a ZnCl$_2$–NaCl (60–40 mol %) melt. Temperature, 450°C; scan rate, 0.002 V/s; with (i) increasing and (ii) decreasing potential.