—Communication—

Application of Rotating Ring Disk Electrode Technique to Study on Dissolution of Nickel in Molten Alkali Chloride at 700°C

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Received March 7, 1986 ; Accepted June 12, 1986

1. Introduction

A rotating ring disk electrode method is one of the most useful electrochemical techniques to detect the reacted species and analyze the reaction mechanism in situ. This method is characterized by the collection number N which was theoretically deduced by Albery¹⁾ under hydrodynamic control of RRDE reactions.

$$N = 1 - F(\alpha/\beta) + \beta^{2/3} [1 - F(\alpha)] - (1 + \alpha + \beta)^{2/3} \{1 - F[(\alpha/\beta)(1 + \alpha + \beta)]\} \quad (1)$$

$$F(x) = (3^{1/2}/4\pi) \ln[(1+x^{1/3})^3/(1+x)] + (3/2\pi) \arctan[(2x^{1/3}-1)/3^{1/2}] + 1/4 \quad (2)$$

where $\alpha = (r_2/r_1)^3 - 1$, $\beta = (r_3/r_1)^3 - (r_2/r_1)^3$ and r_1 , r_2 , r_3 are the radius of the disk electrode and the inner and outer radii of the ring electrode, respectively. It is noted that Eq.(1) does not contain temperature-depending factors. Therefore, if the RRDE method is available to a system of high temperature electrochemistry such as a fused salt, it would become helpful to clarify reaction mechanisms. The purpose of this paper is to confirm the applicability of the RRDE method to dissolution reactions of nickel in fused alkali chloride.

2. Experimental

A pure nickel rod was used as a sample which was shaped into a cylinder of 2 mm in diameter and 10 mm in length. The electrolyte used was an equimolar mixture of KCl and NaCl. 40 grams of the electrolyte was taken in an alumina crucible of 40 mm in diameter and fused in an electric furnace at 700 °C under a flow of Ar gas. The counter electrode was a Pt plate and the reference electrode was an Ag/10 mol%AgCl electrode in a 6 mm ϕ mulite tube. The equipment was schematically drawn in Fig. 1. The assembly of the electrode is given as follows: The disk holder was a cylindrical rod made of sintered boron nitride of 10 mm in diameter and 20 mm in length, on the one cross section of which a nickel disk (2 mm ϕ) and a concentric Pt-ring (4 mm inner and 6 mm outer diameter) were embedded. According to Eq.(1), the theoretical collection number of this electrode was calculated to be 0.46. The rotating axis was made of a stainless tube of 10 mm in diameter and 300 mm in length which was used as a lead of the ring electrode. The disk electrode was screwed with a nickel-made holder which was connected with a carbon steel rod (5 mm ϕ X 350 mm), which played a role of the lead of the disk electrode. Insulation between the stainless tube and the carbon steel rod was attained by a silica tube spacer. A disk sample could be adjusted and replaced with the mechanical screw system. The assembly of RRDE was schematically drawn in Fig. 1 (A). A dual potentiostat was used for polarization of the disk and ring electrodes. Anodic polarization was mainly carried out by the potential sweep method at the sweep rate of 4.2 mV/sec.

3. Results and discussion

In order to determine the ring potential for the collection of the dissolved nickel ions, constant

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Key words: Rotating ring disk electrode, Fused chloride, Nickel dissolution

Fig. 1 Schematic diagram of RRDE assembly (A) and experimental apparatus (B)

Fig. 2 Ring polarization curve at constant disk current (A) and relation between disk and ring current (B)

anodic currents were applied to the nickel disk keeping a rotating speed of 1000 rpm, and then, the ring electrode was polarized in the cathodic direction (Fig. 2). Negative ring current rose up at around -0.23 V and gradually saturated over -0.35 V but no limiting current could be observed. Then, residual current of the ring was measured using an inert carbon electrode as a disk keeping disk current zero. The result was also given in Fig. 2. Difference in two curves donated the real ring current for reduction of the nickel ions dissolved from the nickel disk. It exhibits a limiting current over -0.35 V. When disk current changed, similar ring polarization curves were obtained as long as they were corrected by the residual current (the dotted curve in Fig. 2(A)). Relation between disk and ring currents at -0.5 V was given in Fig. 2(B). A good linearity can be seen and 0.43 is obtained as the slope value which corresponds to the collection number. This value is very close to the theoretical collection number, 0.46. This means that the cathodic ring reaction was the reverse reaction of the anodic dissolution reaction. At the next step, the effect of the rotation speed on the collection number was examined. The results are shown in Fig. 3. In the range of the rotation speed above 700 rpm, the collection number reached the value of 0.43, although a slight decrease in the collection number with the rotation speed was observed above 2000 rpm. This is probably due to less smooth rotation of the RRDE assembly. The effect of temperature on collection number was examined. It can be seen that the slopes are almost invariable both at 700 and 850 °C (Fig. 2 (B)). The result supports that the equation of the collection number is independent of temperature (Eq. (1)). It is concluded that the RRDE method can be applied to molten salt systems at high temperatures. When the ring potential was set at -0.4 V and the rotation speed was kept at 1000 rpm, the nickel disk was polarized in the anodic direction. Figure 4 shows the anodic polarization curve of the disk and the responding ring current curve in Tafel plotting. Tafel linearity of the disk polarization curve is deviated both in the lower and the higher current ranges, but the ring current holds a good linearity in a wide range, although the Tafel slope changes from 0.1 to 0.2 V/decade in the lower current range. Similar results were reported by Sato and Okamoto²⁾ on nickel dissolution in aqueous acidic solutions. They only interpreted the value of 0.1 V/decade by assuming that dissociation of an intermediate adsorbant NiOH_{ad} was the rate-determining step. In the case of the fused chloride mixture, the intermediate may be NiCl_{ad} and the rate-determining step is the chlorination reaction of NiCl_{ad} to a stable nickel chloride complex $[\text{NiCl}_4]^{2-}$ ³⁾. The value of 0.2 V/decade is most likely to deduce the direct 2-electron discharging reaction from nickel to the nickel chloride complex. Thus the following reactions may be assumed.

Validity of the existence of the adsorbant NiCl_{ad} have not been clear. More data should be required for mechanistic discussions, but it is clear that this method is also useful for high temperature electrochemistry.

Reference

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Fig. 3 Effect of rotation speed on collection number

Fig. 4 Anodic polarization curve of nickel and responding ring current (A) and apparent collection number (B)