

Study on the Electrochemical Behavior of Iodide at Platinum Electrode in Potassium Chlorate Solution

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1. Introduction

Radioactive iodine-131, is one of the most hazardous fission products which could be released from fuels of nuclear reactors during the severe accident of nuclear power plants. Due to its high radioactivity, high fission yield (2.8%) and hazardous biological effects, the behavior of iodine has been taken interests in many research groups [1-4].

Iodine is known to be released from the fuels as a cesium iodide form, CsI [5]. And, as nuclear fuels are mostly placed in the water pool, it is easily dissolved in the water after released from the fuels. In water, iodide anion could be oxidized into molecular iodine. As the molecular iodine is a volatile species and the oxidizing rate is affected by many environmental facts such as pH, radiolysis products and temperature, the oxidation reaction of the iodide ion has been considered as an important chemical reaction related to the severe accident of nuclear power plants [1-2].

In present work, the electrochemical behavior of iodide anion was observed by using cyclic voltammetric technique in potassium chlorate solutions. We observed two different oxidation waves in the oxidation potential region. From the comparison with the previous reported results [6], one is regarded as the oxidation of iodide into molecular iodine. The other is evaluated to be the formation of high-valent iodine-containing compounds.

2. Methods and Results

All chemicals were of analytical grade. The electrolyte solution with 1 mM KI, 1M KClO₄ and 1 mM KOH was prepared with ultra-pure MilliQ-treated water (18.2 MΩ from MilliQ Academic). The electrolyte solution was de-oxygenated by injecting with high-purity argon gas for 30 min before use. The pH of the electrolyte solution was maintained to be 10.9.

Electrochemical measurements, cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed by using SP-300 potentiostats (BioLogic Science Instrument, France). A conventional three-electrode system was used in the experiments. A platinum rotating disk electrode with surface area of 0.0314 cm² (Tacussel EDI 101T/ CTV 101T) was used as working electrode, a piece of platinum wire was used as counter electrode and a KCl-saturated calomel electrode was used as the reference electrode. All experiments were done at ambient temperature.

2.1 Electrochemical behavior of iodide

Figure 1 shows the cyclic voltammograms for 1 mM KI in the mixed solution of 1.0 M KClO₄ and 1.0 mM KOH on the platinum disk with scan rate 100 mV and different upper potential limits: 1.0 V (a) and 1.4 V (b). During the positive scan from 0.3 to 1.4 V, two oxidation current waves were observed at 1.0 and 1.4 V vs. SCE, respectively. In addition, one reduction current wave was observed at 0.4 V vs. SCE.

The first oxidation wave was evaluated to correspond with the oxidation of iodide into molecular iodine[6]. The molecular iodine was reported to react with iodide anion. And then, triiodide anion was formed on the electrode. The second oxidation wave was evaluated to correspond to the formation of high-valent iodine-containing compounds like IO⁻[7]. The reduction wave observed at 0.4 V was caused by the reduction of the iodine compound with high-valent.

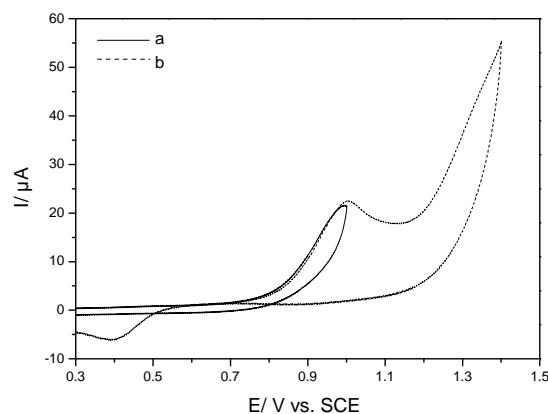


Fig. 1. Cyclic voltammograms with different upper potential limits: a) 1.0 V, b) 1.4 V on the platinum rotating disk electrode in mixed electrolyte solution of 1mM KI, 0.1 M KClO₄ and 1 mM KOH.

2.2 Diffusion coefficient of iodide anion

Figure 2 shows the relationship between the first oxidation current and the rotation speed of disk electrode. The linear relationship in the figure means the first oxidation reaction is controlled by the diffusion of the iodide anion. By using the Levich equation, the diffusion coefficient of the iodide anion was calculated to be $2.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The value is almost the same as the reported ones [8] measured in similar media.

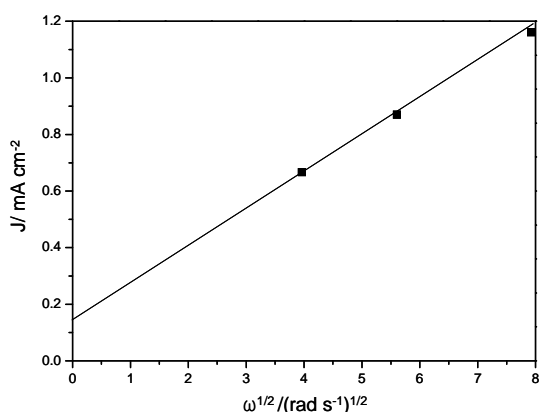


Fig. 2. Levich plot for the oxidation current of iodide on the platinum rotating disk electrode in the solution of 1 mM KI, 0.1 M KClO₄ and 1 mM KOH.

3. Conclusions

Two different oxidation waves of iodide anion were observed in the oxidation potential region. The first one is caused by the formation of the molecular iodine. The other is evaluated to be the formation of high-valent iodine-containing compounds. The diffusion coefficient of the iodide anion was calculated to be $2.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ by using Levich equation.

Acknowledgments

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