

## Effect of Solution pH on Electrochemical Oxidation of Iodide Ion at Platinum Electrode in Sodium Perchlorate Solution

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### 1. Introduction

In first several days during the severe accident of nuclear power plants, radioactive iodine-131 is one of the most hazardous volatile fission products which could be released from fuels of nuclear reactors. Due to its high radioactivity, high fission yield up to 2% and hazardous biological effects, many research groups [1-7] have been studied the chemical behavior of iodine species.

Iodine is reported to be released from the fuels as a cesium iodide form, CsI [8-10]. 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 factors 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 effect of the solution pH on the electrochemical oxidation of iodide anion was carried out using linear sweep voltammetry (LSV) technique in different pH solutions. We confirmed that the electrochemical oxidation reaction of iodide into iodine at Pt electrode is independent on the solution pH.

### 2. Methods and Results

All chemicals were of analytical grade. The electrolyte solution with 1 mM NaI and 0.1 M NaClO<sub>4</sub> was prepared with ultra-pure MilliQ-treated water (18.2 MΩ from MilliQ Academic). The electrolyte solution was de-oxygenated by purging with high-purity argon gas for 30 min before each experiment. The pH of the solution was controlled by HClO<sub>4</sub> and NaOH solution, respectively.

Electrochemical measurements, 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 disk electrode with surface area of 0.0314 cm<sup>2</sup> (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 oxidation of iodide anion

Figure 1 shows the linear sweep voltammograms for NaI in the solution of 0.1 M NaClO<sub>4</sub> on the platinum disk with scan rate 5 mV/s. During the positive scan, two distinct oxidation current waves were observed at 0.45 and 1.2 V vs. SCE, respectively.

During the positive scan in 0.1 M NaI solution, two distinct oxidation current waves were observed at 0.45 and 1.2 V vs. SCE, respectively. The first oxidation wave was evaluated to correspond with the oxidation of iodide into molecular iodine [11-13]. The molecular iodine was reported to react with iodide anion [13]. And then, tri-iodide 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<sup>-</sup> [14]. The decrease of current above 0.5 V is caused by the adsorption of molecular iodine. In low iodide concentration solution, the oxidation behavior was quite different from that of high concentration.

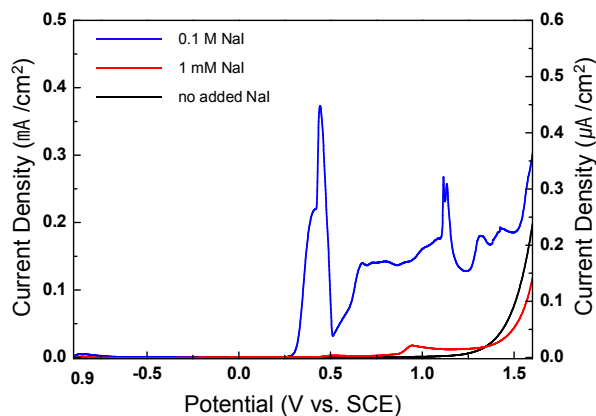


Fig. 1. Linear sweep voltammograms in iodide solution with different concentrations: no added (right ordinate), 1 mM (right ordinate) and 0.1 M NaI (left ordinate) on the platinum disk electrode.

#### 2.2 Effect of the solution pH on the oxidation of iodide ions

Figure 2 shows the linear sweep voltammograms on the platinum disk electrode in different pH solutions. The solution pH was controlled by HClO<sub>4</sub> and NaOH

solution, respectively. We clearly found that the oxidation reaction of iodide ion was independent on the pH range between 4 and 10. Even though the oxidation reaction of iodide ion is not dependent on the solution pH, other reactions such as the reduction reactions of dissolved oxygen and hydrogen peroxide are dependent on the solution pH. Therefore, the oxidation reaction of iodide ion is dependent on the solution pH in the presence of these reducing species.

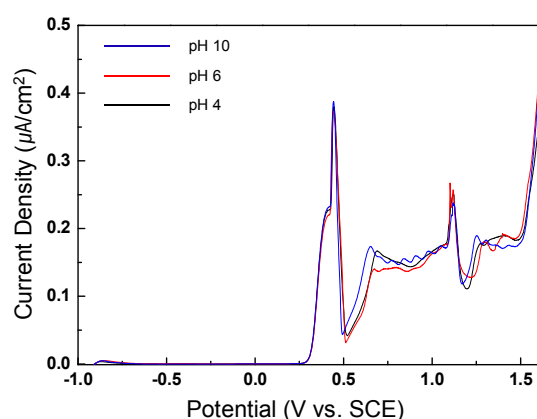


Fig. 2. Linear sweep voltammograms on the platinum disk electrode in different pH solutions.

### 3. Conclusions

By the linear sweep voltammograms obtained at the platinum electrode, it was confirmed that the oxidation of iodide ion starts at the potential above 0.45 V vs. SCE. And the oxidation reaction is independent on the solution pH in the range between 4 and 10.

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