

## **A STUDY ON THE HI CONCENTRATION BY POLYMER ELECTROLYTE MEMBRANE ELECTRODIALYSIS**

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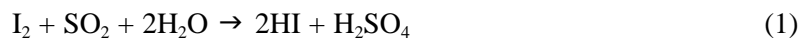
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### *Abstract*

Concentration of HI over HIx solution by polymer electrolyte membrane electro dialysis was investigated using galvanodynamic and galvanostatic polarisation method. For this purpose, HIx solution with sub-azeotrope composition ( $\text{HI} : \text{I}_2 : \text{H}_2\text{O} = 1.0 : 0.5 : 5.8$ ) was prepared. It was noticed that the electrical energy demand for electro dialysis of HIx solution decreases with increasing temperature. From the experimental results, it is concluded that the system resistance crucially affects the electro dialysis cell overpotential and hence the optimisation of cell assembly as well as the selection of low resistance materials should be carried out in order to obtain high performance electro dialysis cell.

## Introduction

Thermochemical water-splitting iodine sulphur (IS) process is considered as the most promising method for large scale, high efficiency, and environmentally benign hydrogen production [1]. The IS process is comprised of three coupled chemical reactions such as Bunsen reaction, sulphuric acid decomposition reaction, and HI decomposition reaction [2]. The reaction scheme is described as follows:



Many works have been done on the evaluation of the thermal efficiency of the IS process by optimizing their closed-cycle loop [1, 3-5]. They reported that the hydriodic acid concentration part is the most energy consuming process since the HIx solution (HI - I<sub>2</sub> - H<sub>2</sub>O mixture) produced from the Bunsen reaction present in an azeotrope composition. And hence the distillation part to concentrate hydriodic acid needs lots of excess thermal energy, giving rise to total thermal efficiency drop in IS process.

To solve these problems, GA researchers [2] adopted an extractive distillation by using phosphoric acid. In this process, the phosphoric acid extracts only I<sub>2</sub> and H<sub>2</sub>O and finally HI can be concentrated. However, it contains phosphoric acid concentration process by steam recompression, making the whole process to be complicated and corrosive. In 2003, Hwang *et al.* [6], tried to concentrate HI in HIx solution by electro-electrodialysis method. They reported that the energy demand of electro-electrodialysis to produce 1mole of hydrogen was much lower than that of steam recompression in GA process and the application of electro-electrodialysis in IS process seems to be very useful with proposing the possibility of high thermal efficiency.

In this respect, the present work discusses the polymer electrolyte membrane electro dialysis method to concentrate the HI over HIx solution. For this purpose, we prepared HIx solution with sub-azeotrope composition (HI : I<sub>2</sub> : H<sub>2</sub>O = 1.0 : 0.5 : 5.8) and the polymer electrolyte membrane electro dialysis was investigated using galvanodynamic and galvanostatic polarisation method.

## Experimental

The activated carbon fiber cloth was cut into the size of 5 cm x 5 cm to form the carbon electrode. The carbon electrode was immersed in ethanol solution overnight to remove the residuals and then dried at room temperature.

The Nafion 117 (Du Pont, USA) was used as a polymer electrolyte membrane. The membrane was pretreated by boiling in 3 wt.% H<sub>2</sub>O<sub>2</sub> solution for 1 h, followed by boiling in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 1h. Thereafter, the membrane was placed in boiling water for 1 h, and the procedure was repeated at least twice to remove completely the sulfuric acid.

The HIx solution was prepared from the mixing of hydriodic acid (55~58 wt.%, Kanto Chemicals Co., Japan) and Iodine (99%, Junsei Chemicals Co., Japan) with mole ratio of HI : I<sub>2</sub> = 1.0 : 0.5. From the titration result of HIx solution, it was confirmed that the mole ratio of as-prepared HIx solution was HI : I<sub>2</sub> : H<sub>2</sub>O = 1.0 : 0.5 : 5.8. This indicated that the HI molarity of starting solution was 9.55 mol kg<sup>-1</sup>-H<sub>2</sub>O, which is lower than the azeotrope composition of 11.11 mol kg<sup>-1</sup>-H<sub>2</sub>O.

A single cell assembly was composed of polymer electrolyte membrane sandwiched with two carbon electrodes, gaskets, and carbon blocks with flow channels for the distribution of reactant HIx solution as shown in Figure 1 (a). The single cell was placed in a mantle heater to maintain a desired temperature. Figure 1 (b) shows the schematic illustration of the experimental arrangements for electrochemical measurements. The volumes of HIx solution (HI : I<sub>2</sub> : H<sub>2</sub>O = 1.0 : 0.5 : 5.8) were 430 and 190 ml in anolyte and catholyte reservoirs, respectively. The reservoirs and all glass lines were cast in double jacket that were heated with silicon oil at the same temperature.

## Results and discussion

Figure 2 displays cell potential measured from the electro dialysis cell as a function of operation temperature. As operation temperature increased from 35 to 90°C, the cell potential decreased from 0.68 to 0.41 V at the applied current of 2 A. This is because high temperatures reduce the amount of electrical energy required to concentrate HI molarity from a thermodynamic standpoint and hence electrical energy demand  $\Delta G$  for electro dialysis of HIx solution decreases with increasing temperature [7]. Furthermore, high temperature operation quite generally favours reaction kinetics decreasing activation overpotential.

In this respect, it is assured that high temperature operation is advantageous for electro dialysis of HIx solution. In this work, the operation cell temperature was selected as 90°C. If not specifically indicated, all the electrochemical measurements in the present study were carried out at 90°C.

Figure 3 illustrates the current-potential curves measured on the electro dialysis cell. The potential exhibited linear increase with the applied current over all current ranges. It is well known [8] that current-potential curve has a characteristic shape and clearly shows three distinct regions with respect to the applied current. In the low current range, the shape of current-potential curve is convex and transformed to linear in the intermediate current range. Then the shape changed to concave in the high current range.

The overpotential in the low current range is ascribed to the activation overpotential, which is caused by the slowness of the reactions taking place on the surface of the electrode. In the intermediate current range, the overpotential is mainly due to the ohmic losses of the system. The appearance of overpotential in the high current range is primarily ascribed to the mass transfer limitation of the involved species.

Under the circumstances, it is reasonable to say that the reaction kinetics on the surface of carbon electrode is facilitated and hence the activation overpotential is not observed. However, the system resistance such as electrode, electrolyte, polymer electrolyte membrane, and carbon block could be dominant, influencing cell overpotential over all current ranges. Therefore, it is necessary to reduce the system resistance by selecting the cell constituents with low resistance and optimising the cell assembly.

It is noticed that the vapour pressure of HI over HIx solution steeply increases right after the azeotrope composition [9]. Accordingly, the thermal burden imposed on the distillation could be drastically diminished. The azeotrope composition of HIx solution is HI : H<sub>2</sub>O = 1.0 : 5.0 (HI molarity: 11.11 mol kg<sup>-1</sup>-H<sub>2</sub>O). However, as mentioned earlier, the HIx solution prepared in this work was of sub-azeotrope composition with HI molarity 9.55 mol kg<sup>-1</sup>-H<sub>2</sub>O. Therefore, we tried to concentrate HI over azeotrope composition from sub-azeotrope composition examining electrochemical behaviour of the cell.

Figure 4 (a) plots the cell potential against elapsed time with applied current of 2 A. The cell potential steadily increased from 0.40 to 0.47 for 2 h. At the same time, the HI molarity increased up to 11.9 mol kg<sup>-1</sup>-H<sub>2</sub>O in catholyte, while that in anolyte decreased up to 8.7 mol kg<sup>-1</sup>-H<sub>2</sub>O. The ratio of HI molarity change between catholyte and anolyte from the starting composition is about 2.6. Taking into account that the volume of HIx solution in anolyte is almost 2.3 times as much as that in catholyte, it can be said that the amount of HI molarity change in two solutions is roughly the same.

From the experimental results, we concluded that electrical energy demand  $\Delta G$  for electro dialysis of HIx solution decreases with increasing temperature. Moreover, the electro dialysis cell overpotential is primarily influenced by the system resistance and hence the thermal efficiency of the cell could be improved by reducing the constituent resistance and by optimizing the cell assembly.

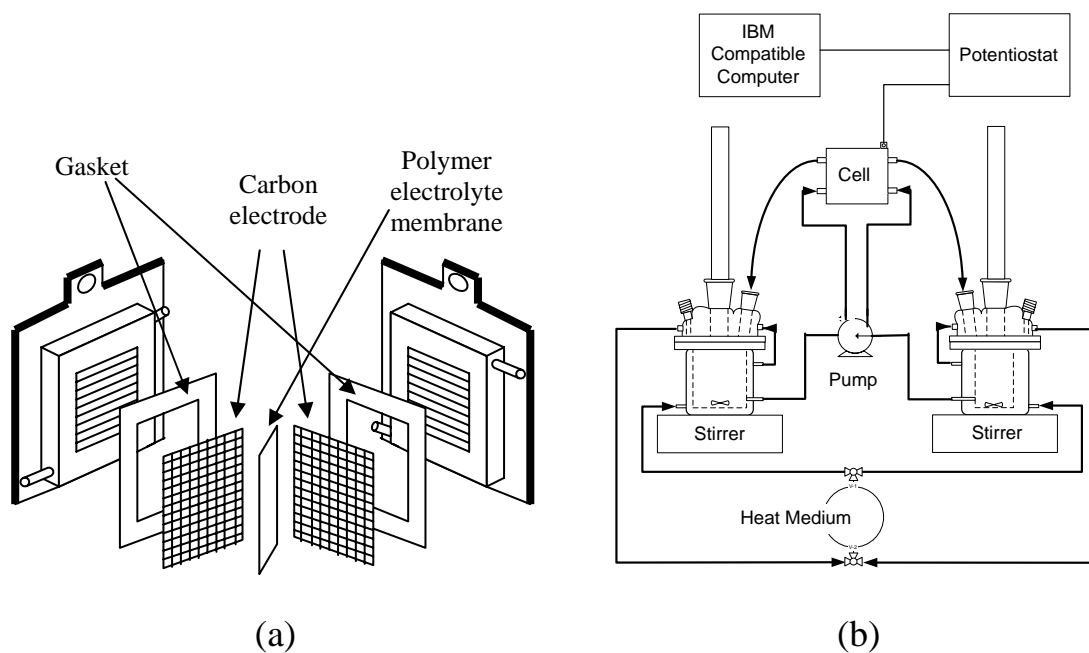
### **Acknowledgement**

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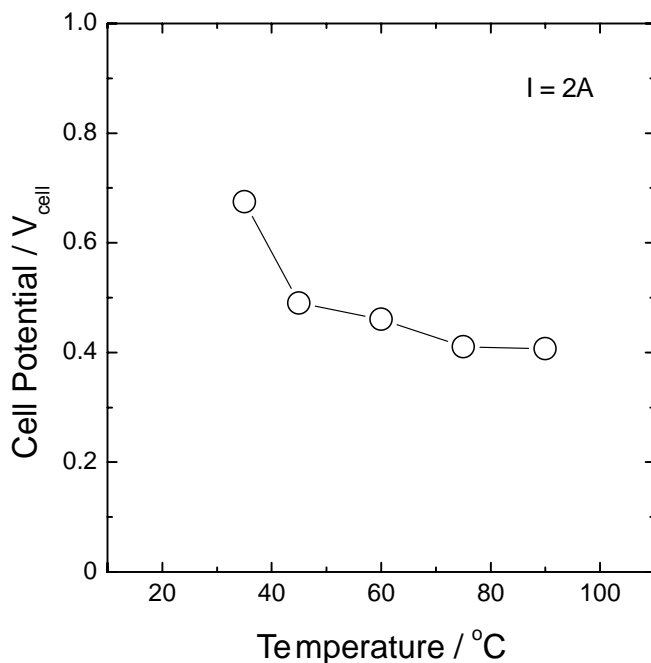
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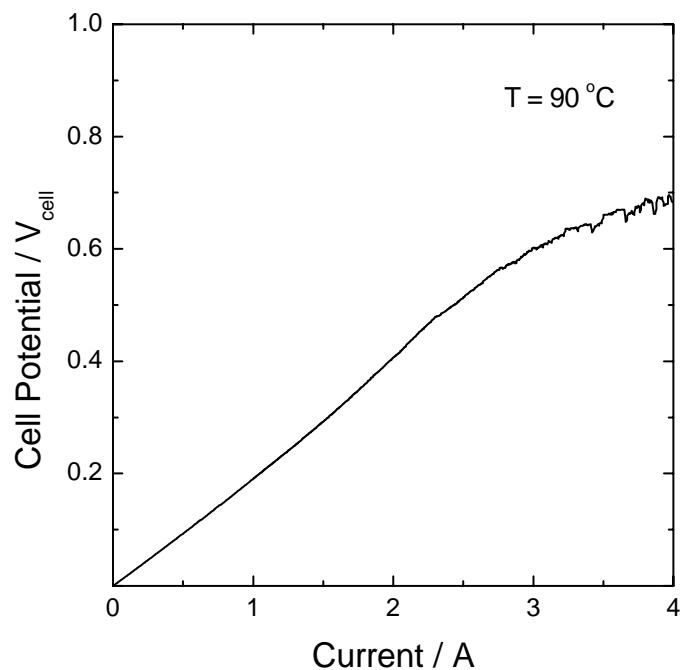
**Figure 1. Schematic diagram of (a) electro dialysis cell and (b) experimental arrangements used for concentrating HI over HIx solution**



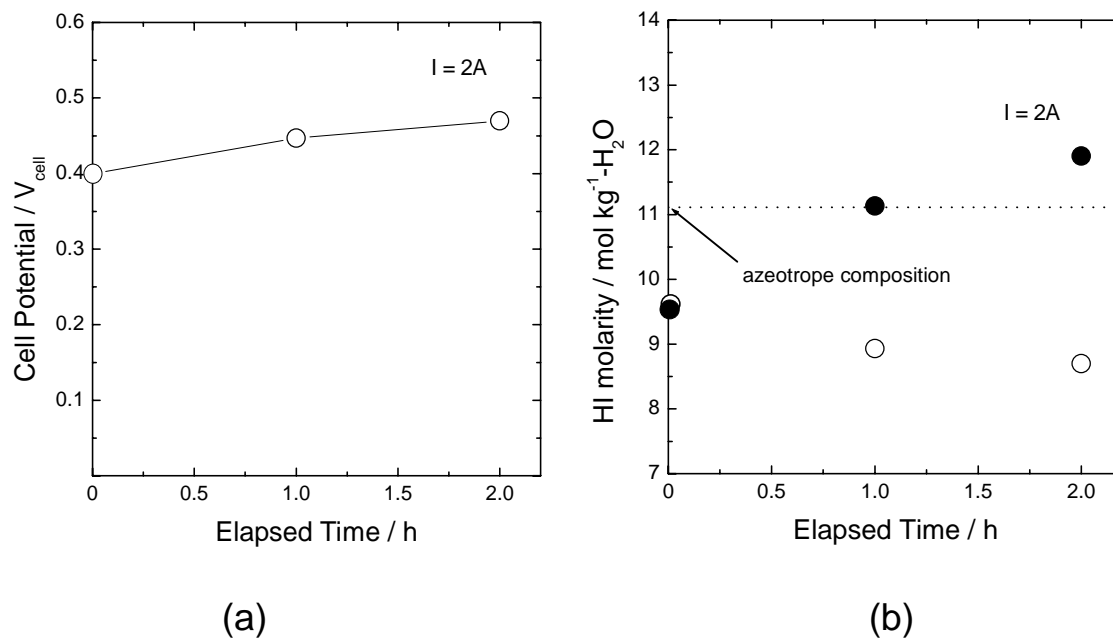
**Figure 2. Plots of cell potential against operation temperature measured on the electro dialysis cell at the applied current of 2A. The apparent area of activated carbon electrode was 25 cm<sup>2</sup>.**



**Figure 3. Galvanodynamic polarization curves measured on the electro dialysis cell at the operation temperature of 90°C.**



**Figure 4. Plots of (a) cell potential and (b) HI molarity against elapsed time measured on the electro dialysis cell at the operation temperature of 90°C. The applied current on the cell remained constant with 2 A throughout the measurement.**



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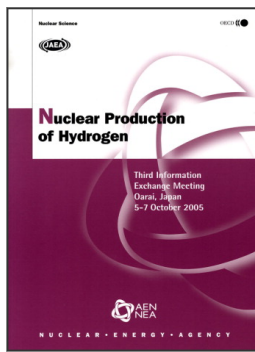
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