Hydrogen production by water electrolysis using solid polymer electrolyte

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Received 20 August 2000; revised 24 January 2002

In recent years, considerable amount of work on the development of highly efficient solid polymer electrolyte composites for water electrolysis has been carried out\(^1\). Generally Nafion-117 (cationic exchange membrane) is used as solid polymer electrolyte (SPE) and platinum and iridium/iridium oxide are found to be suitable materials as cathode and anode respectively for water electrolysis due to their low over voltages. Different techniques like chemical deposition\(^2\), Electro deposition\(^3\), hot press method\(^4\) and deposition of iridium or platinum on porous titanium have been tried by various workers\(^5,6\) to prepare an efficient system. Chemical deposition can be carried out either by saturating Nafion membrane by cationic solution of Ir or Pt and then reducing the noble metal cations by a suitable reducing agent, or by circulating the anionic solution of metal salts to one side of membrane and reducing agent to other side of it. In this note, the chemical deposition of platinum is carried out by former method and iridium is deposited by electroless plating method\(^5\).

Hydrothermal treatment at high temperature to increase the water absorption capacity of the membrane and ion plasma treatment for roughening the surface of membrane, to enhance the adhesive strength of catalyst-membrane are generally carried out before chemical deposition. But we have prepared all SPE composites without ion plasma treatment at different hydrothermal treatment temperatures to observe systematically the effect on the performance of electrolytic cell.

Experimental

Perfluorosulphonic acid polymer membrane (Dupont de Nemours Nafion products) Nafion-117 (eq.wt.1100 and dry thickness 0.178mm) was chosen as SPE. IrCl\(_3\)·H\(_2\)O, Pt (NH\(_3\))\(_2\)Cl\(_2\)H\(_2\)O, NaBH\(_4\) and hydrogen dichloride (GR grade) were supplied by Aldrich chemicals. Before chemical deposition, Nafion membrane (5x5 cm\(^2\)) sample was cleaned by boiling in HNO\(_3\)·H\(_2\)O (1:1 vol) for 30 min and then boiled in deionized water(resistivity =18M ohm cm at 20°C) under pressure at 100 to 150°C for 1 h for hydrothermal treatment.

Deposition of platinum

The chemical deposition of platinum was carried out by the same procedure as described by Millet et al.\(^2\). Nafion was dipped in 0.01M Pt(NH\(_3\))\(_2\)Cl\(_2\)·H\(_2\)O solution for 15 min at room temperature and then the reduction of cationic platinum on membrane was carried out by dipping it in 0.3% NaBH\(_4\) solution for two hours. Generally, two cycles for the deposition are sufficient to prepare a good Pt/Nafion composite with 1.07 to 1.15 mg/cm\(^2\) loading.

But if the efficiency of electrolytic cell is lacking, It may be increased by a third cycle of deposition, the film is dipped in platinum solution only for 5 min. If higher loading of platinum is carried out by repeated cycles, the deposition of platinum takes place too far in the membrane and this causes a decrease in the hydrogen production efficiency of the cell (low faradic yield).

Deposition of iridium

Iridium was deposited on the platinum deposited surface of Nafion in a electrolessplating bath\(^7\) at 70°C. In 250 ml of M/25 solution of IrCl\(_3\)·2H\(_2\)O, 100 ml of M/10 solution of hydrogen dichloride and 1 ml of conc. HCl were added by stirring. The solution was concentrated to 25ml at 90°C. This solution (5 ml) was diluted to 350 ml with water and the pH of the solution was adjusted to 2.8 by N/10 NaOH solution. In this electrolessplating bath the deposition automatically takes place on platinum surface at
70°C. The deposition was carried out for 1 to 4 h by keeping pH of solution between 2.7 and 2.8 using N/10 NaOH solution. The deposits from 1 mg/cm² to 4 mg/cm² were obtained depending upon the time of deposition. Generally, a period of 3 to 4 h is sufficient to give good composite of Pt-Ir.

M/SPE/M (M=PtI r or Pt, SPE = Solid polymer electrolyte or Nafion membrane) composite was sandwiched between two platinum plated titanium current collectors made of titanium gauze (120×110 mesh diameter 0.1 mm). Further titanium gauzes were pressed to M/SPE/M composite by two platinum plated titanium plates (10×10×1 cm³). Titanium plates were insulated from each other by a teflon sheet of suitable thickness as shown in Fig. 1. On the pressed side titanium plates were engraved to 1 mm depth and with same breadth. Each groove is 2 mm apart from the adjacent groove. These grooves ensure sufficient and uniform supply of water during electrolysis and also a escape route of O₂ and H₂ gases during electrolysis. This whole set-up is represented in Fig. 2 as electrolysis cell. The titanium plates were connected to the D.C. power supply, which can work either at constant voltage or at constant current. There are two thermocouples (TC in Fig. 2) inserted in the titanium plates to measure the temperature of electrolysis cell. Tap water was filtered (PF & R.O.) and stored in a tank. It was deionised (DI) (resistivity 18 MΩ cm at 20°C) and pumped to anodic chamber (A) and cathodic chamber (B). Each chamber was made up of copper and teflon coated from inside having capacity of two liters and 3/4 of each chamber was filled with deionized water, which was found to be sufficient to carry out the electrolysis for many hours.

Water from chamber A and chamber B was pumped to the electrolysis cell through heat exchanger (HE) to maintain a constant temperature. After passing through electrolysis cell (EC), excess water, H₂ and O₂ gases were pumped to chamber B and A respectively. O₂ and H₂ gases escaped from the top of chambers A and B respectively and their flow and purity were checked by a flowmeter and a gas analyser.

The whole system was connected to DA (data acquisition and control system) which automatically controls the flow and temperature of water and pressure of the gases. The current and voltage were also monitored by this unit.

**Result and discussion**

The bonding of electrodes (Pt and Ir) on the SPE is critical. In order to realize the efficient composites for SPE water electrolysis, two conditions must be met:

(i) Metallic electrode must be located simultaneously inside the membrane (act as electrocatalyst) and outside on the surface of membrane (act as current collector); and

(ii) metallic electrode must be located not too far inside the membrane to avoid low faradic yield due to gas diffusion through the membrane. Furthermore, these two regions must be in contact to ensure electron transport and good adherence of the electrode under high mechanical tension during gas evolution.

As the electrocatalysts (Pt and Ir) are costly metals their loadings on the SPE should be as low as possible (without decrease of electrolysis cell efficiency) so as to make these cells economically viable.

The Pt/ SPE/ Pt composites prepared with different loadings by depositing Pt as described in the experimental section: Current voltage (CV) curves were plotted as shown in Fig. 3 and the electrolysis was carried out for each composite at 800 mA/cm² (current density) at 80°C for many hours. The required voltage for electrolysis for each composite is summarized in Table 1.

It is clear from Table 1 that two cycles deposition of Pt is sufficient for the efficient working of electrolysis cell.
Similarly composite with different Ir. loading but with same Pt loading (1.07-1.15 mg/cm²) were prepared and electrolysis was carried out for each sample at 800mA/cm² at 80°C and results are summarized in Table 2. CV curves at 25°C and 80°C are plotted in Fig. 3.

The CV curves for all composites having Pt loading 1.15mg/cm² and Ir loading 2.8 mg/cm² coincide with each other, but as the Pt loading is increased, the current efficiency of the cell decreases as in Table 1. On the other hand with the increase of Ir loading the current efficiency remains more or less same but the minimum amount of Ir required for loading is 2.8 mg/cm² as in Table 2.

In these experiments the nafton membranes were pretreated at 110°C for hydro thermal treatment for one hour in water before chemical deposition of Ir or Pt.

The Pt/SPE /Pt and Pt Ir/SPE /PtIr composites were found to be light golden yellow and light gray in colour respectively with smooth spotless shining surface to the naked eye.
If some flaws like dark spots, non-uniformity of colour appeared on the deposited film, it was observed that it does not form a good SPE composite.

SEM photograph of the surface and cross section of IrPt/SPE composite for optimum loading of Pt (1.15 mg/cm²) and Ir (2.8 mg/cm²) were recorded. The porous structure of the layer was seen which is necessary for evolution of gases and absorption of water to membrane. Layer of approximate 5 µm thickness of IrPt was found to be directly bound inside and above the nafion membrane. The deposition of Ir was not only on the outer surface of Pt but also crept deeply inside of the Pt layer as has been revealed by the RDX analysis.

**Hydrothermal treatment**

The process of boiling nafion membrane in water at high temperature is called hydrothermal treatment. This treatment increases the water absorption capacity of the membrane. Generally 100°-150°C are found to be the desirable temperature range. This is because at temperature below 100°C, the adhesive strength between membrane and the deposited metals tended to decrease, and at temperature above 150°C the mechanical strength of the membrane tends to decrease considerably. It has also been observed that the effective resistance of the membrane also decreases slightly with increase in hydrothermal temperatures. In order to find out the effect of hydrothermal treatment on the overall efficiency of the cell, six Pt/SPE/Pt (1.15 mg/cm² loading) composites were prepared, these were pre-treated at temperatues 100-150°C at an interval of 10°C in nickel autoclave at high pressure.

**Table 1**—Dependence of number of cycles of Pt deposition on Nafion and the effect of Pt loading on electrolysis voltage and current efficiency.

<table>
<thead>
<tr>
<th>No of cycle of Pt deposition</th>
<th>Pt loading (mg/cm²) at 800 mA</th>
<th>Electrolysis voltage (±0.01)</th>
<th>Current efficiency* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.53-0.58</td>
<td>2.1-2.4 (not stable)</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>1.07-1.15</td>
<td>2.02 ±0.01</td>
<td>98.7</td>
</tr>
<tr>
<td>3</td>
<td>1.72-1.80</td>
<td>2.02 ±0.01</td>
<td>97.2</td>
</tr>
<tr>
<td>4</td>
<td>2.30-2.38</td>
<td>2.02 ±0.01</td>
<td>90.1</td>
</tr>
</tbody>
</table>

*current efficiency %=[Volume of generated H2 in ml×100]/[Current x 22400 mL]

Each composite was tested for several hours for water electrolysis at 80°C. Current voltage curves for all the samples were found to be same as shown in Fig. 3. But the amount of gas evolution or current efficiency decreases as the hydrothermal treatment temperature increases.

It was observed that the most suitable hydrothermal treatment temperature ranges between 110°C and 120°C. The behaviour for IrPt/SPE/IrPt composite has not been tested but it is assumed that it will be similar to Pt/SPE/Pt composite.

**Surface roughening treatment**

Various techniques like sand paper, sandblast and ion plasma sputtering are used for roughening the surface of membrane. It is considered that this treatment tends to increase the adhesive strength of the catalyst with membrane.

However, it was also observed by Millet et al. that surface roughening treatment has practically no effect on the efficiency of the cell. However, it may decrease the effective thickness of the membrane, thus causing more permeation of gases through the
membrane. The present investigation is carried out without this treatment. The current efficiency and energy efficiency (two parameters to judge the efficiency of electrolysis cell) are found to be 99.2% and 90.3% respectively for Pt and Ir loading of 1.15 mg/cm² and 2.8 mg/cm² respectively at 110°C hydrothermal treatment temperature.

Energy efficiency = \left\{ \frac{1.48v \text{ (thermoneutral voltage)}}{\text{Electrolysis voltage (v)}} \right\} \times \text{current efficiency}

It can be concluded that the procedure described for preparation of M/SPE/M (M= Pt or Ir) composite is simple and reproducible. A good composite can be prepared within seven hours. The composite thus obtained presents good electrochemical properties, low catalyst’s loading, long time stability and high energy efficiency.

References