PRODUCTION OF AN ION-EXCHANGE MEMBRANE-CATALYTIC ELECTRODE BONDED MATERIAL FOR ELECTROLYTIC CELLS

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A good bond is achieved by placing a metal salt in solution on one side of a membrane and a reducing agent on the other side so that the reducing agent penetrates the membrane and reduces the metal. Thus, a solution containing Pt, Rh, etc. is placed on one side of the membrane and a reducing agent such as NaBH₄ is placed on the other side. The bonded metal layer obtained is superior in catalytic activity and is suitable as an electrode in a cell such as for solid polymer electrolyte water electrolysis.
Production of bonded materials between an ion-exchange membrane and catalytic electrode for cells

This invention is concerned with a method of producing an ion-exchange membrane-catalytic electrode bonded material for electrolytic cells. In this method, a solution of metal salts is placed on one side of the ion-exchange membrane and on the other side a reducing agent solution is placed. Then the reducing agents penetrate the metal salt solution by osmosis. As a result, metal layers are formed onto the membrane surface in the metal salt solution.
3. Explanation of Details of This Invention

This patent is concerned with the production of an ion-exchange membrane-catalytic electrode bonded material for electrolytic cells. There are two known methods of bonding catalytic metals onto the ion-exchange membranes. In the first method, catalytic metal powders are thermally pressed onto the membrane surface as described in Jpn. Kokai Tokkyo Koho, 77-78788. In the second one, the ion-exchange membrane is immersed in a solution of reducing agents and then placed into a metal salt solution. The metal is formed on the surface of the membrane. This method is found in Jpn. Kokai Tokky Koho, 67-5014. However, these methods have some difficulties such as

a) in the first method the processes are quite complicated. Some special bonding materials such as teflon (trade mark of Du Pont, Inc. USA) are required. Further, the catalysts are often damaged by surfactants which are contained in the bonding materials.

b) the second method also has a flaw. It is difficult to maintain a constant concentration of the reducing agents on the membrane surface. Therefore, reduction reactions are nonuniform on the surface. As a result, a good bonding between catalytic metals and the ion-exchange membrane is often not obtained.

In order to overcome these problems, the present authors developed the method described below. This method can supply ion-exchange membrane-catalytic electrode bonded materials for electrolysis of solid polyelectrolytes (SPE).

The SPE produces hydrogen efficiently. It is known that hydrogen gas at the anode and oxygen gas at the cathode are generated if bonding materials consisting of positively charged ion-exchange membranes are used. In this SPE method, improvement of bonding between the ion-exchange membrane and catalytic electrodes is essential in order to increase energy efficiency by reducing the electric field recomposition of water.
This invention is based on our observation that a reducing agent can penetrate through ion-exchange membranes continuously. Thus, if a metal salt solution is placed on one side of the membrane and a reducing agent solution is introduced on the other side, the reducing agent penetrates through the membrane and moves into the metal salt solution. As a result of the contact with the metal salt solution, good binding and highly active metallic layers are formed on the surface of the membrane in the metal salt solution side.

In short, this invention is a method to produce ion-exchange membrane catalytic electrode bonded materials for an electric cell forming metallic layers on the surface of the ion-exchange membrane in the metallic salt solution side by having the reducing agent penetrate through the membrane from the other side.

We describe below details of this invention. A cell is divided into two parts, 1 and 2, by an ion-exchange membrane (Figure 1). The metal salt solution is placed in compartment 1 and a solution containing reducing agents in compartment 2. The reducing agents penetrate through the membrane into the metal salt solution. Metal layers are formed by reduction reaction on the surface of the membrane in the metal salt solution. After one side of the membrane is covered by the desired metal, the cell is emptied and washed thoroughly. Then, metal salt and reducing agent solutions are introduced in compartments 2 and 1, respectively. The metal layer is now formed on the surface of the other side of the membrane.

Because of reaction characteristics of cathode and anode in the electrolysis of water, a metal, in general, on one side is different from that on the other side. This invention yields desired results, whether metals on both sides of the membrane are the same or different.
Any cation ion-exchange membrane can be used for our invention. From its oxidative and thermal resistance nature, floride resin, Nation (trade name from DuPont Inc.), manufactured by Du Pont Inc., USA, is preferable. However, good quality bonded materials are also obtained by using syrene based ion-exchange membranes.

As metal catalysts, the platinum family such as platinum, rhodium, palladium, ruthenium, and iridium are preferable because of their activity and antioxidant nature. However, other metals which slow reduction reaction by reducing agents, can be used. For reducing agents, alkali borane such as sodium boron hydride, and organic borane such as dimethyl amino borane, hydrous hydride, sulfate and chlorides are used.

The compatibility and catalytic activity of the metal layers are dependent on the quality of the ion-exchange membrane, metal salts, type of reducing agents, concentration of solutions, and temperature. In order to increase permeability of the membrane, it is recommended that the membrane be treated with hot water. For example, this can be done easily treating Nafion with 50-200°C water. The treatment also increases the bonding ability of metals.

If sodium boron hydride is used as a reducing agent, platinum and rhodium can obtain a sufficient bonding ability at room temperature, while for ruthenium and iridium the temperature should be 50-95°C. For the concentration of the solutions, in general, 1-10% of metal salt solutions and 1-20% reducing agent solutions are used. For catalytic activities, platinum is the best for anode catalysts, while iridium is superior for cathode catalysts. The order of catalytic ability at the cathode is Ir > Rh > Rh-Pt > Pt > Ru-Pt > Ru > Pd. Here Rh-Pt is a blend of two metals, Rh and Pt. If a mixture of their salt solutions is used, such a blend of metals forms a layer on the surface of the membrane. For a single metal solution, if a highly active catalyst having a large surface area is used, the faster the rate of reduction. In general, the rate of reduction reaction depends on temperature, concentration of the reducing agents, and salt concentrations. Further, the
higher the temperature for the membrane treatment, the faster the reduction reaction is. In sum, this invention has several advantages over the conventional methods for producing bonded materials. They are as follows:

a) The present method is economical since it can produce such materials by a single process, compared to the teflon bonding method. Further, there is no interference caused by bonding materials or components contained in them.

b) The present method can control the amount of catalyst easily, since the reducing agent penetrates through the membrane. It can be controlled by specifying the metal salts, the concentration of the reducing agent, temperature, and treatment of the membrane. Moreover, reproductibility of the metal layers are mainly determined by these factors. Therefore, both sides of the membrane can be covered by the same quality of metal layers.

c) The reduction reaction occurs only on the surface of the membrane. Thus, there is no waste of solutions. Since we can control the amount of deposit on the membrane surface, the solutions can be used again. In sum, this invention overcomes various defects found in conventional methods and provides an economical and simple method for the production of ion-exchange membrane-catalytic bonded material for an electrolytic cell.

Below are presented properties of an ion-exchange membrane catalytic bonded material for an electrolytic cell.

The internal resistance consists of resistance of the membrane, contact resistance between membrane and catalyst, and some other resistances. If the same kind of membranes is tested, the membrane resistance is constant. Thus, the values of internal resistance indicate contact resistance. The contact resistance becomes smaller, as the contact between the membrane and catalyst becomes better. Therefore, strength of the bonding may be expressed by the internal resistance.
TABLE I. Values of Resistances in Water Electrolysis at 25°C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Electrode</th>
<th>Ion Exchange Membrane</th>
<th>Internal Resistance ($\Omega$ cm$^2$)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt / Pt</td>
<td>0.28</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rh / Pt</td>
<td>0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>G.E. Electrode</td>
<td>0.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SPE Electrolyte</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nafion 125</td>
<td>0.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Key: 2--Catalytic Electrode; 3--Ion-Exchange Membrane; 4--Internal Resistance; 5--Notes; 6--Cathode/Anode; 7--Nafion 125; 8--Electrodes were produced by the present method; 9--Manufactured by G.E. Inc.; 10--SPE catalytic electrodes for water electrolysis; 11--Electrodes were manufactured by the conventional methods (A); 12--Published by G.E.; 13--Electrodes were produced by the conventional method (B); NaBH4 was used for the reducing agent.

The internal resistance appearing in Table II shows that the bonding is quite good compared to the electrodes prepared by other methods.

TABLE II. Excess Charge during Water Electrolysis.

<table>
<thead>
<tr>
<th>No.</th>
<th>Electrode</th>
<th>Ion Exchange Membrane</th>
<th>Excess Voltage ($V$)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt / Pt</td>
<td>0.04</td>
<td>-0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rh / Pt</td>
<td>+0.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nafion</td>
<td>+0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pt / Pt</td>
<td>-0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rh / Pt</td>
<td>+0.43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Key: 14--Table II. Excess Charge during Water electrolysis; 15--Catalytic Electrode; 16--Ion-Exchange Membrane; 17--Excess Voltage; 18--Volt; 19--Notes; 20--Anode; 21--Cathode; 22--Nafion; 23--The negative sign for the excess voltages corresponds to that for the anode and the positive for the cathode.
In this table, the catalytic bonded material is prepared by the present method, in No. 1, while in No. 2 we used ones produced by the conventional method. As seen from the table, excess voltages at both the cathode and anode are lower for the present method than that for the conventional method. This confirms that the material prepared by the present method is energetically superior to that produced by the conventional method.

The ion-exchange membrane-catalytic electrode bonded material, produced by the current method, can be used in a variety of electrochemical equipment such as SPE water electrolysis, fuel battery, oxygen concentrator, and ion-exchange membrane-catalytic electrode. The following application is one of them. It is noted that the use of the current method is not confined to these special cases only.

**EXAMPLE 1.**

The ion-exchange membrane, Nafion, was treated in 100°C water for 60 minutes. It was set in the cell. 10\% aqueous solution of sodium borane hydride was poured into one side of the cell and 3\% aqueous solution of platinum chloride was placed in the other side of the cell. The reaction was carried out for 5 minutes. The metal layer on the surface of the membrane was analyzed. The results are as follows: platinum content $4 \text{ mg/cm}^2$, metal thickness $0.006 \text{ mm}$, and relative surface resistance $10^{-1} - 10^{-2}\Omega\cdot\text{cm}^2$.

**EXAMPLE 2.**

The membrane was treated as described in Example 1. 15\% aqueous solution of hydrazine and 3\% platinum chloride solution were used. The reaction time was about 30 minutes. The results were metal content $5 \text{ mg/cm}^2$ and thickness $0.007 \text{ mm}$.
EXAMPLE 3

Styrene based ion-exchange membrane, Neocepta, manufactured by Tokuyama Sode KK, Japan, was used. 5% sodium borane chloride and 4% rhodium chloride solution were introduced in the cell. The reaction time was about 30 minutes. The content of rhodium was 3 mg/cm² and thickness was 0.005 mm.

EXAMPLE 4

After the platinum layer was deposited on one side of the membrane, as described in Example 1, 2% ruthenium chloride solution was poured into the opposite side of the cell membrane. 8% borane hydride solution was placed in the platinum layer side of the cell. The metal layer contained 5 mg/cm² of ruthenium, and its thickness was 0.006 mm.

4. Cell

The schematic illustration of our cell is displayed. Here, 1 and 2 are inner compartments, and 4 is the ion-exchange membrane.

![Figure 1.](image)

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