Combinatorial investigation of Pt-Ru-Sn alloys as an anode electrocatalysts for the direct alcohol fuel cell

조합촉매 기법을 응용한 직접 알코올 연료전지(Direct Alcohol Fuel Cell) Anode 3상 측매(Pt-Ru-Sn) 개발에 대한 연구

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1. Introduction

Ethanol[1], 1-propanol[2], and 2-propanol[3] are also liquid fuels which are easily available. These fuels for Direct Alcohol Fuel Cells (DAFCs) are inexpensive and less toxic than methanol. Particularly, ethanol is an attractive alternative to methanol as a fuel for fuel cells since in some countries, such as Brazil, an already well-established infrastructure for the use of ethanol in automobile combustion engines exists so that an introduction of direct ethanol fuel cells for electrotraction purposes may be possible without requiring any modification of the infrastructure[4]. But the present development of direct alcohol fuel cells is not so satisfying as DMFCs. There are several obstacles for DAFCs to overcome before their commercialization. One of the main problems of DAFCs is the poor performance of electrocatalysts, especially anode catalysts at lower temperatures because of the anode surface poisoning by CO-like intermediates[5]. Making alloys with a second or a third metal is a convenient way to modify electrocatalytic properties of Pt in order to overcome poisoning effects. Notable enhancement of the electrocatalytic activity of platinum based electrocatalyst has been observed by introducing a second metal: Pt-Ru, Pt-Sn, Pt-Pd, Pt-W[6]. One way to develop new electrocatalysts is applying the combinatorial electrochemistry to this area. The first report of combinatorial electrochemical screening was that of Mallouk and co-workers [7]. In this study, we applied the combinatorial chemistry to develop the anode electrocatalysts. Pt-Ru-Sn metal alloys are tested as the anode electrocatalysts for the direct alcohol(methanol, ethanol and 2-propanol) fuel cell.
2. Experimental

Electrode arrays were prepared by dispersing 0.5 M aqueous solutions of three metal salts (H₂PtCl₆, RuCl₃, Aldrich, and SnCl₂, Junsei) onto a Teflon-coated Toray carbon sheet, using manually prepared solution mixtures. The completed array was reduced by 0.5 M sodium borohydride, and the reduced array was thoroughly washed with nanopure water.

The electrolyte solution was composed of 100 μM quinine as a proton indicator, 6 M of reactant alcohol, and the diluted H₂SO₄ which was added to adjust the pH to 7. Each composition was used as a working electrode. Cyclic voltammetry experiments were conducted between 0.0 and 1.6 V RHE at a sweep rate of 1 mV/s. The most active working electrode was selected by the brightest spot of the array obtained by fluorescence emission excited by UV of 254 nm [8].

Four carbon-supported platinum-based electrocatalysts designated on combinatorial array in Fig. 1 such as Pt(80)Ru(20)/C, Pt(50)Sn(50)/C, Pt(20)Ru(70)Sn(10)/C and Pt(50)Ru(30)Sn(20) were prepared for the electrochemical characterization experiment.

Fig. 1 Combinatorial array for alcohol electro-oxidation; Note: inside of dotted area denotes the active compositions for each alcohol (methanol, ethanol and 2-propanol) electro-oxidation.

3. Result and Discussion

The fluorescence images of Pt–Ru–Sn alloy electrodes for alcohol(methanol, ethanol and 2-propanol) electro-oxidation at different activation voltages are shown in Fig. 2. We have successfully identified the active area for the electro-oxidation of each alcohols. The active area for each alcohols is shown in Fig. 1. In the case of 2-propanol, the active range was very broad, and initial
activation potential was lower than methanol and ethanol. The similar information has been reported by Qi et al. (2002). The activation overpotential of 2-propanol is less than 0.04V, but that of methanol is around 0.3V [3]. Table 1. shows the composition of each candidate electrocatalysts chosen from active area of each alcohols. Though these electrocatalysts were not the best composition for each alcohols, we chose the edge composition of each alcohols to improve the availability of combinatorial electrochemistry. Electro catalyst-1 is composed of PtRuSn(80:20:0) for electro-oxidation of methanol. For ethanol and 2-propanol,

Fig. 2. Combinatorial screening results of Pt-Ru-Sn electrode assembly for electro-oxidation of each alcohol by fluorescence imaging.
(a) Methanol  (b) Ethanol  (c) 2-propanol

Table. 1 The best composition of electrocatalyst for oxidation of each alcohol

<table>
<thead>
<tr>
<th>Metal composition (molar ratio)</th>
<th>Pt</th>
<th>Ru</th>
<th>Sn</th>
<th>Target alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electro catalyst-1</td>
<td>8</td>
<td>2</td>
<td>0</td>
<td>Methanol</td>
</tr>
<tr>
<td>Electro catalyst-2</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Electro catalyst-3</td>
<td>2</td>
<td>7</td>
<td>1</td>
<td>2-propanol</td>
</tr>
<tr>
<td>Electro catalyst-4</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>For all alcohol</td>
</tr>
</tbody>
</table>
Table. 1 The best composition of electrocatalyst for oxidation of each alcohol the candidate composition is PtRuSn(50:0:50) and PtRuSn(20:70:10) designated as Electrocatalysts-2 and Electrocatalyst-3 respectively. Electrocatalyst-4 is active for all alcohol, and the composition is PtRuSn(50:30:20).

Single cell performance test results were shown in Fig. 3. As identified in combinatorial test, PtRu(8:2)/C, PtSn(5:5)/C and PtRuSn(2:7:1)/C catalyst show higher activity to methanol, ethanol and 2-propanol respectively in the single cell test.

Fig. 3. The single cell performance of the prepared Pt–based electrocatalysts at 88oC,

(a) Methanol (b) Ethanol (c) 2-propanol

As one can observe in Fig. 3 (b), the open-circuit voltage of DEFC with the electrocatalyst Pt:Ru:Sn=5:0:5 approaches to 0.722V, about0.06V more than the fuel cell employing other electrocatalysts, and the maximum peak power density is 35.3mW/cm² and the overall performance was superior to other electrocatalysts at 88°C.
Fig. 3 (c) shows the cell performance of direct 2-propanol fuel cell. The performance of the cell operating on 2-propanol at 88°C is substantially higher than the cell operating on methanol and ethanol at current densities of < 200mA/cm². For example, the cell voltage at 120 mA/cm² is ~200 mV higher when operating with 2-propanol than that with methanol. Similar observations were reported by Qi et al. [3]. To the best of our knowledge about a direct alcohol fuel cell, operating with 2-propanol reached the highest performance. Unfortunately, the highest performance of the cell operating on 2-propanol rapidly drops when the current density exceed 200 mA/cm². The cell voltage oscillate around 0.3V at current densities higher than 200mA/cm². At high cell voltage, the current may be generated by the oxidation of evolved hydrogen which was generated by dehydration of 2-propanol. But at low cell voltage, the current may be generated by the deep oxidation of acetone or 2-propanol [3].

4. Conclusion

Combinatorial electrochemistry was applied to identify the optimum composition of ternary metal (Pt,Ru and Sn) electrocatalyst for the low-temperature direct alcohol fuel cells fed by methanol, ethanol and 2-propanol. Electrochemical characterization method was investigate the effect of alloy metal to Pt-based electrocatalysts. It was found that Pt(80)Ru(20), Pt(50)Sn(50) and Pt(20)Ru(70)Sn(10) shows the best performance for the oxidation of methanol, ethanol and 2-propanol respectively. It was reconfirmed by single cell performance test.

5. Reference


6. Acknowledgement

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