Since the reaction rate of the oxygen reduction reaction (ORR) at the cathode is much lower than that of hydrogen oxidation reaction (HOR) at the anode, the cathodic ORR has become the most challenging step in a fuel cell. Up to now, Pt is the best catalyst for the ORR due to its high catalytic activity. However, two drawbacks of Pt-based catalysts, such as the high cost and the insufficient electrochemical durability, have limited the further commercialization of this technology. Therefore, looking for new non-precious metal alternative catalysts to replace Pt becomes the current important issue.

In this regard, carbon-based transition metal macrocycle complexes catalysts become one of the most promising candidates to replace Pt/C catalyst, especially these catalysts synthesized after thermal treatment show higher catalytic activity. For revealing the mechanism of ORR and improving the ORR activity, we should know the active sites in these catalysts. So far, there is a consensus that carbon, nitrogen and transition metals are the active site in these catalysts. In this work, with carbon-supported copper phthalocyanine tetrasulfonic acid tetrasodium salt, CuTSPc/C, as a target, the role of transition metal in macrocycle complex was investigated by acid-leaching procedures.

CuTSPc/C catalysts were prepared by combining a mixture of 40mg CuTSPc and 60mg carbon black in a mortar, milling by adding 10ml methanol for 2h, then was vacuum-dried at 40°C for 1h to remove methanol. The resulting powders were placed in a quartz boat and pyrolyzed at 700°C for 120min at a rate of 20°C min⁻¹ in a flowing nitrogen atmosphere. This catalyst as-prepared is thus designated as CuTSPc/C-700. In order to remove the metal Cu, the catalyst was further disposed with an acid-washed procedure (acid-leaching effect) after heat-treatment. In detail, the CuTSPc/C-700 catalyst was refluxed in 0.5M H₂SO₄ at 80°C for 8h, then the suspension was washed with deionized water and centrifuged until the supernatant to neutral, and finally dried at 60°C in an oven overnight under ambient air conditions. This catalyst is designated as CuTSPc/C-700AL. The electrocatalytic activity was investigated using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) employing rotating disk electrode (RDE) technique and rotating ring-disk electrode (RRDE) technique in 0.1 M KOH.

To determine whether the metal Cu is removed after acid-leaching, EDX analysis was performed to analyze the elemental composition of the catalyst samples before and after acid-leaching, the corresponding results are summarized in Table 1. As can be seen from Table 1, the catalyst sample consists of C, O, Cu and S before acid-leaching. After acid-leaching, there is an increase in C and S content and a decrease in O content. In particular, the content of N and Cu cannot be detected. Since for CuTSPc/C, N is a light element compared to S, the presence of N may be covered. However, the absence of metal Cu indicates that the metal Cu has been removed basically after acid-leaching.

Figure 1 shows the polarization curves of the CuTSPc/C-700 catalyst before and after acid-leaching. It can be seen that the ORR activity of the CuTSPc/C-700 AL decreased greatly. The half-wave potential for CuTSPc/C-700 AL was negatively shifted more than 30mV compared to CuTSPc/C-700. Compared with the results of Table 1, the absence of metal Cu has negative effect on the ORR activity. Therefore, it can be concluded that the presence of metal Cu is beneficial for ORR active sites.

References

Table 1. Elemental quantification analysis of CuTSPc/C-based catalysts

<table>
<thead>
<tr>
<th>Catalyst samples</th>
<th>Atomic concentrations, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>CuTSPc/C-700</td>
<td>68.20</td>
</tr>
<tr>
<td>CuTSPc/C-700AL</td>
<td>91.02</td>
</tr>
</tbody>
</table>

Figure 1: Polarization curves of the CuTSPc/C-700 catalysts before and after acid-washed in an oxygen-saturated 0.1mol·L⁻¹ KOH solution. Scan rate: 5mVs⁻¹. Electrode rotation rate: 1500rpm.