Templated Non Precious Cathode Catalysts Prepared by Transition Metal and Poly(ethyleneimine) for Oxygen Reduction Reaction in Alkaline Electrolyte

Jingjing Shi¹, Pan Xu¹, Ming Fu Zhen², Jinli Qiao^{1*}

 College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, China
Zhejiang Geely Automotive CO.,LTD, Shanghai 201501, China)

*qiaojl@dhu.edu.cn

Non precious metal (NPM) catalysts, which are cheap and abundant, have been reported as promising candidates of replacing Pt for the oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cells. Certain types of N-containing transition metal catalysts have showed high activity for oxygen reduction in alkaline media, especially for Fe- and Co- centered catalysts¹⁻³. However, compared to Pt-based catalysts for practical application in fuel cells, both the ORR activity and stability of these catalysts have to be significantly improved.^{4,5}

It is believed that the high surface area, high porosity and proper pore structure of catalyst usually lead to high catalytic activity for the ORR. Template method has drawn great attention to obtain the specified morphology and predetermined microstructure^{6,7}. In this paper, we choose template method to synthetize polyporous NPM catalysts. Nanoscale SiO₂ was employed as sacrificial supports to create pores, while poly(ethyleneimine) (PEI) as source of N and C.

The M-PEI (M/PEI = 1/3, M = Fe, Co, Ce) catalysts were prepared by homogeneously dispersion of metal and PEI precursors onto the surface of SiO2 (the metal loading with respect to silica is 15wt.%). SiO₂ was etched by 40wt.% HF after dried at 85°C for 24h, then the resultant powder was pyrolized in an N2 atmosphere at 800°C for 1h. The vacated SiO_2 particles lead to creation of pore. The final powder was washed to be neutral by purified water and then dried overnight. Base on this method, we prepared M-PEI catalysts with high porosity. The kinetics and electrocatalytic activity on the M-PEI catalysts have been measured using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and rotating disk electrode (RDE). All these tests were carried out in a glass cell consisting of a three-electrode system in 0.1M KOH at the ambient solution temperature.

Figure 1 shows the cyclic voltammograms of Fe-PEI, Co-PEI and Ce-PEI catalysts, respectively. It can be seen that Co-PEI catalysts showed much better ORR activities than that of Fe-PEI and Ce-PEI catalyst. Although the ORR peak potentials of Co-PEI (-0.02 mV) and Fe-PEI (-0.054 mV) electrodes were similar, the peak current density on Co-PEI electrode is 200% higher than that on Fe-PEI electrode. Both are much higher than that of Ce-PEI catalyst based on their peak potential and peak current densities. Since almost all of the transition metals can be removed by HF, the difference in ORR performances on these catalysts was probably due to fact that the transition metal played in promoting formation of active sites, instead of forming active sites themselves.

Figure 2 shows the polarization curves of the above three electrodes. Clearly, Co-PEI was found to show the highest

ORR activity among the catalysts studied. The onset potential at 0.1V and the half-wave potential at 0V were obtained for Co-PEI catalyst.

References

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Fig. 1 Cyclic voltammograms of M-PEI (M=Fe, Co, Ce) catalysts in 0.1M KOH. Scan rate: 50 mV s⁻¹. The overall loading of the mixed catalyst was 141.2 μ g cm⁻².



Fig. 2 Polarization curves of M-PEI (M=Fe, Co, Ce, M/PEI=1/3) catalysts in an O-saturated 0.1M KOH solution. Scan rate: 5mV/s. Electrode rotation rate: 1500 rpm. The overall loading of the mixed catalyst was 141.2 µg cm⁻².