Development of Carbon-Based Noble-Metal-Free Fuel Cell Catalyst

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Introduction

There has been an increased demand for a catalyst that efficiently functions with far less or no noble metals in the cathode of a olymer electrolyte fuel cell (PEFC, Fig. 1), being one of the most promising new energy systems which could help to improve the global environment by substituting conventional energy systems. At present, the PEFC is in practical use, for instance, for electric vehicles on a very limited scale using the catalyst consisting of platinum and a carbon support (Pt/C), but widespread use will begin with the development of catalysts free from resource limitation and cost inflation. Carbon materials with Fe ion coordinated by N atoms (Fe–N_x moiety, Fig. 2 [1]) embedded on the surface as the active site have been most extensively studied and are one of the promising candidates for the active and reliable noble-metal-free PEFC cathode catalyst. The research group of Osaka Municipal Technical Research Institute and collaboration partners recently formed the noble-metal-free cathode catalysts by carbonizing catalase and hemoglobin. Especially, the abundance and inexpensiveness of hemoglobin would be advantageous for the PEFC widespread use. Hemoglobin could be abundantly obtained (about 2 million tons per year), especially from the meat industry that produces more than 200 million tons of meat per year around the world and discarding blood containing hemoglobin as waste. We also developed another method for the formation of the noble-metal-free cathode catalyst with the Fe–N_4 moiety by heat treatment of the mixture of glucose, Fe salts, and amino acids or purine and pyrimidine bases, which are closely related to natural compounds, and often commonplace, safe, and inexpensive. The activity and the durability of these catalysts are insufficient at present; however, important information about their improvement has been obtained and the improvements have been done steadily.

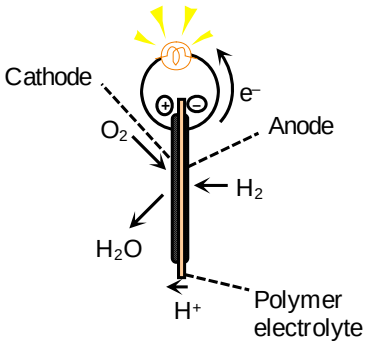

Fig. 1 Schematic representation of polymer electrolyte fuel cell.

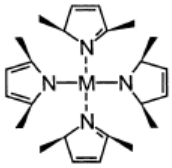

Fig. 2 Model of Fe–N_x moiety as active site for oxygen reduction. ▬ : connection to carbon surface. M: center metal ion (Fe(II)). [1]

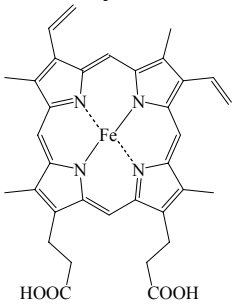

Fig. 3 Molecular structure of protoheme.

Formation of carbon-based noble-metal-free fuel cell catalyst from proteins [2]

The heat treatment of catalase and hemoglobin, which contain protoheme (Fig. 3), produced the carbon materials with the Fe–N_x moiety as the active site for oxygen reduction. The activity increased with an increase in the heat-treatment

temperature by the pore development inside the carbon material, although the yield of the carbon material became extremely low for the heat treatment at the excessive high temperature. The maximum temperatures for catalase and hemoglobin were 800 and 825 ºC, respectively. However, even the carbon material obtained at the temperature showed much lower activity and durability than Pt/C.

The improvements of the activity and the durability were achieved by the modification of the heat treatment. The formation of the precursor of the carbon material by the heat treatment below 600 ºC and the heat treatment of the precursor at 900 ºC led to the increase of the active Fe center. In addition, the introduction of CO_2 in the second heat treatment developed the pores inside the carbon material, which resulted in the increases in the active site on the pore surface and its reactivity. The durability was also enhanced by the generation of the ordered structure around the Fe–N_x moiety in the carbon materal, which was based on the results of the extended X-ray adsorption fine structures (EXAFS) at the Fe K-edge.

Use of amino acids, purine base, and pyrimidine base for generation of Fe–N_x moiety [3]

The formation of the carbon-based noble-metal-free fuel cell cathode catalysts were achieved by using mixtures of glucose, amino acids, purine bases, pyrimidine bases, and Fe salts, which are commonplace, safe and inexpensive natural organic compounds. The heat treatments of the mixtures at 150 ºC for dehydration and 1000 ºC for carbonization produced the carbon materials with the Fe–N_x moiety as the active site for oxygen reduction. Figure 4 shows the relationships between the cell voltage and the currents generated by fuel cells formed using the three kinds of the carbon materials (GGI1000, G3GI1000, and G4GI1000) in the cathodes [4]. They were formed from the mixture of glucose, glycine, and Fe lactate. The molar ratios of glycine to glucose in the starting mixture were 1, 3, and 4 for GGI1000, G3GI1000, and G4GI1000, respectively. The performance was improved by changing the ratio from 1 to 3. The durability of the fuel cell was also dependent on the content of the starting mixture. The EXAFS results indicated that the generation of the ordered structure around the Fe–N_x moiety in the carbon materal enhanced the durability, which was similar to the carbonized hemoglobin.

Summary

It has been shown that the carbon-based noble-metal-free fuel cell catalysts were formed from the natural organic compounds. The important information on the enhancement of the catalytic activity and the durability has been obtained. The further improvements would be attained by trying various starting materials and investigating various heat-treatment conditions in the future studies.

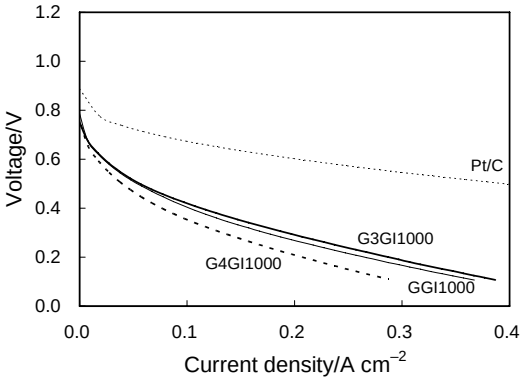

Fig. 4 Relationships between cell voltage and currents generated by fuel cells whose cathodes were formed from GGI1000 (thin line), G3GI1000 (thick line), G4GI1000 (thick dotted line), and Pt/C (thin dotted line). Cell temperature: 80 ºC.

References

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