

PREPARATION OF ELECTROCHEMICALLY ACTIVE CARBONS FOR OXYGEN REDUCTION BY CARBONIZATION OF MIXTURES OF METAL COMPLEXES AND FURAN RESIN

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Introduction

Proton exchange membrane fuel cell (PEMFC) is regarded as a promising option for the energy supply in the future. Because this type of fuel cell works at considerably lower temperatures than the conventional fuel cells, a plenty of platinum is required as the catalyst to promote the reactions, i.e. oxidation of fuels and reduction of oxygen. Since the latter reaction has a very large overpotential, the requirement of the large amount of platinum is a serious problem.

Commonly platinum catalysts are loaded on carbon blacks, for example Vulcan XC-72. In these cases the carbons are recognized as inert catalyst supports. If these supports become to have oxygen reduction activity, the required amount of platinum would be reduced.

Previously we have found the electrochemical activity of the carbons prepared in the presence of iron species, such as ferrocene [1,2]. Such carbons could show a comparable activity for a redox reaction of ferricyanide/ferrocyanide to a platinum electrode. This encouraged us to study the possibility of the carbons prepared by such ways for the oxygen reduction catalysts.

In the present study, we prepared carbon materials in the presence of different types of metal complexes with different transition metals and ligands, and investigated the activities of the carbons for the electrochemical reduction of oxygen in an acidic media.

Experimental

A furan resin (Hitafuran VF-303s, Hitachi Chemicals Co. Ltd.), the precursor for carbon, was mixed with a metal acetylacetonate (MAA, M=Fe, Co, Ni) in an acetone solution, then it was solidified by introducing a small amount of trichloroacetic acid followed by heating at 80°C for 24 h. These were subjected to carbonization by heating at 1000°C for 1 h in a nitrogen stream. The furan resins incorporated with cobalt phthalocyanine or iron phthalocyanine (CoPc or FePc) were also prepared in the same manner. In all cases the metal loading levels were set at 3 wt% on the basis of resin precursors. The carbons are referred by the name of the metal complexes introduced. The carbonized

samples were pulverized with a planetary ball mill. The pristine carbon sample was also prepared (FR).

The structures of the obtained carbons were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The electrochemical activities of the carbons for oxygen reduction were investigated by a rotating electrode voltammetry. A small amount (14 μ g) of the carbon samples were spread on the disk electrode (3 mm diameter) made of glass-like carbon by using a Nafion solution as a binder. The electrolyte was 1 M H₂SO₄ saturated with O₂ at room temperature. The carbon working electrode was rotated at 1500 rpm and was subjected to the voltammetry by sweeping the potential from the open circuit potential (OCP) to -0.1 V vs Ag/AgCl at a rate of 0.5 mV/s.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the obtained samples. The carbon sample prepared without metal complexes, FR, showed a broad diffraction pattern. In the (002) diffractions of the samples prepared in the presence of metal complexes, it was observed that the developments of a sharp diffractions that were superimposed on the diffractions, depending on the kinds of the metals and of the ligands. In order to compare the developments of these sharp diffractions, the (002) regions were separated into two contributions mathematically. The area fractions of the broad and the sharp components are presented in Table 1. The largest development of the sharp diffraction was obtained for NiAA. Acetylacetonates tended to show the distinct developments in the sharp diffractions than the phthalocyanines.

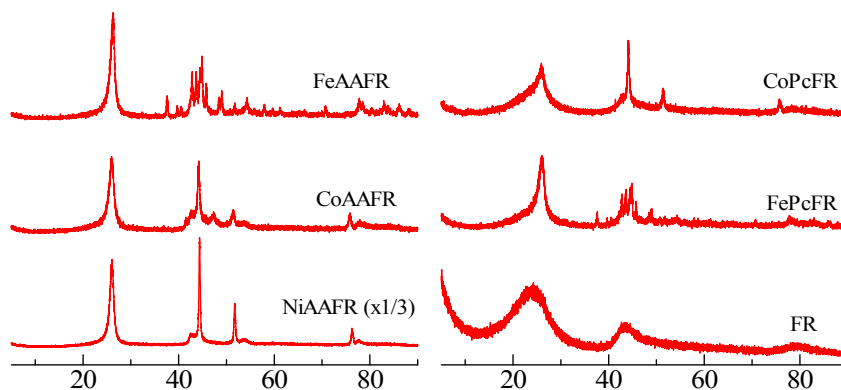


Figure 1. X-ray diffraction patterns of the prepared samples.

Table 1. Representative TEM images of the prepared carbons.

	Fractions from XRD		O ₂ reduction	
	broad	narrow	E _{O₂} (V)	i _{0.3V} (μA/cm ²)
FeAA	0.6	0.4	0.25	5.1
FePc	0.63	0.37	0.38	24.3
CoAA	0.54	0.46	0.37	29.6
CoPc	0.81	0.19	0.46	121
NiAA	0.48	0.52	0.2	0

Figure 2 shows the representative TEM images of the metal-introduced carbons. The characteristic features of these samples were the shell-like carbon structures. Some of them showed the carbons surrounding the metal particles. Since such well developed shell-like structures were found in the carbons with higher fractions of the sharp (002) X-ray diffractions, we identified the sharp (002) X-ray diffractions as the diffractions originated from such shell-like carbons.

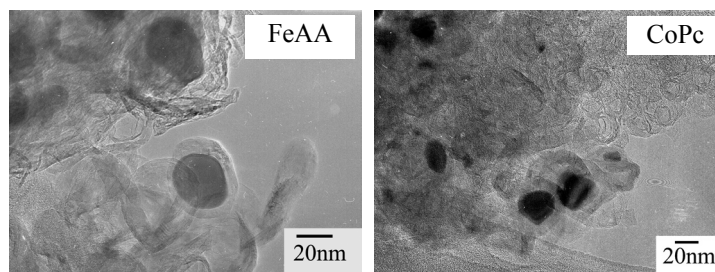


Figure 2. Representative TEM images of the prepared carbons.

Representative examples of oxygen reduction voltammograms of the carbons are presented in Figure 3. When the electrode potential was lowered from the OCP of the electrode, the increasing reduction currents were observed. The potential at which the reduction current of 10 μA/cm² was attained was defined as the O₂-reduction potential (E_{O₂}) here. We also evaluated the activities of the carbons by the current density at 0.3 V vs. Ag/AgCl (i_{0.3V}). The carbons prepared in the presence of metal complexes showed higher activities than FR. The electrochemical activities of carbons for oxygen reduction depended on the kinds of the metals and the kinds of the complexes. In general, the carbons with cobalt complexes showed larger activities than the corresponding iron complexes containing carbons. Among them, the CoPc showed the highest activity as presented in Table 1.

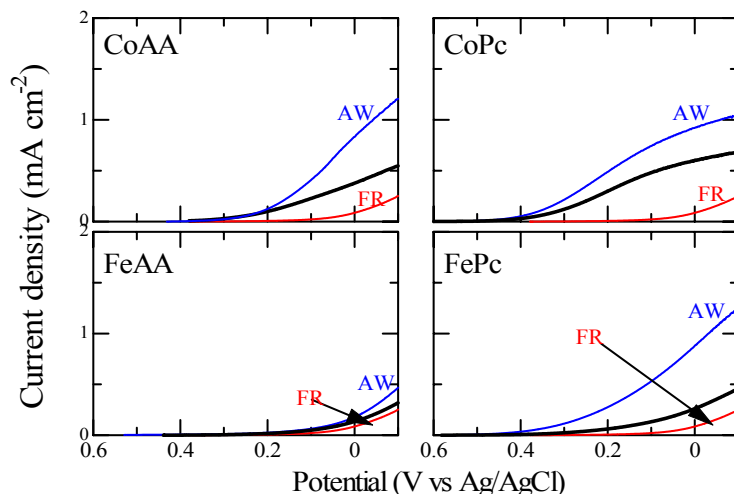


Figure 3. Hydrodynamic voltammograms for oxygen reduction by using the carbons as working electrodes.

Iron or cobalt phthalocyanines are known as active electrocatalysts for oxygen reduction [3]. Hence, there is a possibility of the metal species remained on the carbons surfaces act as the active center for the electroreduction of oxygen. Acid washing of the obtained samples were conducted in order to remove such surface metal species. After this treatment, it was impossible to detect the metal species by an X-ray photoelectron spectroscopy. Figure 3 also showed the voltammograms of such acid washed samples, indicated by AW. The electrochemical activities of the carbons were not reduced by the acid washing, rather the activities showed increases in the activity. These results indicated that the activities obtained in the present study did not originate from the metal species remained on the carbon surfaces but from the nature of the carbon surfaces induced by the metal complexes during carbonization.

Conclusions

Carbonization of furan resin with cobalt phthalocyanine could give a carbon material with electrochemical activity for oxygen reduction. This activity was concluded to come from the changes in the nature of the carbon surfaces, not from the metal species remained on the carbon surface.

Acknowledgments

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References

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