ELECTROCHEMICAL BEHAVIOR OF SURFACE-MODIFIED CARBON FIBERS

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Introduction

Modification of carbon materials by fixation of acidic surface oxygen complexes improves their performance when they are used either as adsorbents or catalysts [1]. Unlike the solution-phase oxidative treatment with nitric acid the oxidation by ammonium peroxydisulfate causes the fixation of stronger acidic surface groups, and does not change the surface area of the original carbon [2]. At the same time, the oxidizing treatment affects the electrochemical behavior of carbon materials in aqueous solutions [3].

The objective of the present work is to study the electrochemical behavior of carbon fiber (CF) electrodes with different surface functionality prepared by oxidative and non-oxidative treatments.

Experimental

PAN-based carbon fiber (Toho Rayon Co., LTD) was used for modification. Before the modification a sizing agent was removed by acetone. Conditions of surface treatment are presented below (see Table 1). Oxidation was achieved by treatment with 1M $(NH_4)_2S_2O_8$ at different temperature and time conditions. The non-oxidative treatment was performed by heating CF in hydrogen and argon gas flow. Measurement of equivalent surface groups was completed by the method described in [4]. Cyclic voltammograms were recorded at one selected scan rate 10 mVs^{-1} in oxygen and helium-saturated 0.15M NaCl aqueous solution using Ag/AgCl electrode as a reference.

Results and Discussion

The results obtained from analysis of equivalent surface groups are listed in the Table 1. The temperature of oxidizing treatment influences the concentration of oxygen containing functional groups on the surface of CF. A greater degree of surface functionality was developed by oxidation at 50°C even in a reduced time.

Figs. 1-3 show a set of cyclic voltammetry data recorded at the CF with different concentration of surface acidic groups in oxygen and helium-saturated solutions. The oxidative and heating treatments affect the shape of cyclic voltammograms. The CV curves recorded at bare and modified electrodes in oxygen-saturated solution (Fig. 1) in comparison with those in oxygen-free media (Fig. 2) demonstrate the electrocatalytic ability of oxidized CFs, as evidenced by well-defined wave. This wave is not appeared on the curves recorded in inert atmosphere and could be attributable to the voltammetric reduction of dissolved oxygen. The limiting current corresponding to this wave decreases with the oxidizing treatment in relation to that of the unoxidized sample. The limiting current is clearly lower for CF oxidized at 25 °C and 70 °C than recorded for specimens treated at 50 °C. For the reduced sample the electroactivity is not detected (Fig. 1b). The pH-dependent experiments show the decrease of the electrochemical activity in acidic solutions (Fig.3). Additionally, it was observed the increase of the double-layer charge current at oxidized CF electrodes (Fig.2) under condition when the electrochemical (Faraday) processes are minimized.

Conclusions

Reasonably high concentration of surface oxides on PAN-based CF was achieved by oxidizing treatment with ammonium peroxydisulfate. The concentration of oxygen surface groups depends on the temperature of oxidizing treatment. The preliminary studies showed that the condition of surface modification treatment affects the electrochemical behavior and double layer capacity of prepared CF. CFs oxidized with ammonium peroxydisulfate possess the electrocatalytic ability while presence of the electrochemically active species in solution media. The pH of the solution influences the electroactivity of prepared carbon fibers.

References

1. Tarkovskaya IA, Oxidized carbon. Kiev.1981: 196.
2. Moreno-Castilla C, Ferro-Garsia MA, Joly JP, Bautista-Toledo I, Carrasco-Marin F, Rivera-Utrilla J. Activated carbon surface modifications by nitric acid, hydrogen a peroxide, and ammonium Peroxydisulfate Treatments. Langmuir 1995,11: 4386-4392.
3. Biniak S, Dzielendziak B, Siedlewski J. The electrochemical behaviour of carbon fibre electrodes in various electrolytes. Double layer capacitance. Carbon 1995;33(9):1255-1263.
4. Yamakawa T. Reports of the Resources Research Institute. Japan. 1968. 70:29.

Acknowledgments

Researches are sponsored by Science Technology Agency of Japan.

Table1 Development of surface functionality and surface potential on treatment of PAN-based carbon fibers

Treatment of carbon fibers	Sample	Time of treatment (hours)	Temperature of treatment (°C)	Acidic functionality (meq/g)
Carbon fiber	CF	-	-	0.17
Liquid-phase oxidation (1 M $(NH_4)_2S_2O_8$)	FO25	48	25	2.14
	FO50	24	50	2.75
	FO70	4	70	2.37
Gaseous reduction (H_2)	FR	2	950	0.02
Heat treatment (Ar)	FAr	1	500	0.04

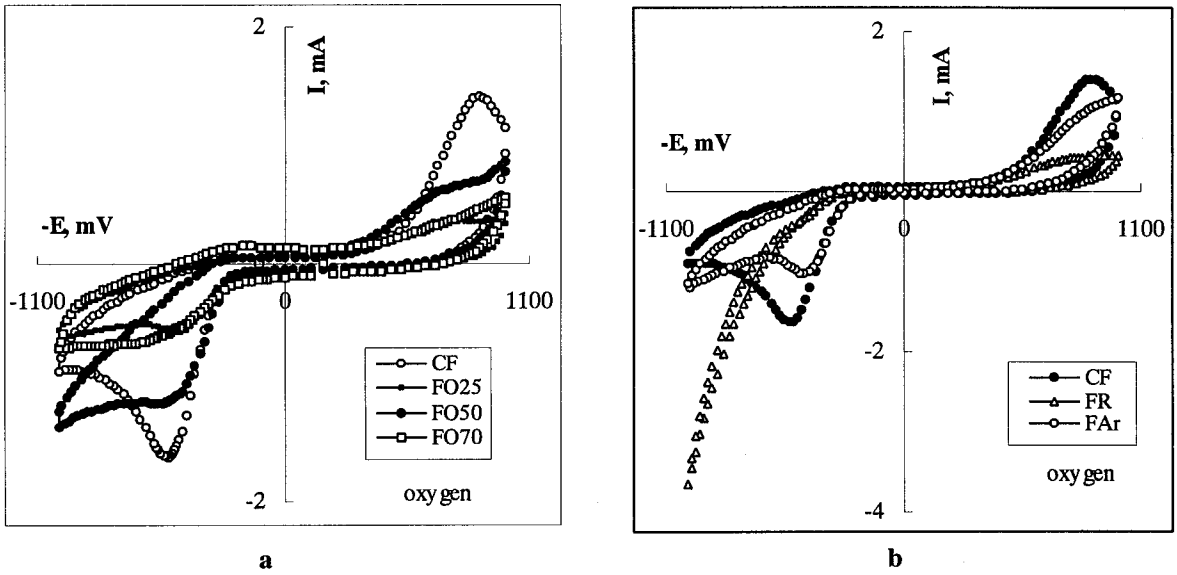

Figure 1. Cyclic voltammograms (CV) recorded at oxidized (a) and heat-treated (b) CF electrodes in oxygen-saturated 0.15M NaCl, pH=6.

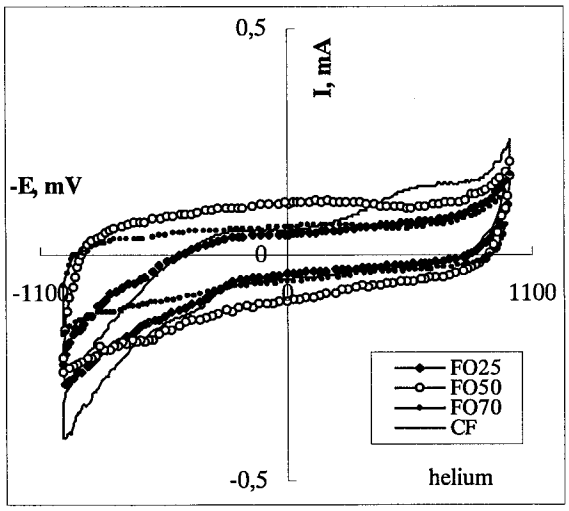

Figure 2. CV recorded at oxidized CF in helium-saturated 0.15 M NaCl, pH=6.

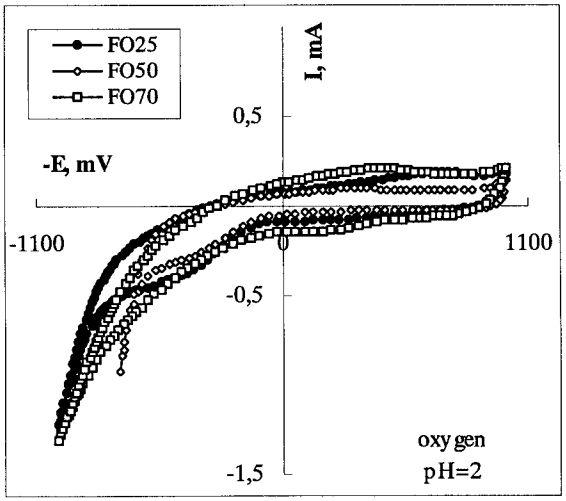

Figure 3. CV recordedat oxidized CF in oxygen-saturated 0.15 M NaCl, pH=2.