

IMPROVING THE ELECTROCHEMICAL PERFORMANCE OF CARBON FILAMENTS BY SOLVENT CLEANSING

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INTRODUCTION

The kinetics and reversibility of electrochemical processes strongly depend on the surface of the electrodes. Therefore, surface treatments are commonly applied to electrode materials. These treatments include changes in the surface functional groups, surface crystallographic structure and surface roughness. They may involve chemical treatment, heat treatment, laser treatment, plasma treatment, polishing or other surface activation. In particular, in the case of carbon materials, acid treatment [1-6], heat treatment [7, 8], laser treatment [9, 10] and electrode polishing procedures [11] have been employed. These treatments tend to increase the oxygen-containing functional groups on the surface of the carbon. In the case of high temperature heat treatment in an inert or reducing atmosphere or in vacuum, graphitization of the carbon can take place, thus changing the crystallographic structure both in the surface and in the bulk. In the case of heat treatment in the presence of oxygen, oxidation of the carbon occurs, thus increasing the amount of oxygen-containing functional groups on the surface and even converting the carbon to CO or CO₂ gases (thereby roughening the surface). In contrast to the surface modifications mentioned above, this paper involves surface cleansing. Cleansing refers to the removal of undesirable materials from the surface through washing in a solvent. Cleansing is a form of surface treatment which has not previously been applied to carbons. In this work, cleansing was found to greatly improve the electrochemical behavior of vapor-grown carbon filaments (consistently increasing the electrode rate constant to as high as 0.02 cm/s) due to the fact that a tarry residue remains on the surface of these filaments after the filament growth process, which involves a carbonaceous gas.

EXPERIMENTAL

Electrochemical performance was assessed by

cyclic voltammetry (CV) via the Fe²⁺/Fe³⁺ redox couple. A Bioanalytical Systems (BAS) CV cell was used. The test solution comprised 6 mM potassium ferricyanide (or potassium hexacyanoferrite (III) in IUPAC nomenclature) [K₃Fe(CN)₆], the electroactive species, in 1 M potassium nitrate [KNO₃] in water, the supporting electrolyte. The solution was purged with argon prior to electrochemical testing through a gas inlet tube. A saturated calomel electrode served as the reference and a platinum wire as the auxiliary electrode. The working electrode was a purchased BAS holder normally used for carbon paste. The carbon filaments were packed into the holder cavity at a pressure of 10 MPa without the use of any binder, unless noted otherwise. The circular carbon filament electrode had a surface area of 0.08 cm². The CV current densities were calculated by dividing the measured current by the area of the electrode outer surface. Voltammograms began sufficiently negative of the ferricyanide potential to allow reduction of the electroactive species in solution to ferrocyanide. Cycling then began with the oxidation half cycle at scan rates of 20 - 200 mV/s.

RESULTS AND DISCUSSION

A tarry residue (mainly polyaromatic hydrocarbons, as determined by gas chromatography/mass spectrometry) remained on the surface of vapor-grown carbon filaments (Grade ADNH, 1500 Å diameter, obtained from Applied Sciences Inc., Cedarville, Ohio). Cleansing in solvents effectively removed the tarry residue, improving the electrochemical reversibility and increasing the electron transfer rate, k_s (Table 1). Cleansing also decreased the electrical contact resistivity between adjacent filaments at a given contact pressure (thereby decreasing the filament compact's volume resistivity) and improved filament compactability at a given compaction pressure.

Even higher packing density (and therefore the

**TABLE 1 CARBON FILAMENT CYCLIC VOLTAMMETRY RESULTS
OBTAINED AT POTENTIAL SCAN RATE OF 200 mV/s**

Filament type	Treatment	Peak separation	Rate constant ^a	Packing density ^b	Resistivity ^c
		ΔE (mV) (± 10)	k_s (cm/s) (± 0.0005)	(g/cm ³) (± 0.002)	($\Omega \cdot \text{cm}$)
ADNH	As received	530	Irreversible	0.465	0.041
ADNH	Acetone cleansed	200	0.0037	0.680	0.020
ADNH	Acetone cleansed/chopped	130	0.0082	0.737	—
ADNH	Methylene chloride cleansed/chopped	90	0.0209	0.820	—

^a At a scan rate of 200 mV/s.

^b After compression at 10 MPa and subsequent pressure release.

^c At 7 MPa pressure for the filament compact, as determined by the four-probe method.

subsequent CV) was achieved by placing the cleansed filaments in a rotary blender filled with acetone and chopped by blending for 3 min. This additional increase in packing density is due to the large decrease in fractional spring-back. Furthermore, chopping decreased the residual current density and increased k_s (Table 1). The improved electrochemical behavior after chopping is partly due to the increased packing density.

The improvement in electrochemical performance realized by cleansing in methylene chloride was significantly greater than that achieved by cleansing in acetone. The rate constant k_s reached 0.02 cm/s after methylene chloride cleansing and chopping.

CONCLUSIONS

Vapor-grown carbon filaments were found to be covered with a tarry coating (mostly polyaromatic hydrocarbons), which degraded electrochemical behavior. The tarry coating increased the contact resistivity between adjacent filaments in a filament compact at a given contact pressure. The removal of the tarry coating was achieved by solvent cleansing. The coating removal caused the exposure of oxygen-containing functional groups on the surface of the carbon filaments and improved filament compactability, and decreased filament-filament contact resistivity. Acetone cleansing was effective, though further improvement in electrochemical reversibility and compactability was observed by cleansing in methylene chloride. Chopping of the filaments in a liquid medium using a blender further enhanced filament compactability, thereby further

improving the electrochemical performance.

ACKNOWLEDGEMENT

This work was supported in part by New York State Energy Research and Development Authority.

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