

IMPROVING THE ELECTROCHEMICAL BEHAVIOR OF CARBON BLACK AND CARBON FILAMENTS BY OXIDATION

C.A. Frysz^a and D.D.L. Chung^b

^aWilson Greatbatch Ltd.

10,000 Wehrle Drive

Clarence, NY 14031

^bComposite Materials Research Laboratory

State University of New York at Buffalo

Buffalo, NY 14260-4400

Introduction

Carbon blacks are used for current collectors, conductive additives or electrocatalysts in batteries and fuel cells [1-4]. Except for ascertaining parameters important for the electrochemical oxidation of carbon black [1], essentially no work had been conducted relative to the electrochemical behavior of oxidized carbon black [5,6]. It is the objective of this paper to study the electrochemical behavior of carbon black. A related objective is to improve its electrochemical performance as measured by changes in the electron transfer rate k_s via thermal and chemical oxidation. Another objective is to compare the electrochemical response of thermally and chemically oxidized carbon black with that of thermally and chemically oxidized carbon filaments (made catalytically from carbonaceous gases).

Experimental

The carbon materials investigated were carbon black (425 Å mean particle size, Shawinigan acetylene black from Chevron, Houston, Texas), carbon filaments (grade ADNH, 1500 Å in diameter, greater than 100 µm in length from Applied Sciences Inc., Cedarville, Ohio), and carbon fibers (same as in Ref. 8, i.e., Thornel P100, radially structured, unsized, high-modulus, mesophase-pitch-based graphite fibers, 10 µm diameter, with a graphite basal plane skin, from Amoco Performance Products, Atlanta, Georgia).

Thermal oxidation was conducted by heating in air at 250-600°C for 0.5-5 h.

Chemical oxidation was achieved by immersing the carbon in an acid medium in a beaker. The mixture was stirred for 10 min, and then was filtered. That cleansing was occurring was evident by a yellow to brown discoloration of the acid medium. The carbon was returned to the beaker containing deionized water before stirring for an additional 5 min, then filtering again. This process was repeated until the filtrate tested neutral with litmus paper. The carbon was allowed to air dry in a low humidity environment (< 1% R.H.) overnight before testing. The acids used to chemically oxidize carbon filaments (in order of decreasing relative strength, determined from the dissociation constant) were HCl, HNO₃, H₂SO₄, H₃PO₄ and CH₃COOH. (HCl is not classified as an oxidizing acid, so the effects of the HCl may not be oxidation, even though the HCl treatment is grouped with the other acids under chemical oxidation.)

Cyclic voltammetry (CV) was conducted using the Fe(CN)₆^{-3/4} redox couple and the method of Ref. 7. The rate constant for electron transfer (k_s), the capacitance (C) and the electrochemical area (A) were calculated from the CV data [7].

Results and Discussion

The burn-off data at 600°C show that carbon black is less resistant to thermal oxidation than carbon fibers. TGA (in air) shows that carbon fibers are most oxidation resistant, followed by carbon black and then carbon filaments.

No redox peak is present for the as-

received carbon black. However, the redox peaks are clearly observed after thermal oxidation to a burn-off of 16%. The peaks begin to become more visible, even at the lowest burn-off of 1%, improving in shape as burn-off increases. The reaction remains irreversible or quasi-reversible until the 16% burn-off is reached. The 16% burn-off gives the best electrochemical reversibility. Burn-off of carbon filaments in air to a 15% weight loss also demonstrates enhanced electrochemical behavior. The peak separation ΔE decreases from 530 to 110 mV, and the redox reaction is rendered reversible with a k_s value of 0.0110 cm/s.

Chemical treatment improves the reversibility of the redox reaction of both carbon black and carbon filaments. The improved electrochemical performance is attributed to either an increase in the adsorbed oxygen from the acid solution on the surface of the carbon, the formation of carbon complexes favorable to electrochemical performance, or, specifically in the case of carbon filaments, the removal of the tarry coating present on their surface exposing oxygen containing surface functional groups. Of the acids having a 10% concentration, the highest k_s was achieved with HCl, whether used to treat carbon black or carbon filaments. This was expected since HCl is the strongest of the acids evaluated. Of the acids having a 10% concentration used to treat carbon filaments, CH_3COOH resulted in the next highest k_s . This was unexpected, since CH_3COOH is the weakest of the acids evaluated. This result is attributed to the nature of the surface functional group formed. The most dramatic improvement was observed for carbon filaments treated with 50% HCl; the electrochemical response changed from irreversible to reversible, and k_s (0.0371 cm/s) is the highest of all the treatments applied.

Thermal and chemical oxidation treatments significantly decrease the capacitance of the carbon black. The effect on capacitance is believed to be due to improved compactability, which is due to morphology changes.

Thermal oxidation of carbon filaments results in large increases in capacitance and electrochemical area. The additional oxygen on the filament surface after thermal oxidation

results in increased capacitance and electrochemical area. Chemical oxidation of carbon filaments, however, results in lower capacitances and electrochemical areas compared to the as-received version, and much lower compared to thermal oxidation.

Conclusions

Oxidation changed the electrochemical behavior of carbon black, carbon filaments and carbon fibers from irreversible to reversible. Thermal oxidation of carbon black (16%) yielded a higher k_s than did chemical (HCl or HNO_3) oxidation. For carbon filaments, chemical oxidation using 50% HCl gave the most beneficial effect of the acids tested, increasing k_s to a higher value than can be achieved by either thermal oxidation or solvent cleansing. Thermal oxidation of carbon fibers to a 17% burn-off gave higher k_s than thermal oxidation to burn-offs of 7% or 22%.

References

1. Kinoshita, K., *Carbon Electrochemical and Physicochemical Properties*, 1988, Wiley, New York, 87, 297.
2. Randin, J.P., *Encyclopedia of Electrochemistry of the Elements*, 1976, Vol. VII, A.J. Bard, Ed., Dekker, New York.
3. Yeater, E., Molla, J. and Gupta, S., *Proceedings of the Workshop on the Electrochemistry of Carbon*, 1983, S. Sarangapani, J.R. Akridge and B. Schumm, Eds., The Electrochemical Society, Pennington, New Jersey, 123.
4. McCreery, R.L., *Electroanalytical Chemistry*, 1991, A.J. Bard, Ed., Vol. 17, Dekker, New York, 280.
5. Konoshita, K. and Bett, J.A.S., *Carbon*, 1973, 11, 403.
6. Hallum, J.V. and Drushel, H.V., *J. Phys. Chem.*, 1958, 62, 110.
7. Shui, X., Frysz, C.A. and Chung, D.D.L., *Carbon*, 1995, 33, 1681.
8. Frysz, C.A., Shui, X. and Chung, D.D.L., *Carbon*, 1994, 32, 1499.