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Characterization and Electrochemical Properties of Electrosynthesized Carbonaceous Fibers

by

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13. ABSTRACT (*Maximum 200 words*)

Carbonaceous fibers with diameters ranging from 0.1-5 microns and lengths up to several hundred microns spontaneously form during cathodic electrodecomposition of CCl_4 in nonaqueous solvents (CH_3CN or CH_2Cl_2) containing tetrabutylammonium salts. The fiber morphology is dependent on current density, CCl_4 concentration, and electrode surface preparation. X-ray photoelectron spectroscopic measurements revealed that the fibers consist primarily of carbon, with some nitrogen, chlorine, and oxygen impurities. X-ray and electron diffraction showed the fibers to be amorphous.

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Introduction

Carbon fibers and films are useful materials for several different electrochemical applications, including stable electrodes for electrochemical synthesis and battery applications.[1] Carbon materials are usually deposited by physical methods such as sputtering, or the decomposition of hydrocarbons at high temperatures. Carbon films have also been formed electrochemically, either by reduction of halogenated hydrocarbons[2-4] or reduction of fluorinated polymers.[5]

We have recently discovered a method by which carbonaceous materials are deposited in the form of small fibers, which due to their unusual morphology may have applications in several fields. The deposition proceeds through the reduction of carbon tetrachloride in an organic solvent. The net reaction can be written as:

$$CCl_4 + 4e^- \rightarrow C_{(s)} + 4Cl^-$$

Carbon fibers are formed at the cathode as a result of this reaction. The fibers have diameters from 0.1-5μm, and lengths up to several hundred microns. The fibers have been grown on Ni, Cu, Ag, Pt, or Fe substrates, with the morphology being dependent on current density, CCl_4 concentration, and electrode surface preparation.

Preparation

Working electrodes with areas of approximately 0.25 cm^2 were cut from 99.5% purity metal foils (Johnson Matthey Electronics, Aldrich Chemicals). The electrodes were polished with 1μm alumina or 85 μm SiC. Solvents were distilled under nitrogen from the appropriate drying agent, and CCl_4 was vacuum distilled before use.[6] The electrolytic deposition solutions typically consisted of 30 mL of solvent (CH_3CN or CH_2Cl_2), 1 mL of CCl_4, and 1.5g of tetrabutylammonium tetrafluoroborate ($TBABF_4$) or 1.3g of bis-(triphenylphosphoranylidene) ammonium chloride (PPNCl) (Aldrich Chemicals). All electrodeposition experiments were carried out in a two-compartment cell under either argon or nitrogen atmospheres. The platinum counter electrode was separated from the working and reference electrodes by a glass frit. The applied current density was typically 3-5 mA/cm^2 and the galvanostatic depositions were carried out for 30-60 min.

Results

Figure 1 shows an electron micrograph of fibers formed on a copper substrate from a solution of CH_3CN and $TBABF_4$. The fibers are approximately 0.1-5 microns in diameter and range in length up to 200 microns. The size and density of fibers is dependent on electrode preparation, with coarse polishing (85 μm SiC) resulting in dense clumps of fibers while smoother polishing (1 μm alumina) results in scattered, individual fibers. Fiber growth is suspected to be nucleated at defect sites on the electrode surface.

The fibers lack any discernible long range crystalline order, as seen by selected area electron diffraction and powder X-ray diffraction.

X-ray photoelectron spectroscopic measurements for samples prepared in acetonitrile solution indicate that the fibers consist primarily of carbon, although significant quantities (5-10%, calculated using the relative peak areas and previously determined sensitivity factors) of Cl, O, and N are also present.

Infrared (IR) spectra of the material feature a peak at 2210 cm^{-1} which implies acetylene or $C\equiv N$ groups. Incorporation of a $C\equiv N$ species could result from acetonitrile encapsulation; however a peak at 2150 cm^{-1} was also seen from samples prepared in methylene chloride, implying the existence of $C\equiv C$ species. The aliphatic C-H stretches in the IR at 2881 and 2967 cm^{-1}, and C-H bending modes at 1460 and 1387 cm^{-1} arise from intercalated tetrabutylammonium ions.

Cyclic voltammetry experiments show reversible ion exchange can take place as the potential is scanned. Figure 2 shows the IR spectrum of a fiber sample doped initially with tetrabutylammonium ions. As the potential is swept between 0.0 volts and -0.62 volts vs. Ag/AgCl in acetonitrile containing 0.1M PPNCl, the tetrabutylammonium ion is exchanged with the bis-(triphenylphos-phoranylidene) ammonium ion. After cycling, a second IR spectrum, also shown in Figure 2, shows that tetrabutylammonium ions have been partially replaced.

Heat treatment of the fibers at temperatures up to 500°C show the disappearance of aliphatic CH groups, as measured by infrared spectroscopy. X-ray diffraction experiments show the fibers remain amorphous after heating to these temperatures.

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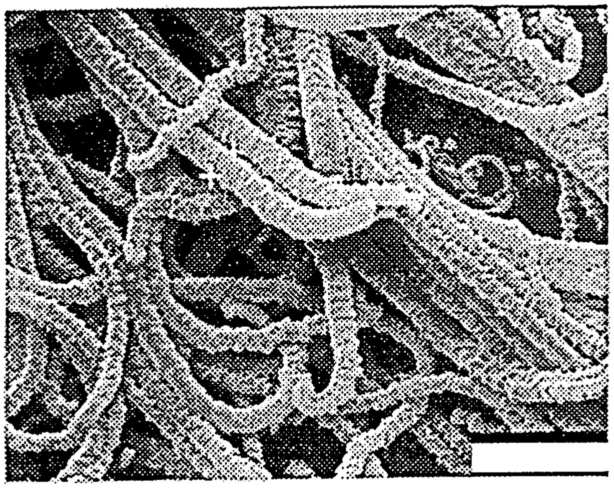

Figure 1: SEM micrograph of electro-deposited carbonaceous fibers. Bar at lower right represents 12 microns.

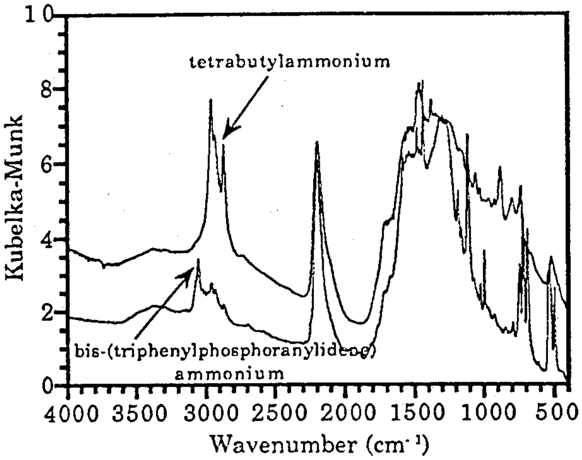

Figure 2: Infrared spectra before (top) and after (bottom) cyclic voltammetry experiments, showing cation replacement.