

Characterization and Ion Incorporation of Electrosynthesized Carbonaceous Fibers

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Introduction

Carbon fibers are typically prepared via high-temperature pyrolysis of polymeric precursors. Examples include poly(acrylonitrile), in which the polymeric fibers are carbonized at temperatures of up to 1600°C.¹ The high temperature preparation of these fibers adds considerably to their cost.

We have recently discovered a process in which carbonaceous fibers form spontaneously, at room temperature, upon electroreduction of carbon tetrachloride in an organic solvent. The net reaction can be summarized as:



This process is similar to that used by Kavan,² in which fluoropolymers are reduced to carbonaceous materials. These fluoropolymer-derived materials do not show fibrous morphology, however.

The deposited fibers from the present work have diameters ranging from 0.1-5 microns and lengths up to several hundred microns. The production of fibers was observed on Ni, Cu, Ag, Pt, or Fe substrates, with the morphology being dependent on current density, CCl₄ concentration, and electrode surface preparation.

Preparation

Working electrodes with areas of approximately 0.25 cm² 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 CCl₄ was vacuum distilled before use.³ The electrolytic deposition solutions typically consisted of 30 mL of solvent (CH₃CN or CH₂Cl₂), 1 mL of CCl₄, and 1.5g of tetrabutylammonium tetrafluoroborate or 1.3g of bis-(triphenylphosphoranylidene) ammonium chloride (Aldrich Chemicals). All electrodeposition experiments were carried out in a two-compartment cell, with the counter electrode separated from the working and reference electrodes by a glass frit under either argon or nitrogen atmospheres. Current density for deposition was typically 3-5 mA/cm² 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 using CH₃CN. The fibers are approximately 0.1-5 microns in diameter and range in length up to 200 microns. The size and density of fibers were dependent on electrode preparation. Fiber growth is suspected to be induced 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 indicated 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 spectra (IR) of the material feature a peak at 2210 cm^{-1} which implies acetylene or $\text{C}\equiv\text{N}$ groups. Incorporation of a $\text{C}\equiv\text{N}$ species could result from acetonitrile encapsulation. 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 ion.

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

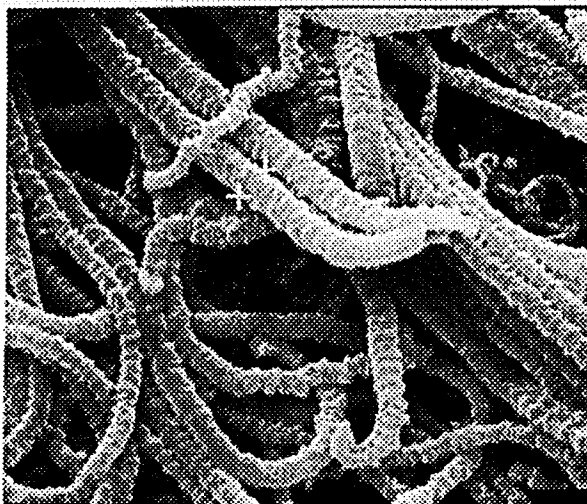


Figure 1: SEM micrograph of electro-deposited carbonaceous fibers. Bar represents 4 microns.

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.

Further cyclic voltammetry, heat treatment, and characterization experiments are currently underway.

References

1. Pierson, H.O. *Handbook of Carbon, Graphite, Diamond, and Fullerenes* (Noyes Publications, Park Ridge, 1993), p. 166-196.
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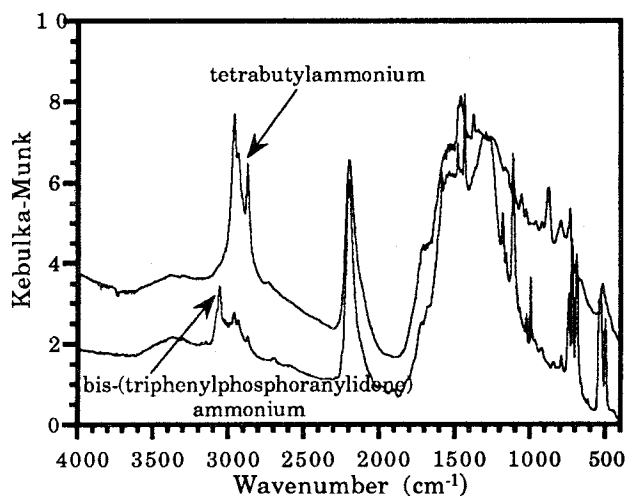


Figure 2: Infrared spectra before (top) and after (bottom) cyclic voltammetry experiments, showing cation replacement.