# METAL-CARBON AND CARBON-CARBON NANOCOMPOSITES FOR LITHIUM-ION BATTERIES AND STRUCTURAL APPLICATIONS

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**Keywords**: *Li-ion, battery, magnesium, nanocomposite, carbon nanotubes, anode, electrolyte*

## 1 Introduction

Magnesium-carbon, aluminum-carbon and carbon-carbon (nano)composites are attractive lightweight materials for both structural aircraft components and Li-ion battery anodes. This multi-functionality may allow the airframe to serve as a power/energy source for a variety of applications, including hybrid and electrical engines for aerial vehicles. Improving fundamental understanding of the complex structure-property relationships of these composites at the nano-scale will open new avenues in fine tuning their microstructure and chemistry to achieve high strength-to-weight ratio and high power characteristics and long cycle life when used as battery electrodes.

## 2 Experimental

### 2.1 Synthesis

*2.1.1. Metal Nanowires*

Free standing aluminum [1] and magnesium nanowires were grown using a low pressure chemical vapor deposition (CVD) performed in a hotwalled reactor at 100-300 ºC. Depositions were performed in a quartz process tube onto various metal foils, including copper, nickel, stainless steel, and aluminum. The delivery of organometallic precursor vapors was provided by ultra high purity argon gas flowing through a packed bed or a bubbler system. The deposition pressure was maintained at the level of less than 2 Torr, as controlled by a convection gauge.

*2.1.2. Metal-Carbon Nanocomposites*

Metal-carbon nanocomposites were produced by electrodeposition of metals on carbon fibers or carbon nanotubes following the procedure described in [2]. The hermetically-sealed three electrode cells with aluminum (for Al deposition) or Mg (for Mg deposition) reference and counter electrodes were used inside an argon dry box (<1 ppm $H_2O$). For comparison purposes, metal-carbon composites were also produced *via* ball-milling of metal and carbon powder inside an argon-filled vacuum-tight container. The electrochemical performance of these samples was compared to that of the nanocomposites prepared *via* electrodeposition.

*2.1.3. Carbon-Carbon Nanocomposites*

Vertically aligned carbon nanotubes (CNT) were grown in a low-pressure (2-10 Torr) CVD reactor on quartz substrates using acetylene as a precursor gas. We utilized iron (II) chloride catalyst powder, as described in Ref. [3]. This method produces a high yield of vertically aligned CNTs (VACNTs) along the reaction chamber with measured growth rates in excess of ~0.1 $mm \cdot min^{-1}$. The CNT length in the range of 0.5-2 mm could easily be obtained (Figure 1) within minutes of the deposition time. In addition, this method does not require catalyst pre-deposition, which reduces the process cost and sample preparation time.

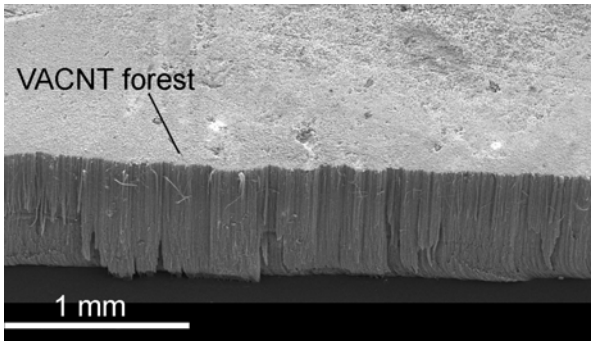


Figure1. SEM micrograph of VACNT.

Carbon-carbon composites were synthesized by CVD deposition of carbon on a produced CNT paper or fabric using acetylene and propylene as precursor gases. The deposition was performed in the temperature range of 700 - 900 ºC.

### 2.2 Material and Structural Characterization

The structural and chemical characterization of the produced composites was performed using X-Ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). XRD experiments using Cu-$K_\alpha$ radiation were performed with a X'Pert PRO Alpha-1 diffractometer (Panalytical, USA) equipped with a monochromator. SEM and EDS measurements of the samples morphology, diameter and composition were performed using a LEO 1550 microscope (LEO Electron Microscopy Group, DE). ImageJ software was employed for the SEM image analysis to determine the nanowire diameter distributions [4]. TEM experiments were performed using a JEOL 100CX II (JEOL, Japan) using a 100 kV electron beam. Tensile tests (Instron, USA) have been performed using in order to evaluate the mechanical properties of the selected composites electrodes.

### 2.3 Electrochemistry

For electrochemical testing 16.5 mm diameter electrodes were prepared for 2016 coin cells and assembled in an argon dry box (<1 ppm $H_2O$). The counter and reference electrode was battery grade metallic lithium. Cyclic voltammetry was performed using Solartron 1480 MultiStat (Solartron Analytical, USA) multichannel potentiostat in the potential range from 10 mV to 2V at different scan rates. Charge-discharge tests have been performed using multichannel SB2000 cycler (Arbin Instruments, USA) in the same range at the current rates of 1 to 0.02 C. Electrochemical impedance spectroscopy studies have been performed using Solartron 1287 Electrochemical Interface coupled with Solartron 1255B Frequency Response Analyzer (Solartron Analytical, USA) to evaluate the structural changes within each electrode with cycling.

## 3 Results and Discussion

### 3.1 Aluminum and Magnesium Nanowire Synthesis

Freestanding metal nanowires (Figures 2, 3) were successfully grown on various metal foils. They exhibited narrow diameter distribution, which was found to show little dependence on the synthesis temperature or on a metal substrate selected.

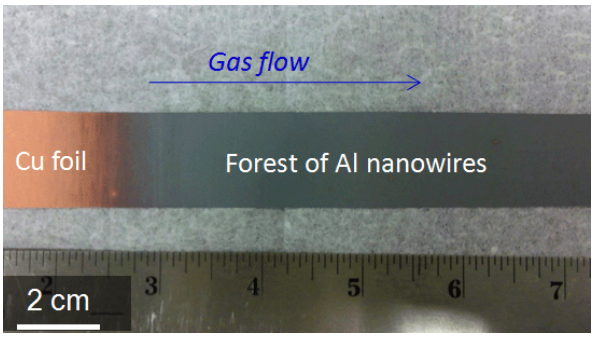


Figure 2. Optical micrograph showing uniform large-area deposition of Al nanowires on a Cu foil. Reproduced from Ref. [1] with permission.

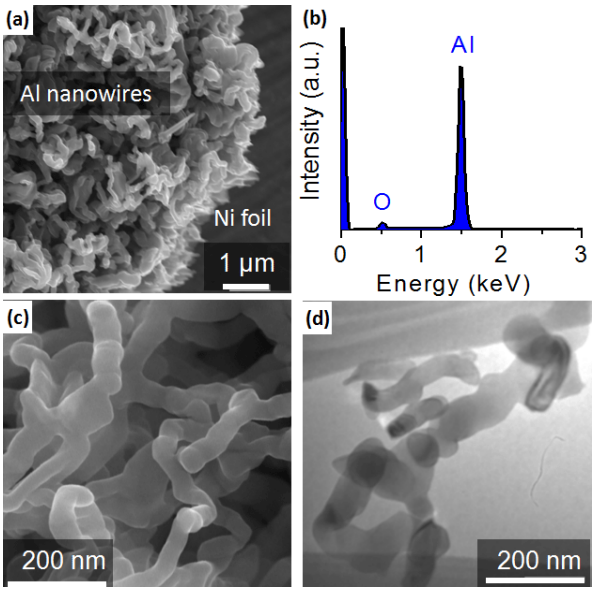


Figure 3. Curved Al nanowires grown on metal foils at 125 °C: (a, c) SEM micrographs showing a top view of Al nanowire forest, (b) a typical EDS spectrum taken at a nanowire region, (d) low-resolution TEM micrograph showing short curved Al nanowires. Reproduced from Ref. [1] with permission.

The specific Li insertion capacity of the selected nanowire samples was found to approach 1100 mAh/g, which exceeds conventional graphite anodes by over 200%.

### 3.2 Aluminum-Carbon and Magnesium-Carbon Nanocomposites

The produced metal-carbon composites exhibited significant electrochemical activity (Figures 4, 5) and reversible specific capacity in excess of 650 mAh/g, when tested with selected electrolytes as anodes for Li-ion batteries.

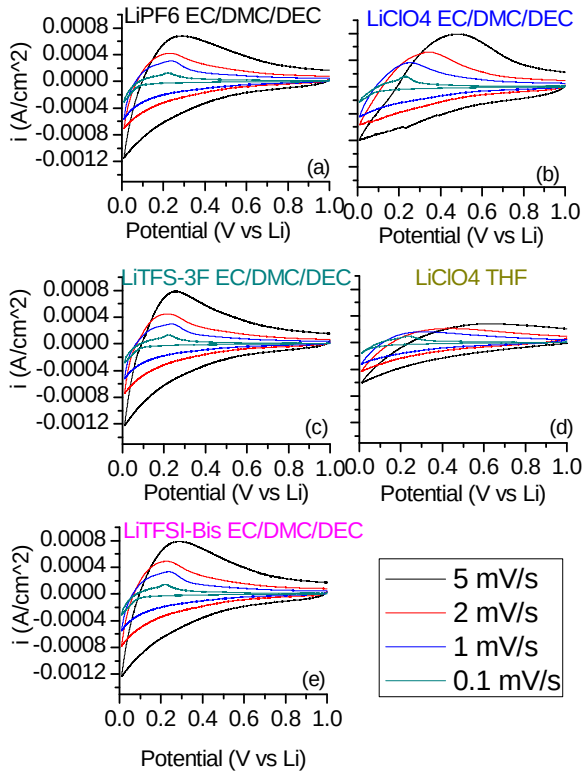


Figure 4. Cyclic voltammetry of magnesium-carbon nanocomposite anode for a Li-ion battery showing the kinetic limitations for the electrolyte based on THF solvents and $LiClO_4$ salts.

We found, however, that both electrochemical stability and activity of the metal-carbon composites was found to strongly depend on the electrolyte composition (Figure 4).

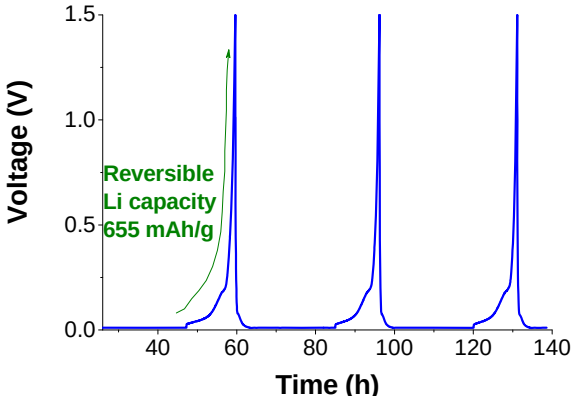


Figure 5. Electrochemical charge-discharge profiles of a typical magnesium-carbon nanocomposite anode for a Li-ion battery.

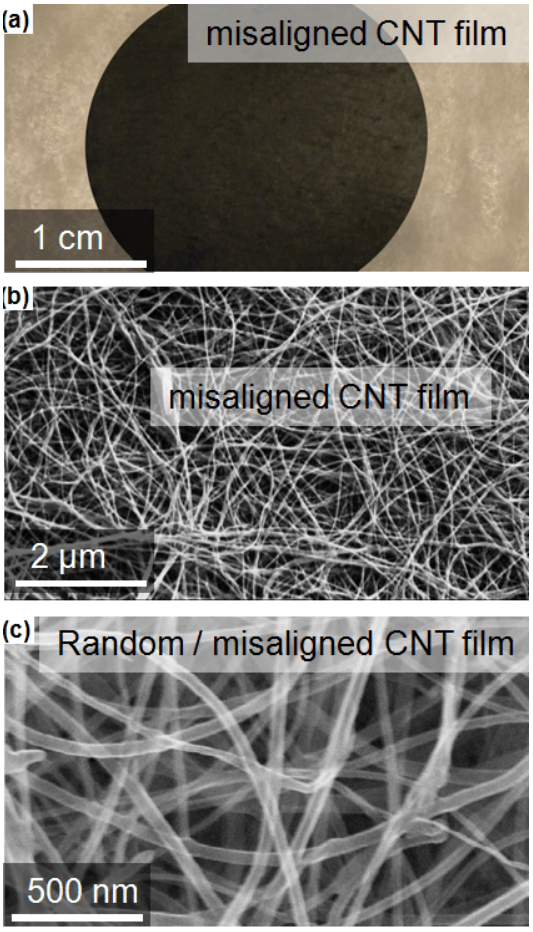


Figure 6. Thin mats of misaligned CNT films: (a) optical and (b, c) SEM images.

Mechanical test methods have been designed using a tapered tensile test specimen to provide localized deformation. The tensile test specimen design was based on ASTM D638. Laser cutting using a computer controlled $CO_2$ laser was implemented to insure reproducibility in geometry. Mechanical properties of the carbon-metal composites were found to strongly depend on the quality of the carbon-metal interface and the composite uniformity.

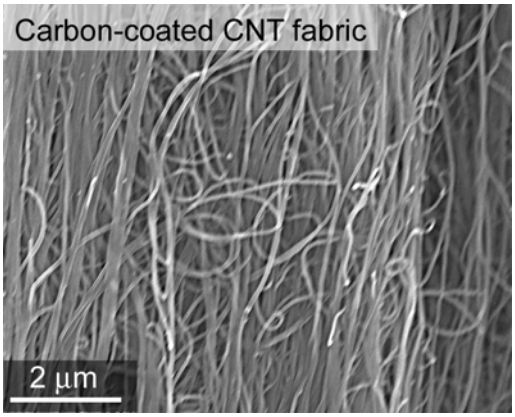


Figure 7. SEM micrograph of CVD carbon – coated CNT fabric used in multifunctional carbon-carbon composite anodes for Li-ion batteries.

### 3.3 Carbon-Carbon Nanocomposites

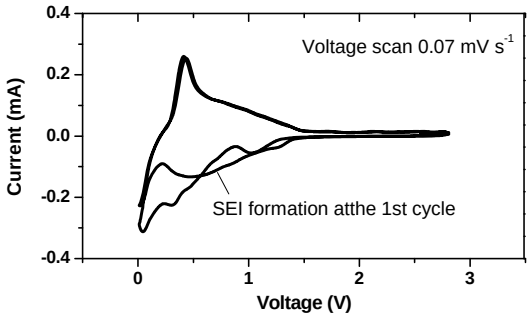


Figure 8. Cyclic voltammetry of a carbon – coated CNT fabric.

We have utilized both aligned and misaligned (Figure 6) CNT mats/paper/fabric for the nanocomposite formation. Carbon deposition on the CNT paper and fabric was very uniform (Figure 7). It resulted in the significant strengthening of the CNT paper samples and dramatic improvements in their electrochemical stability when used as Li-ion anodes. Figure 8 shows a typical cyclic voltammetry curve of the carbon-carbon composite anode. Formation of the solid electrolyte interphase (SEI) at below 1 V vs. Li/Li+ is evident in the first cycle. Due to relatively large specific surface area (SSA) of the composite formation of the SEI may contribute to significant irreversible capacity losses. However, these losses can be minimized provided the composite SSA is reduced or the composite is prelithiated. On a positive note, the obtained specific capacities reach ~280 mAh/g, which is comparable to that of the currently used graphites. But in contrast to traditional graphites, very high rate capability could be achieved. In addition, these composites could be used for load-bearing applications.

### 4 Summary

Nanostructured metal-carbon and carbon-carbon nanocomposites exhibit attractive mechanical and energy storage properties. In our talk we will discuss the most critical parameters that are required for their stable applications in multifunctional electric energy storage systems.

### Acknowledgement

This work was partially supported by US Air Force Office of Scientific Research (AFOSR). K. Evanoff was supported by the Robert Shackelford fellowship. The authors greatly appreciate the helpful discussions and advice of Prof. Inoue with the CNT growth part of the project.

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