

Coaxially Coated Vertical Carbon Nanofiber Arrays as 3D Multifunctional Electrodes for Battery-Supercapacitor Hybrids

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PI: Jun Li

Kansas State University

Objective:

The objectives of this proposed work are: (1) establishment of the fabrication of a set of unique hierarchical electrode materials by combining dissimilar functional nanomaterials in a unique three-dimensional (3D) architecture which forms ternary vertical nanowire arrays; (2) study of their properties for electrical energy storage in a battery-supercapacitor hybrids based on lithium chemistry; and (3) development of scalable production strategies for such high-performance energy storage technologies.

Methods:

This proposed work takes an approach of stepwise assembly of nanomaterials with different functionalities in a hierarchical vertical nanowire array. The proposed ternary structure was fabricated on a nanostructured template, i.e. a vertically aligned carbon nanofiber (VACNF) array that is grown on a proper metal foil with Plasma enhanced chemical vapor deposition (PECVD). A layer of active energy materials (such as Si, TiO₂, LiCoO₂, MnO₂, etc.) is then coaxially deposited on the VACNFs as a thin shell. If necessary, an electrical conductive polymer is then deposited as the outer layer. The highly conductive VACNFs serve both as a 3D brush-like nano-template and as a good current collector. The nanostructured shell significantly reduces the diffusion path length and enables fast reactions for supercapacitors and Li-ion batteries. The combination of the stable VACNF core and conductive polymer outer layer makes it possible to accommodate the large volumetric change of the shell materials during charge-discharge cycles.

Conformal shell materials with a radial thickness of ~50 to 200 nm have been successfully deposited using various methods, including electrochemical deposition (for MnO₂)[1], magnetron ion sputtering (for Si, Mn and TiO₂)[2, 3], chemical vapor deposition (CVD) (for TiO₂)[4-6], and pulsed laser deposition (PLD) (for LiCoO₂). Depending on the materials, deposition techniques and conditions, the deposited shell presents a variety of intriguing nanostructures. Figure 1 shows the SEM and TEM images of

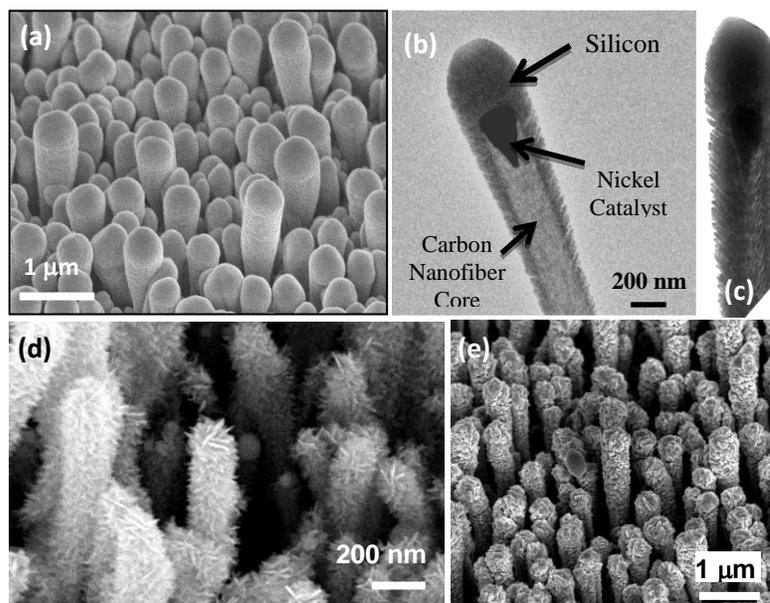


Fig. 1 The structure of the various vertical core-shell nanowire structure by depositing Si (a-c), TiO₂ (d), and LiCoO₂ on vertically aligned carbon nanofibers. Panels (b) and (c) are TEM images while the rest are SEM images.

some example shell structures, including feather-like Si shell by ion sputtering (Fig. 1a-c), need-like TiO₂ shell by CVD from organometallic precursors (Fig. 1d), and nanoparticulated shell of LiCoO₂ by PLD (Fig. 1e).

Highlight of Results:

While the large surface area and short reaction path length, nanostructured electrode materials can potentially provide solutions to high-performance electrical energy storage. Such electrodes combine the high energy capacity of batteries with the high power output of supercapacitors. However, they suffer from poor electronic conductivity and unstable electrical connection after charge-discharge cycles, limiting the overall performance and stability.

We have demonstrated that the core-shell hierarchical structure of Si and TiO₂ on highly conductive and mechanically stable VACNFs can dramatically improve the power density and cycle life. Fig. 2 shows the representative half-cell test results of a Si/VACNF anode with 500 nm nominal Si thickness sputtered onto a ~3 μm tall VACNF array. There are three remarkable characteristics. (1) The specific Li storage capacity (normalized to the Si mass) is ~3,000 to 3,500 mAh/g, matching the maximum value reported by experimental observations for amorphous Si. Clearly all Si in the shell is active. (2) The specific capacitance retains at this level as the C-rate was increased from C/2 to 5C (or C/0.2). Such charge-discharge

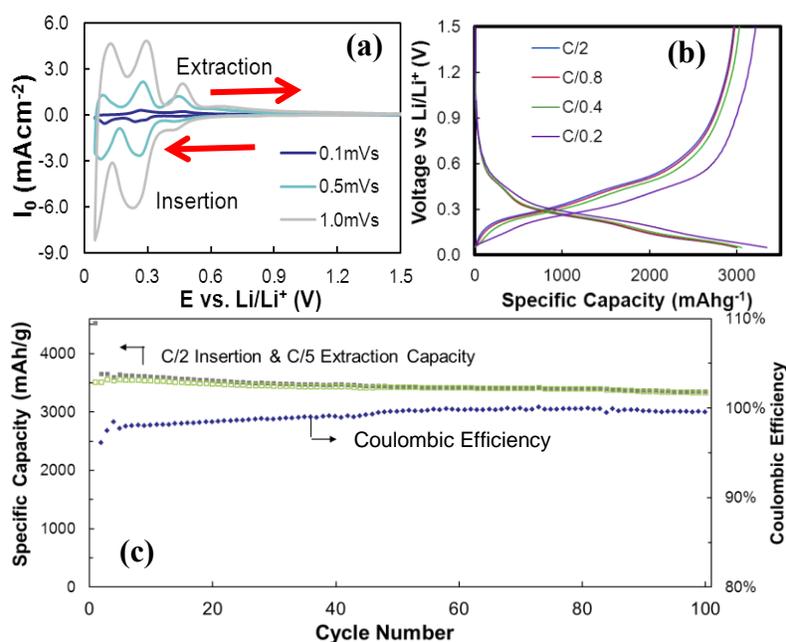


Fig. 2 Characteristics of Si/VACNF core-shell structure as a high-performance lithium battery anode. (a) Cyclic voltammograms showing Li⁺ insertion and extraction below ~0.5 V vs. Li⁺/Li. (b) The galvanostatic charge-discharge profile showing almost invariant specific capacity of Si shell as the C-rate was increased from C/2 to C/5 (or C/0.2). (c) The specific capacity of the Si shell over 100 charge-discharge cycles.

rate is much higher than previous studies with Si nanowires.[7] (3) More importantly, the electrode is remarkably stable with less than 8% drop in the specific capacity after 100 cycles. The Coulombic efficiency actually increases during cycling, reaching a value over 99% after ~50 cycles. Our results of the electrodes based on TiO₂/VACNF core-shell structure showed similar high-power characteristics which remain stable even at 32C rate over hundreds cycles. For both of these two types of electrodes, a solid electrolyte interphase (SEI) was formed as the electropotential was lowered to 1.0 V (vs. Li/Li⁺) or below. The SEI may serve well as the outer polymer film to form a dynamic ternary structure that further stabilizes the core-shell structure.

In contrast, the cathodes based on LiCoO₂/VACNF performed well in the first few charge-

discharge cycles but then quickly fade away in the following cycles. We are investigating this issue at this moment. It is likely a suitable polymer coating is needed to stabilize the electrode material.

Field Impacts:

The core-shell structure or the ternary composites can be used either as cathodes or anodes depending on the shell materials. For example, Si and TiO₂ are good anode materials while LiCoO₂ is a good cathode material. Combining them together may lead to a remarkable high-performance lithium-ion battery. Such battery may present extremely high specific power (at >10 C rate) which approach the properties of supercapacitors. Our goal is to achieve unprecedented power density, energy capacity, and significantly improved cycle life. The materials fabrication is based on scalable processing technologies including PECVD, MOCVD, PLD, and electrodeposition, which are all suitable for industrial manufacturing. Scalable manufacturing was explored through collaboration with Prof. Judy Wu's group in the University of Kansas. It will make significant impact to the electrical energy storage technologies. Along this direction, a strong collaboration with Catalyst Power Technologies Corp. and NASA Ames Research Center has been established in order to push this further in manufacturing and commercialization. Two patents have been filed to secure the intellectual properties.

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