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Anomalous capacity increase at high-rates in lithium-ion battery anodes based on silicon-coated vertically aligned carbon nanofibers

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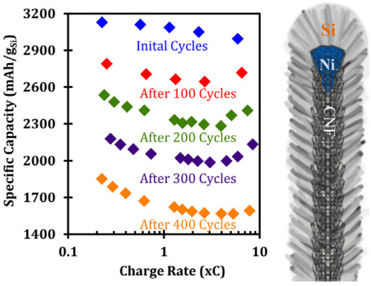
HIGHLIGHTS

- Si-coated VACNFs Li-ion battery anode is characterized at high current rates.
- The high-power capability and long cycling efficiency of nano-hybrid electrode is discussed.
- A new phenomenon of increasing capacity at increasing current at high rates is presented.

GRAPHICAL ABSTRACT



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ABSTRACT

This study reports of a multi-scale hierarchical lithium-ion battery (LIB) anode that shows a surprising increase in storage capacity at higher current rates from ~3C to ~8C. The anode, composed of forest-like vertically aligned carbon nanofibers coaxially coated with Si shells, is shown to obtain a storage capacity of 3000–3500 mAh $(g_{Si})^{-1}$ and greater than 99% coulombic efficiency at a 1C (or C/1) rate, leading to remarkable stability over 500 charge–discharge cycles. In contrast to other studies, this hierarchical LIB anode shows superior high-rate capability where the capacity decreased by less than 7% from ~C/8 to ~3C rates and, more importantly, increased by a few percent from ~3C to ~8C rates, displaying a new phenomenon that becomes more evident after going through long cycles. Electron microscopy, Raman, and electrochemical impedance spectroscopy reveal that the electrode structure remains stable during long cycling and that this enhanced property is likely associated with the combination of the unique nanocolumnar microstructure of the Si coating and the vertical core–shell architecture. It reveals an exciting potential to develop high-performance lithium-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) have become the most important electrical energy storage (EES) systems for today's portable electronics due to their high specific energy densities. Further increasing energy density and, more importantly, power density, by

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improving the structure, composition, and assembly of electrode materials is critical to broader application, including the ever-increasing fledgling market of electric vehicles. Since inception in the early 1990's, the vast majority of commercial LIBs utilize a pair of intercalation compounds (graphite and metal oxides such as $LiCoO_2$ or $LiFePO_4$) as the electrodes [1]. While being able to provide sufficient energy storage capacity and long cycling lifetime, these electrodes are not suitable for new applications demanding greater energy density at a higher power rate. This has triggered an extensive study on an assortment of novel materials and various nanoscale electrode architectures [2–5], and of which, Silicon (Si) has been identified as one of the best materials for LIB anodes. Si presents an extremely high theoretical Lithium (Li) storage capacity (4200 mAh g^{-1}), a very low lithiation potential (0.2–0.4 V vs. Li/Li^+), and is naturally abundant and environmentally benign [6–8]. In the amorphous state, the maximum obtainable capacity is ~3800 mAh g^{-1}; ten times that of graphite (372 mAh g^{-1}) [8]. However, unlike the staged intercalation of graphite anodes, Li forms alloys directly with Si during charging, causing up to 320% expansion in volume that induces severe anisotropic stress [9]. This stress leads to fracturing and loss of electrical connection that consequently reduces the capacity of Si thin-film electrode after only tens of cycles [10–12]. Various nanostructured Si materials including nanoparticles, hollow spheres, egg yolk, etc. have been employed to reduce the effect of the internal stress and make use of their large specific surface area and short Li^+ diffusion length in solids [7–9]. Among them, long Si nanowires (NWs) were found able to accommodate the large volumetric changes in both axial and radial direction, which effectively minimizes the fracture, providing greater than 3000 mAh g^{-1} capacity at C/20 rate and dramatically enhanced cycling lifetime [9]. However, the charge–discharge rate on Si NW anodes was limited, mostly by the low electrical conductivity of amorphorized Si [8,9]. Hybrid core–shell NWs utilizing a highly conductive and stable NW or nanotube core to support a Si shell has recently been explored toward improving the power rate while maintaining the high capacity and good cycle stability [8,13–20]. However, as the power rate was increased, the obtained capacity still sharply dropped [8,13,16,18], for example by 50% or more from ~C/5 to 5C with Si-carbon nanotube (CNT) core shell structures [19,20].

In our previous study [21], we reported the fabrication and initial characterizations of core–shell NW arrays composed of a forest-like arrangement of vertically aligned carbon nanofibers (VACNFs) that were coaxially coated with intrinsic Si by magnetron sputtering. That study was concentrated on the ultra high capacity obtained at normal power rates (C/10 to 2C). This report is focused on the understanding of the performance at higher rates (up to ~10C) of this core–shell NW anode, detailing how the pine-needle-textured Si shell improves the capacity retention at very high power rates, which is desirable for advanced LIB hybrids.

2. Experimental

Experimental conditions are briefly described below. More details can be found in the supplementary information. Pure copper foils were deposited with a 300 nm thick chromium layer followed by a 30 nm nickel catalyst layer. These Ni/Cr/Cu sheets were then cut into 18 mm diameter disks for vertically aligned carbon nanofibers (VACNFs) growth using DC-biased plasma enhanced chemical vapor deposition (PECVD) following the procedure in literature [21–24]. VACNFs have an average length of 3.0 μm, an average diameter of 150 nm, and ~1.1×10^9 CNFs cm^{-2} areal density. Pure Si was deposited onto the VACNF arrays to form the core–shell NW arrays by high vacuum magnetron sputtering to a nominal Si thickness of 465 nm (equivalent to the film thickness deposited on a flat surface). A reusable electrochemical cell (El-Cell, Hamburg, Germany) was used for all half-cell tests with the Si-coated VACNF disks as the working electrode, a Li disk as the counter electrode, and a Li wire as the reference electrode. A specially designed Kel-F ring was used to separate the working electrode from the polyethylene fiberglass spacer to avoid crushing the core–shell NWs, leaving an exposed working electrode area of 17.5 mm in diameter. The electrolyte consisted of 1.0 M lithium hexafluorophosphate ($LiPF_6$) in a mixture of 1:1:1 volume ratio of ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonate, with 2% vinylene carbonate added. The charge–discharge measurements of Si-VACNF hybrids were set from 1.5 to 0.050 V vs (Li/Li^+) to minimize Li^+ intercalation into VACNF cores. Our previous study has demonstrated that the contribution to the total capacity by Li^+ intercalation into VACNF core is negligible (<10%) [21].

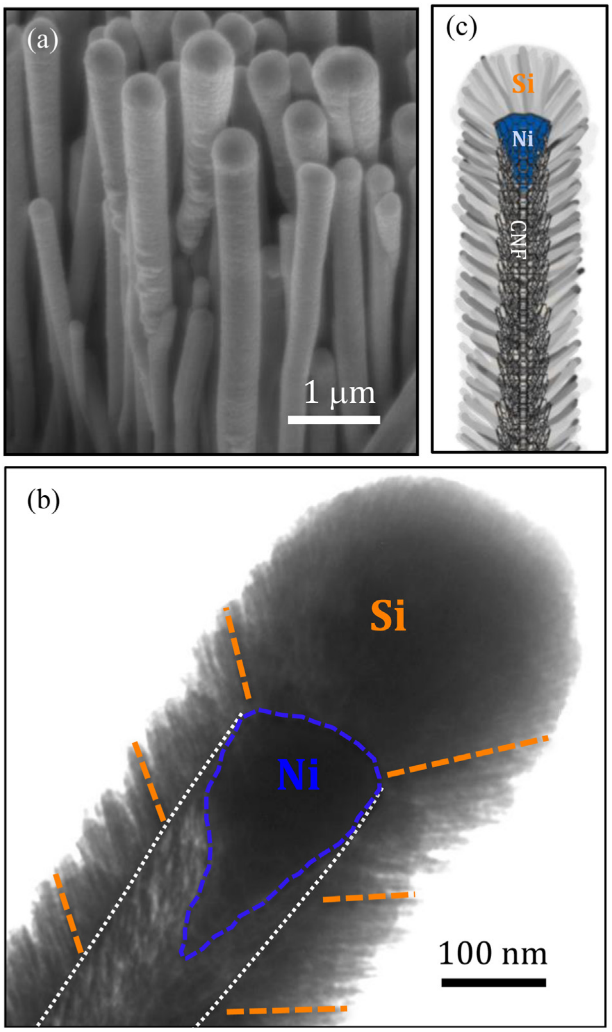

Fig. 1. A SEM image (a) showing a landscape view of the uniform coaxial coating of Si shells on the random CNF array. A TEM image (b) and a schematic (c) that illustrate the nanocolumnar microstructure of Si shell and the conical graphitic stacking structure of the VACNF core. Sputtering deposition of Si created the nanocolumnar microstructure extending out from the CNF shaft (highlighted by white dotted lines) at an upward oblique angle (highlighted by orange dashes) while the Si at the CNF tip showing a solid amorphous feature. A nickel catalyst particle (outlined by the blue dotted line) is shown at the CNF tip. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)