$Li_2Fe_xMn_yCo_zSiO_4$ nanoparticles incorporated CNTs as a novel high capacity cathode for lithium ion batteries

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Current state-of-the-art lithium ion batteries mostly utilize metal oxides as cathode material with $LiCoO_2$ as the most popular and commercially successful representative [1-2]. These metal oxides however, due to their intrinsic material properties, have reached their limit in further enhancement of LIB performances. Specifically, they have limited average potential versus Li/Li^+, mostly well below 4V except $LiMn_2O_4$. And their specific capacity is well below 180mAh/g with the exception of $LiNiO_2$. These metal oxides are also "hot" cathode materials due to the thermal runaway reaction; therefore, there is also a concern for safety. High-performance LIB remains the preferred cost-effective technology that would address a much broader range of energy source/storage for both military and civil applications with LIB being one of the most promising battery technologies that can provide higher energy density than other alternative. It also does not suffer from the memory effect observed in Ni-Cd batteries and the loss of charge is relatively slow when not in use.

This paper reports on the innovative research utilizing multi-walled carbon nanotubes (CNT) as nano-architectured current collector array grown directly on a flexible graphite foil. Nanoparticles of the high-performance ternary orthosilicate, **$Li_2Fe_xMn_yCo_zSiO_4$**, are dispersed in the porous 3D network of CNTs. The CNT/ $Li_2Fe_xMn_yCo_zSiO_4$ hybrid electrode acts as the cathode, where ***x+y+z=1***. This novel approach of using nano-structured, vertical-aligned CNT network provides a high surface area of attachment for $Li_2Fe_xMn_yCo_zSiO_4$ nanoparticles and to minimize the contact resistance at the active material/current collector interface, thereby, maximizing the charge efficiency and the energy density of the cathode. The ternary orthosilicate compound offers a theoretical capacity of ~**330mAh/g**, and our additive/binder free fabrication approach allows for greater mass loading. The nano-architected 3D CNT array structures provide shorter and simpler diffusion paths for lithium ions. Moreover, the porous structure provides elasticity to accommodate dimensional changes during Li-ion intercalation/deintercalation and thus provides excellent cyclability.

Thermal chemical vapor deposition process in a tube furnace is used for growing vertically aligned multi-walled CNTs directly on the flexible and conductive graphite substrates. The input gas mixture consists of $H_2/CH_4/NH_3$ gases, at a temperature of ~750°C. Conventional, low cost sol-gel process was used to synthesize ternary orthosilicates with different stoichiometries, using various ratios of citric acid, iron (III) citrate, manganese acetate, lithium acetate, cobalt carbonate, TEOS (tetraethyl orthosilicate) and ethanol. The 'sol' obtained is then dried to evaporate the water and ethanol. The gel thus formed is further dried overnight in a tube furnace under inert atmosphere. The 'dry gel' product formed is ground in a mortar and is then calcined at high temperature under inert atmosphere.

SEM micrographs of the fabricated $Li_2Fe_xMn_yCo_zSiO_4$ nanoparticles dispersed on CNTs is shown in figure 1, revealing uniform coating. Electrochemical characterization was performed by fabricating pouch-cells consisting of Li foil anode and CNT/ $Li_2Fe_xMn_yCo_zSiO_4$ on graphite as the cathode with a PE separator and 1M $LiPF_6$ in EC:DMC electrolyte. Charge discharge curve for one such LIB cell was recorded at 1C rate and can be seen in figure 2, showing a high specific capacity approaching the theoretical value of **330mAh/g**, at an average voltage of ~**4.1V**, resulting in a very high specific energy value of ~**1350Wh/kg**. Material characterization using techniques of differential scanning calorimetry (DSC), energy dispersive X-ray spectroscopy (EDS), RAMAN spectroscopy, X-Ray diffraction (XRD), and (ICP-MS) has also been performed. Using AC Impedance Spectroscopy, a Nyquist plot was recorded and used to calculate the ESR value of ~7Ω.

Detailed fabrication and characterization of the novel CNT/ $Li_2Fe_xMn_yCo_zSiO_4$ cathode and its performance characteristics will be presented.

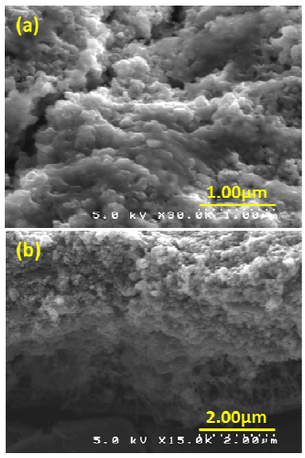

Figure 1. SEM micrographs of $Li_2Fe_{0.7}Mn_{0.15}Co_{0.15}SiO_4$ after dispersing into the CNT network. (a) SEM image from the top surface of the electrode showing uniform particle size distribution; (b) A tilt view of the electrode cross section showing incorporation of the nanoparticles into the CNTs.

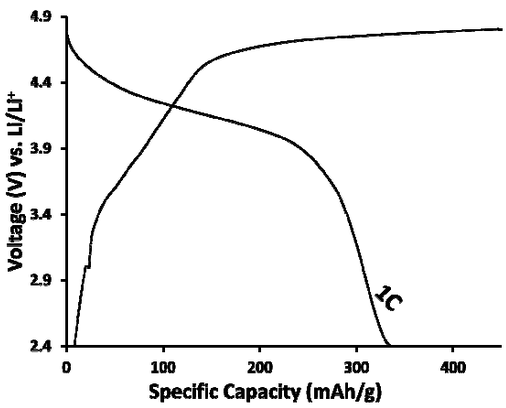

Figure 2. Charge/discharge curves recorded using the CNT/ternary orthosilicate cathode at 1C rate showing a very high specific capacity, approaching the theoretical value of 330mAh/g.

References:

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