A novel nano-structured ternary orthosilicate on carbon nanotube as lithium ion battery cathode

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Currently lithium-ion battery (LIB) is one of the most promising battery technologies that can provide higher energy density than other batteries [1-2]. 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. Hence, high-performance LIB remains the preferred technology that would address a much broader range of energy source/storage for military, industrial, and transportation applications if advanced cathode materials with high specific capacity and energy density could be realized.

This paper reports an innovative nanostructured LIB cathode whereby a novel nanoparticles of the high-performance ternary orthosilicate, $Li_2Fe_xMn_yCo_zSiO_4$, are dispersed in the porous 3D network of vertically aligned multiwall CNTs, served as nano-architecture current collector array, grown directly on a flexible graphite foil. The CNT/ $Li_2Fe_xMn_yCo_zSiO_4$ hybrid electrode acts as the LIB cathode, where x+y+z=1. The 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 while the ternary orthosilicate compound offers a high theoretical capacity of ~330mAh/g. The nanostructured cathode also provides shorter Li^+ diffusion lengths and tolerant to volume-change of the active material cause by charge/discharge of Li-ions. Thereby improved stability and safety of the cell.

Hot filament chemical vapor deposition process is used for growing vertically aligned multiwall CNTs directly on the graphite substrate in $H_2/CH_4/NH_3$ gas mixture at 750°C and 15 torr chamber pressure. Conventional Sol-Gel process was used to synthesize ternary orthosilicates with different stoichiometry, using various ratios of citric acid monohydrate, iron (III) citrate hydrate, manganese acetate tetrahydrate, lithium acetate dihydrate, cobalt carbonate, and TEOS-tetraethyl orthosilicate and ethanol. The 'sol' obtained is then dried to evaporate the water and ethanol. The gel thus formed is further dried in a tube furnace at 100°C for 24 hours under an Ar flow. The 'dry gel' product formed is ground in a mortar and is then calcined at high temperature under Ar flow.

The relationship between the stoichiometry of the transition metals (x, y, z) and the overall discharge capacity in a pouch-cell package using lithium foil anode and 1M $LiPF_6$ in EC:DMC electrolyte have been studied, including charging-discharging at high C-rates. Differential scanning calorimetry was used to study the thermal stability and identify the thermal runaway behavior of these compounds. We have identified the optimum stoichiometric composition and demonstrated excellent performance of the fabricated cathode in Li-ion pouch-cell. Material characterization of the cathodes include scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), RAMAN spectroscopy, X-Ray diffraction (XRD), and (ICP-MS).

A SEM image of the fabricated $Li_2Fe_xMn_yCo_zSiO_4$ nanoparticles dispersed on CNTs is shown in figure 1, revealing uniform coating. The charge/discharge curves for the CNT / ternary orthosilicate LIB cell operated at 1C, 2C, 5C and 10C rates can be seen in figure 2, demonstrating high specific capacities at these C-rates. These results exceed the state-of-the-art LIBs in both specific energy as well as specific power. Using AC Impedance Spectroscopy, a Nyquist plot (figure 3) was recorded and used to calculate the ESR value of ~7Ω.

Fabrication and characterization of the CNT/ $Li_2Fe_xMn_yCo_zSiO_4$ cathode and its performance characteristics will be discussed.

References

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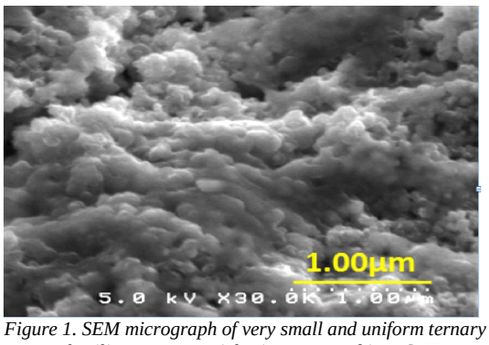

Figure 1. SEM micrograph of very small and uniform ternary orthosilicate nanoparticles incorporated into CNTs synthesized on graphite substrate.

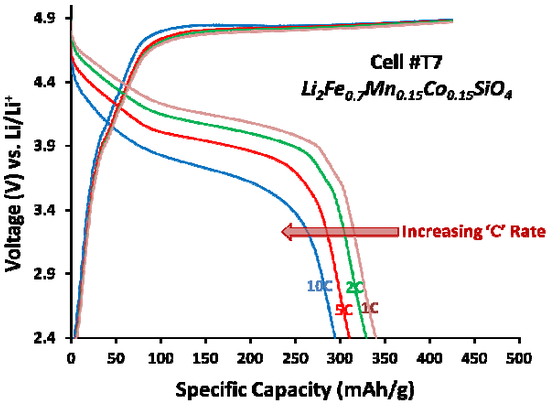

Figure 2. Charge/discharge curves recorded using the CNT/ternary orthosilicate at different C rates of 1C, 2C, 5C and 10C.

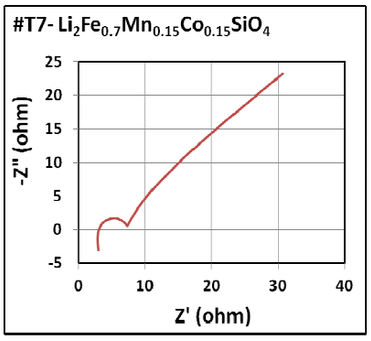

Figure 3. Nyquist plot recorded A.C. Impedance spectroscopy showing an ESR value of ~7Ω