Sonochemical Deposition of Lithium Alloying Nanoparticles on the Surface of Spherical Carbon Anodes for Li-Ion Batteries

Vilas G. Pol, ¹ Sanketh R. Gowda, ¹ Jianguo Wen, ² Dean J. Miller², and Michael M. Thackeray ¹ Electrochemical Energy Storage Department, Chemical Sciences and Engineering Division, ² Electron Microscopy Center, Argonne National Laboratory, Lemont, IL 60439, USA

While graphite is the preferred material for the negative electrode (anode) of Li-ion batteries[1], there is a need to increase capacity of the anode to enhance the energy density of these batteries. Prior research efforts to increase the capacity of graphite anodes have focused on fabricating Sn-C fibers by electrospinning[2], Sn-C composite nanoparticles[3], as well as designing tinencapsulated hollow spherical carbon structures[4]. Usually, carbon-tin composites suffer from the aggregation of Sn particles upon cycling detachment/isolation of Sn particles from the carbon matrix, thereby leading to capacity fade. Hence, it is believed that improving the dimensional stability of metal or alloy particles/clusters during Li insertion/extraction reactions is an important factor that will enhance cycling stability and electrochemical performance.

We have recently reported the electrochemical properties of hard carbon spheres, synthesized by autogenic reactions[5]. The spheres are comprised of disordered carbon planes and cycle, on average, at a higher potential than pure graphite in lithium cells, thereby offering enhanced safety; they provide a steady reversible capacity of ~250 mAh/g at a 1C rate. In this presentation, we will report on our recent efforts to enhance the specific capacity of the carbon sphere electrodes by using a rapid sonochemical process to deposit lithium-alloying Sn and Sb nanoparticles on the surface of the spheres. Typically, the as-prepared spheres were dispersed in ethanol using ultrasonic irradiation for 1 minute, followed by the addition of SnCl₂ and SbCl₃ precursors, respectively. The final slurry was sonicated for 7 min. under a flow of argon gas using a 40% ultrasonic horn intensity (20 kHz, 20W/cm²). After separating the ethanol component, the product was dried at about 100 °C and further heated in an inert argon filled glove box at 500 °C for 3 hrs; exposure of the particles to air oxidized the Sn nanopoarticles to SnO2, whereas the Sb particles remained unaffected. The composite-carbon sphere electrode is therefore referred to as 'CS-SnO₂-Sb'.

The morphological and structural characterization of the CS-SnO₂-Sb materials was carried out by SEM and TEM techniques (Fig. 1a, b). The thin, <10 nm thick SnO₂/Sb layer on the surface of the spheres remained intact after the heat-treatment process. The powder X-ray diffraction pattern of the CS-SnO₂-Sb product confirmed the presence of tetragonal SnO₂ and hexagonal Sb crystals on the surface of the particles. Energy dispersive X-ray analysis revealed that there was about 13 wt.% of SnO₂ and Sb on the surface of the spheres.

The variation in the capacity of the composite-carbon spheres as a function of current was monitored in Li/CS-SnO₂-Sb cells (Fig. 1c). More than 400 mAh/g was delivered at a C/6 rate, about 315 mAh/g at a C/1.5 rate, and more than 200 mAh/g at a C rate. It will be shown that capacities >400 mAh/g can be obtained by sonochemically tailoring the loading of lithium-alloying elements on the surface of commercial graphite products.

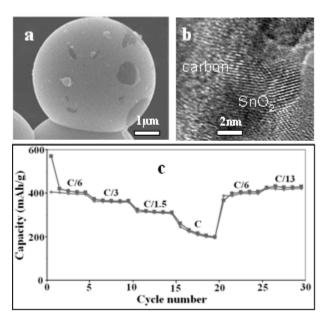


Figure 1. a) Scanning electron micrograph of a composite CS-SnO₂-Sb product, b) High resolution transmission electron micrograph of a composite CS-SnO₂-Sb surface, c) Capacity vs. cycle number plot for a Li/CS-SnO₂-Sb cell at various current rates.

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