University of Fribourg / Faculty of Science and Medicine / Department of Chemistry

Sn/SnO_2 alloy anode@carbon based composite material for high energy lithium ion batteries

Sivarajakumar Maharajan

Tin based anode materials are one of the most promising high energy anode materials for next-generation lithium ion batteries (LIBs) due to its high theoretical capacity of 790 to 991 $mAhg^{-1}$ or 1030 to 7313 $mAhcm^{-3}$, multiple times that of commercial graphite anode materials (372 $mAhg^{-1}$ or 833 $mAhcm^{-3}$). However, the huge volume expansion upon lithium ion insertion (up to 230 to 260%) causes cracking of the active material, consequently leading to the loss of conductivity at the electrode and to quick capacity fading. This greatly hinders the practical application of Sn as anode material in lithium ion batteries. We have developed a 'Nano-rattle' type Sn/SnO_2 nanoparticles encapsulated in carbon shell which features a buffer volume (void) to sustain the volume changes during lithiation and delithiation for many number of cycles and avoid the pulverisation or cracking of particles leading to capacity fade. The nano-rattle synthesis has been attempted by two major approaches. The first approach mostly resulted in $Sn@SiO_2@C$ and $SiO_2@C$ with the silica remaining partially unremoved and the Sn nanoparticles escaping from the particle cores during the high temperature post-thermal calcination step. In our second approach, the hollow silica spheres are formed and the Sn/SnO_2 nanoparticles and impregnated by a melt-diffusion method to yield a high specific capacity of around 2100 $mAhg^{-1}$ for the first cycle. The Coulombic efficiency of the following cycles was above 90% to yield around 400 $mAhg^{-1}$ after 25 cycles for C/10 and 20 cycles for C/5. However, the rate capability still needs to be improved, as it fades at high C-rates like C/2 and 1C due to the high surface reactivity during fast charge and discharge.

Jury:

Prof. Dr. Katharina M. Fromm (thesis supervisor)

Prof. Dr. Robert Dominko (external co-examiner)

Prof. Dr. Alke Fink (internal co-examiner)

Dr. Nam Hee Kwon (internal co-examiner)

Prof. Dr. Marco Lattuada (president of the jury)