

Colloidal Nanocrystals for Li-ion and Na-ion Batteries

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Introduction. Lithium(Li)-ion batteries (LIBs) remain the most prominent rechargeable, electrochemical energy storage technology [1], with tremendous importance not only for portable electronics rapidly growing sector of environmentally-benign electrical mobility [2]. There is also a growing recognition that renewable energy sources require large scale-batteries located, for instance, next to solar cell power plants. Conceptually identical Sodium(Na)-ion batteries (SIBs) have recently received a revived interest as a viable alternative to LIBs due to much greater natural abundance and more even distribution of Na reserves as compared to Li. SIBs are therefore expected to replace LIBs in future large-scale energy storage facilities.

Presently, great research efforts are focused on nanostructuring of the active anode materials, by producing nanowires, nanoparticles and nanocrystals (NCs), in order to mitigate the effects of volumetric changes and to enhance kinetics of the conversion and alloying reactions. With regard to SIBs, it is important to note an even greater need for efficient anode materials, because Silicon does not reversibly store Na-ions at ambient conditions, Graphite shows negligible capacities of 30-35 mAh g⁻¹, while other carbonaceous materials exhibit capacities of less than 300 mAh g⁻¹ at rather low current rates and suffer from the low tap density. Fully contrary to the present situation with LIBs, there is much greater progress for cathodes than for anodes in SIBs.

Antimony nanocrystals as anode materials for SIBs and LIBs (Figure 1) [3]. In the elemental form, antimony (Sb) has long been considered as a promising anode material for high-energy density LIBs owing to its high theoretical capacity of 660 mAh g⁻¹ upon full lithiation to Li₃Sb. Recently, this material has also been demonstrated to store same amount of Na ions. We present colloidal synthesis of Sb NCs with mean size tunable in the 10-20 nm range and with narrow size distributions of 7-11%. In comparison to microcrystalline Sb, 10nm and 20nm Sb NCs exhibit enhanced rate-capability and higher cycling stability as anode materials in rechargeable Li-ion and Na-ion batteries. All three particle sizes of Sb possess high and similar Li-ion and Na-ion charge storage capacities of 580-640 mAh g⁻¹ at moderate charging/discharging current densities of 0.5-1C (1C-rate is 660 mA g⁻¹). At all C-rates (0.5-20C, e.g. current densities of 0.33-13.2 Ag⁻¹), capacities of 20nm Sb particles are systematically better than for both 10nm and bulk Sb. At 20C-rates, retention of charge storage capacities by 10 and 20nm Sb NCs can reach 78-85% of the low-rate value, indicating that rate capability of Sb nanostructures can be comparable to the best Li-ion intercalation anodes and is so far unprecedented for Na-ion storage.

Tin-Germanium nanorods and their Li-ion storage properties (Figure 2).¹ We also present a facile colloidal synthesis of Sn-Ge heterostructures in the form of nanorods with a small aspect ratio of 1.5-3 and a length smaller than 50nm. In the two-step synthesis, pre-synthesized Sn nanoparticles act as a low-melting point catalyst for decomposing Ge precursor, bis[bis(trimethylsilyl)amido]Ge(II), and for crystallization of Ge via solution-liquid-solid growth mechanism. Creation of such Sn-Ge nanoheterodimers can serve as a well-controlled method of mixing these nearly immiscible chemical elements for the purpose of obtaining Sn-Ge nanocomposite electrodes for high-energy density Li-ion batteries. Comparable mass content of Sn and Ge leads to synergistic effects in electrochemical performance: high charge storage capacity above 1000 mAh g⁻¹ at a relatively high current density of 1A g⁻¹ is due to high theoretical capacity of Ge, while high rate-capability is presumably caused by the

enhancement of electronic transport by metallic Sn. At a current density of 4 A g^{-1} , Sn-Ge nanocomposite electrodes retain up to 80% of the capacity obtained at a lower current density of 0.2 A g^{-1} . Temporally separated lithiation of both elements, Sn and Ge, at different electrochemical potentials is proposed as a main factor for the overall improvement of the cycling stability. This can also serve as a general strategy for other active materials (Si, Ge, metal oxides etc.).

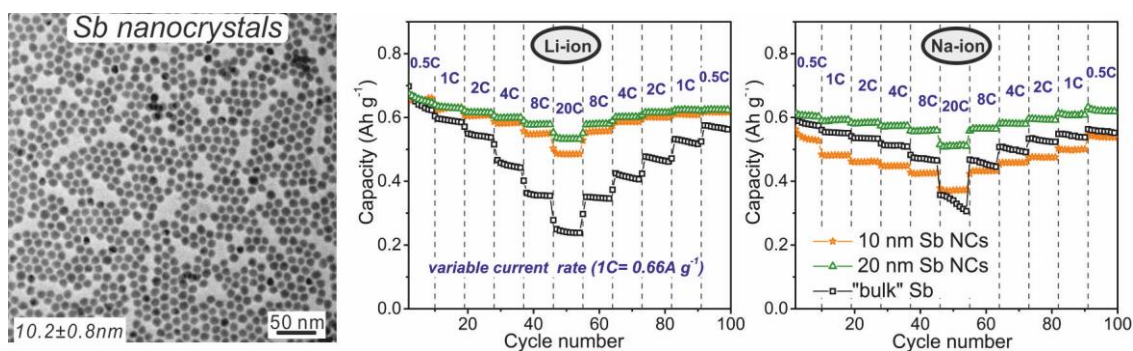


Figure 1. Rate-capability tests of Li-ion and Na-ion half-cells employing Sb anodes made from monodisperse colloidal Sb NCs and from microcrystalline powders. The data for 10nm Sn NCs are shown for comparison. All anodes had same composition of Sb(64%)/CB(21%)/CMC(15%) and were cycled at room-temperature under variable current rate of 0.5-20C (1C=0.66 Ah g⁻¹, 9 cycles at each C-rate, first cycle at 0.1C).

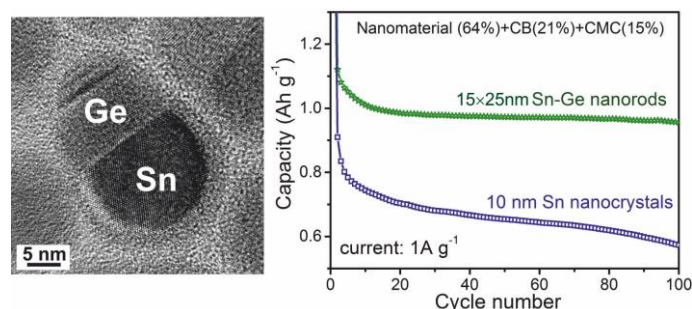


Figure 2. Reversible discharge capacities for anodes containing 64wt% of Sn-Ge NRs (15×25nm) and, for comparison, 64wt% of Sn NCs.

References:

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