

Nanoparticle/Graphene Composites: Toward High-Performance Anode Materials for Lithium-ion Batteries

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Lithium-ion batteries (LIBs) were first commercialized by Sony in 1990 and now are the most popular power sources for cell phones, laptop computers, digital cameras, and hybrid electric vehicles owing to their long cycling stability and high energy density relative to Ni-MH, Ni-Cd, and Pb-acid batteries. Lithium ions can be reversibly extracted from the cathode and inserted into the anode while maintain the structure of the electrode materials (Figure 1). Since the charging and discharging processes depend on the insertion/extraction of lithium ions in the electrodes, the physical and chemical properties of the electrode materials are crucial to the performance of the battery.¹ To improve the performance of LIBs, numerous efforts have been devoted to developing new electrode materials or designing new structures of electrode materials.^{2,3}

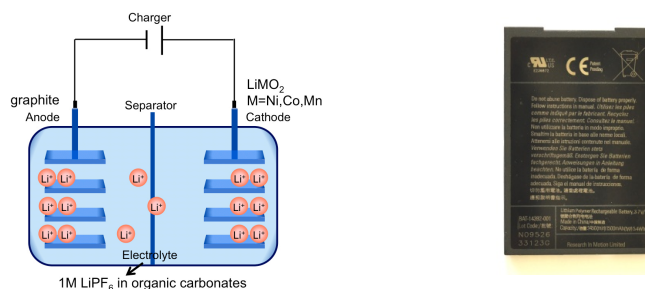


Figure 1. (Left) Schematic illustration of the charging process of a rechargeable lithium ion battery. (Right) Photograph of a commercial lithium ion battery for powering a BlackBerry device.

For anode materials, graphite is commonly used in LIBs due to its high Coulombic efficiency (the ratio of the extracted lithium to the inserted lithium) and relatively low cost. But six carbon atoms are required to accommodate each lithium ion, resulting in a relatively low specific capacity (372 mAh/g). To achieve higher lithium storage capacities, many metals and metal oxides like Si (4200 mAh/g), Ge (1600 mAh/g), Sn (990 mAh/g), SnO₂ (790 mAh/g), and Co₃O₄ (890 mAh/g) have been developed to replace graphite as advanced anode materials.⁴⁻⁸ A major challenge when employing these substances as anode materials is that they suffer from large volume variation (up to 400%) during the lithium insertion/extraction process, which leads to pulverization of the electrode and a very rapid decay in capacity.⁹

One possible approach to solve this problem is to make nanoparticle/graphene composites. Graphene, a one-atom-thick planar sheet of sp²-hybridized carbon, not only has high surface area (~2,600 m²/g) and superior electrical conductivity, but also possesses mechanical flexibility and chemical resistance.^{10,11} Thus, graphene-based materials hold great promise for energy related applications.¹²⁻¹⁴ In the anode of LIBs, graphene sheets can act as matrices for metal and metal oxide nanoparticles, which greatly enhance the capacity and cyclic performance of the electrodes. When Si nanoparticles are well dispersed in and supported by a 3D network of graphene sheets, the Si/graphene composites exhibit high lithium ion storage capacity and cycling stability (>1,500 mAh/g after 200 cycles).⁵ In situ synthetic approaches based on the coordination

between precursors and functional groups on the surface of graphene can lead to a more intimate contact between nanoparticles and graphene sheets. Wang *et al.*⁶ applied this method to get a homogeneous distribution of Sn nanoparticles in graphene sheets. The anode showed enhanced capacity and reversibility compared to electrodes prepared from bare graphene or Sn nanoparticles separately. After 100 cycles, the Sn/graphene electrode retained a capacity of 508 mAh/g. For comparison, the capacity of a bare graphene electrode decayed to 255 mAh/g, and a bare Sn electrode failed after 10 cycles (Figure 2).

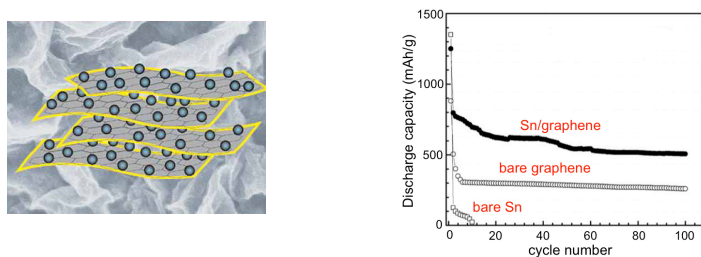


Figure 2. (Left) Schematic diagram of Sn/graphene composite. (Right) A comparison of cycling performance of anodes prepared from Sn/graphene composite, graphene and Sn.

Although graphene buffers the changes in nanoparticle volume well, nanoparticles are still prone to aggregation upon cycling. Confining individual nanoparticles within a single graphene shell can solve this problem. Through the coassembly of graphene and Co_3O_4 by electrostatic forces, Yang *et al.*⁸ have synthesized graphene-encapsulated Co_3O_4 nanoparticles. The effective encapsulation of electrochemically active metal oxide nanoparticles by graphene sheets leads to remarkable lithium storage performance. The high lithium storage capacity is attributed to the synergistic relationship between the nanoparticles and the graphene layers; nanoparticles keep the neighboring graphene sheets separated, while the graphene sheets confine the nanoparticles, which limits the volume expansion upon lithium insertion and prevents the aggregation of nanoparticles.

Nanoparticle/graphene composites have been demonstrated to be promising high-performance anode materials for LIBs. Much more effort, however, is still needed to understand the relationship between nanoparticles and graphene sheets in the electrochemical process. It is worthwhile to try other nanoparticles with different morphologies and prepare other architectures of nanoparticle/graphene composites to achieve higher lithium storage capacity and better cycling performance of the electrode.

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