Graphene-based flexible anode materials for lithium ion batteries

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Introduction

Graphene based flexible materials are highly demanded in lithium ion battery (LIB) research. When used as anode for LIBs, this type of assembly brings several evident advantages over traditional procedure for electrode fabrication. The binder (an insulator) and the current collector (usually copper foil) are not needed, improving the specific capacities of a "whole" LIB. Graphene papers (GP) are also mechanically strong and flexible and therefore, could be used in thin film battery fabrication.

However, the existing data have demonstrated that the specific capacities of GPs are much lower than those of graphite due to the barrier for Li diffusion resulting from close stacking of the graphene nanosheets (GNS) in the papers [1,2]. This impedes the practical applications of GPs in LIBs. As such, many approaches have been proposed to improve the Li storage capacities of graphene-based papers [3,4]. Whereas high capacities (over 1000 mAh g^{-1}) were achieved, these approaches inevitably diminish the mechanical strength of the papers. To date, it still remains a significant challenge to improve the charge capacities of GPs and simultaneously, preserve their mechanical strength and flexibility. This presentation reports our systematic research on fabrication of mechanically strong flexible graphene-based anode materials and understanding of their electrochemical properties in LIBs [5,6]. The flexible anodes include graphene-carbon nanotube (GN-CNT), graphene-MoS_2 (GN-MoS) and graphene-silicon nanowires (GN-SiNW).

Experimental

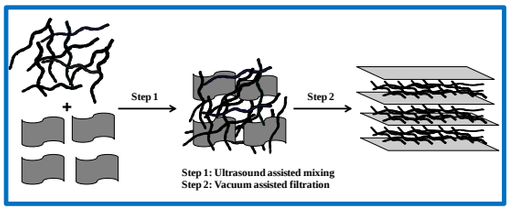
Graphene oxide was prepared by the modified Hummers method. Typically, graphite was oxidized with $KMnO_4$, $NaNO_3$, and H_2SO_4. As synthesized graphite oxide was dispersed in deionized water to give rise to a 0.5 $mg.ml^{-1}$ dispersion, and was then exfoliated by ultrasonication. The obtained dispersion was centrifuged to obtain a homogeneous graphene oxide dispersion. Commercial CNTs were dispersed with Triton X-100 as a surfactant in DI water to form a dispersion through ultrasonication. The obtained dispersion was purified by centrifuge to remove impurities and tangled CNTs. MoS_2 nanosheets were fabricated through exfoliation of commercial MoS_2 powder in N-methyl-pyrrolidinone (NMP) by ultrasonication. The suspension was centrifuged at 2000 rpm. The upper part 2/3 dispersion was collected for further use. Si Nanowires (SiNWs) were fabricated by chemical etching of Si wafer.

To fabricate the flexible graphene based papers, the GNS were mixed with a second nanosized component in water followed by suction filtration. The as-synthesized papers were mildly annealed at 900 °C before characterization and tests.

The samples were characterized using Raman, FE-SEM, TEM and HRTEM. Cyclic voltammetry tests were on CHI electrochemistry workstation over a potential range of 0.01 to 3.0 V (vs. Li/Li^+). Charge-discharge characteristics were tested galvanostatically between 0.01 and 3.0V (vs. Li/Li^+) at room temperature using an Arbin BT-2000 Battery Test System.

Results

The graphene papers (without nanocomponent) only offer maximum capacities of ~180 mAh g^{-1} due to the barrier for lithium ion diffusion in the papers. In the presence of the second nanocomponents, the capacities were improved evidently. The GN-CNT papers deliver maximum capacities of ~350 mAh g^{-1}; in contrast, the maximum capacities for the GN-MoS papers are only ~210 mAh g^{-1}, whereas the capacities of MoS_2 can be over 1000 mAh g^{-1}. The GN-SiNW papers exhibit the highest capacities among all the anode materials, i.e., ~600 and ~450 mAh g^{-1} for the first cycle and the 40th cycle, respectively.



Schematic 1 Fabricatin of graphene based flexible papers by suction filteration (with GN-CNT papers as an example).

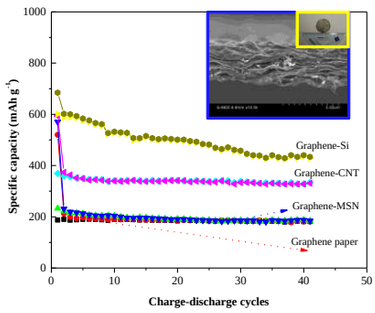


Figure 1 Electrochemical performances of various graphene based flexible papers.

Conclusion

Following these results, it is concluded that preventing restack of the graphene nanosheet is crucial to achieve high lithium storage capacity for graphene based flexible electrode, and very high capacities (~600 mAh g^{-1}) can be obtained when graphene is hybridized with a suitable 1D nanocomponent. The flexible graphene based materials have high potential to be used in LIBs, particularly, flexible thin film batteries.

References:

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