Evaluation of Carbon Nanotube-Encapsulated Silicon and Germanium Nanowires as Proposed Lithium-Ion Battery Anode Materials

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Lithium-ion rechargeable batteries are widely used for a portable energy storage device, typically in the consumer electronics and increasingly in the automobile industry as well. There is still a pressing need for new electrode materials with higher capacity and energy density, however. Germanium (Ge) and Silicon (Si) are very attractive anode materials to improve the performance of Li-ion batteries, because they may be attributed to remarkable theoretical capacities (Ge:1600 mAh/g, Si: 4200 mAh/g) [1,2]. These high capacities correspond to the maximum lithiations $Li_{22}Ge_5$ and $Li_{22}Si_5$, compared to that of graphite, used in the current technology, with a theoretical capacity of only 372 mAh/g, corresponding to the maximum lithiation LiC_6[3,4]. However, Ge and Si show huge volume expansions upon lithiation (up to 300%), which causes the pulverization of Si film-type or particle-type anode materials during alloying/dealloying cycles. Recently, group IV nanowires such as silicon (SiNW) and germanium (GeNW) have been utilized to reduce the volume expansions[5]. The use of these nanostructured anode materials do not completely solve the problem, because their low cyclability (limited to about 10 cycles) means that capacity fading of the anode still remains in a critical problem.

The low cyclability may stem from the aggregation encountered with nanosized materials during alloying /dealloying processes[6]. Consequently, the introduction of carbon nanotubes (CNTs) encapsulating GeNW or SiNW may address the low cyclability issue. DFT calculations with SnNW encapsulated by CNT have reported favorable results[7], so the outlook for the usage of Si and Ge is promising. It is planned to assess CNT-encapsulated SiNW and GeNW for Li-ion battery applications using energetic, structural, electronic and dynamic calculations, through DFT methodology. Band structures will be used to determine whether the heterostructured anode materials are semiconducting or metallic. Multiple chiralities and diameters of CNTs will be considered. The energetics of the CNT/NW nanostructured composites will be evaluated using the DFT calculation. The band structures and density of state were evaluated for each system to show the matrix effect of the CNT encapsulation on the conductivity of the NWs.

Reference

[1] C.K. Chan, X.F. Zhang, Y. Cui, Nanoletters, 2008, 8, 307-309.
[2] W. Wang, P.N. Kumata, ACS Nano, 4, 2233-2241.
[3] J.R. Dahn, Phys. Rev. B, 1991, 44, 9170.
[4] A. Satoh, N. Takami and T. Ohsaki, Solid State Ionics, 1995, 80, 291-298.
[5] C.K. Chan, H. Peng, G. Liu, K. Mcilwrath, W.F. Zhang, R.A. Huggins, Y. Cui, Nature nano, 3, 31-35.
[6] K.T. Lee, Y.S. Jung, S.M. Oh, J.Am.Chem.Soc. 2003, 125, 5652-5653.
[7] M.F. Ng, J. Zheng, P. Wu, J. Phys. Chem. C, 2010, 114, 8542-8545.