High Throughput Synthesis of Silicon Nanotubes: A High Capacity and Stable Anode System

Rigved Epur[1] and Prashant N. Kumta[1,2,3]

[1]Mechanical Engineering and Materials Science Department, Swanson School of Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, 15261

[2]Department of Bioengineering, Swanson School of Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

[3]Department of Chemical and Petroleum Engineering, Swanson School of Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Bulk crystalline silicon undergoes colossal volume changes (>300%) during lithium alloying and de-alloying leading to pulverization of the active material. Such mechanical failure results in loss of electrical contact with the current collector causing rapid decrease in capacity and consequent failure of the battery. Several approaches have been developed to address this problem which involve the use of nano-sized silicon particles [1], active-inactive matrices [2], amorphous silicon composites [3] and strain engineered 1-D dimensional nanostructures [4-6]. Silicon nanotubes have attracted a lot of interest as a stable anode for lithium ion batteries. The hollow nanotube structure of silicon accommodates the large mechanical strain generated during the charge-discharge processes making it less favorable to decrepitation and pulverization. However, the current methods used to synthesize the hollow silicon nanotubes involve chemical infiltration and electro-spinning methods which require expensive precursors that suffer from low yield [7, 8].

In this work, a simple and large scale synthesis of hollow silicon nanotubes using inexpensive precursors and processing methods has been achieved. First, scalable quantities of inorganic nanowires ***(IoNw)*** were synthesized using hydrothermal synthesis involving an inorganic precursor. Amorphous silicon (Si) was later deposited on these nanowires in a CVD reactor by thermal cracking of silane (SiH_4) gas to form ***IoNw/Si*** nanocomposite. These core-shell structures were then dispersed in acid to leach off the core nanowire template to form hollow 1-dimensional structures of silicon.

Fig-1 (a) & (b) show the SEM images of the hollow silicon nanotubes synthesized by the above described method. The diameters of the nanotubes range from 0.6 µm to 1 µm and the lengths of the tubes vary from 5 µm to 100 µm. A sharp peak at 480 cm^{-1} was observed in the Raman spectra (Fig-1c) which is characteristic of amorphous silicon. These hollow nanostructures were mixed with binder and conductive additives to form slurry based electrodes and tested in a half cell configuration against lithium foil. These hollow silicon nanostructures exhibit a high first discharge capacity of ~2420 mAh/g at a current density of 300 mA/g between the voltage range 0.01-1 V vs. Li^+/Li (Fig-1d). A relatively high first cycle irreversible loss of 24% was observed due to possible SEI formation owing to the large surface area of the silicon nanotubes. At high current rates (2A/g), the silicon nanotubes exhibit capacities in the range 1300-1700 mAh/g with a capacity retention of 88% at the end of 50 cycles corresponding to a capacity fade of 0.23% loss per cycle. These nanostructures exhibiting high specific capacity and cyclability are developed using a cost effective and scalable approach enabling them to be a promising silicon based anode system for the next generation of lithium-ion batteries.

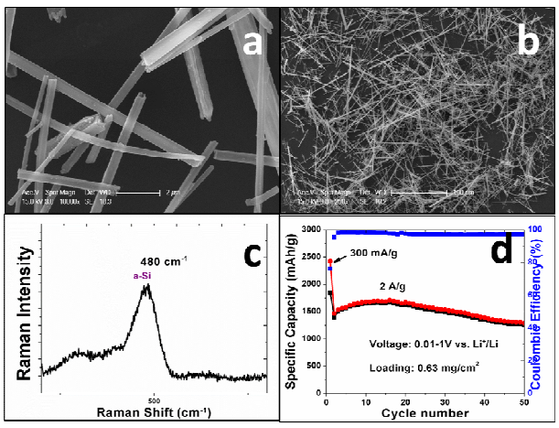

Fig-1: (a) & (b) SEM images (c) Raman spectra and (d) electrochemical characteristics of silicon nanotubes.

Acknowledgements:

The authors gratefully acknowledge financial support of the DOE-BATT (DE-AC02-05CHl1231) and NSF (CBET-0933141) programs. The authors also acknowledge the Edward R. Weidlein Chair Professorship funds for support of this research.

References

[1] X.H. Liu, L. Zhong, S. Huang, S.X. Mao, T. Zhu, J.Y. Huang, Acs Nano 6 (2012) 1522-1531.

[2] I. Kim, P.N. Kumta, G.E. Blomgren, Electrochemical and Solid State Letters 3 (2000) 493-496.

[3] M.K. Datta, J. Maranchi, S.J. Chung, R. Epur, K. Kadakia, P. Jampani, P.N. Kumta, Electrochimica Acta 56 (2011) 4717-4723.

[4] L.-F. Cui, R. Ruffo, C.K. Chan, H. Peng, Y. Cui, Nano Letters 9 (2008) 491-495.

[5] W. Wang, R. Epur, P.N. Kumta, Electrochemistry Communications 13 (2011) 429-432.

[6] W. Wang, P.N. Kumta, ACS Nano 4 (2010) 2233-2241.

[7] M.H. Park, M.G. Kim, J. Joo, K. Kim, J. Kim, S. Ahn, Y. Cui, J. Cho, Nano Letters 9 (2009) 3844-3847.

[8] H. Wu, G. Chan, J.W. Choi, I. Ryu, Y. Yao, M.T. McDowell, S.W. Lee, A. Jackson, Y. Yang, L.B. Hu, Y. Cui, Nature Nanotechnology 7 (2012) 309-314.