

Enhanced Performance of Sn/Graphene Composite Anodes by Surface Treatment

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Sn/graphene (Sn/G) nanocomposites have shown their promise as high energy density Li ion battery anodes for hybrid electric vehicles (HEVs) [1]. However, due to its high surface area, graphene is prone to catalytic solid electrolyte interphase (SEI) formation, thereby resulting in a large initial capacity loss [2]. Furthermore, the formation of unstable SEIs on the graphene surface could lead to further decomposition/reformation of SEIs that degrade Coulombic efficiency with continued cycling. To improve stable SEI formation on carbonaceous anodes, various approaches have been taken including mild chemical oxidation, physical surface coating, and thermal treatments [3]. Here we report two new strategies: chemical grafting of aryl species and electrophoretic deposition of graphene oxide (GO) to generate artificial SEIs on Sn/G composite anodes. Both methods enhance the cycling performance of Li half cells.

Sn/G composites were fabricated by Sn particle deposition on aminophenyl functionalized graphene nanopowder via reduction of SnCl_2 with NaBH_4 [4]. Sulfophenyl treated Sn/G (ST-Sn/G) and aminophenyl treated Sn/G (AT-Sn/G) were prepared by means of grafting sulfophenyl ($-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$) and aminophenyl ($-\text{C}_6\text{H}_4-\text{NH}_2$) groups to Sn/G electrodes with diazonium chemistry. Graphene oxide treated electrode (GOT-Sn/G) was fabricated by electrophoretic deposition of GO on Sn/G.

Preliminary battery cycling results shown in figure 1 indicate enhanced performance of Sn/G anodes after surface treatment. As-fabricated Sn/G gave a capacity of 441mAh/g at the 30th cycle, while the GOT-Sn/G and AT-Sn/G delivered capacities of 633mAh/g and 577mAh/g. A significant increase in capacity was observed for ST-Sn/G. At the 30th cycle, the capacity of ST-Sn/G was almost twice that of as-fabricated Sn/G (853mAh/g vs. 441mAh/g). Electrochemical impedance spectroscopy (EIS) and 1st cycle differential capacity profiles (dQ/dV) were used to analyze the mechanism behind the improved capacity. As shown in figure 2, dQ/dV profiles of ST-Sn/G and AT-Sn/G reveal that the grafted species were reduced in-situ at $\sim 1.5\text{V}$ vs Li/Li^+ during the 1st cycle discharge, before conventional SEI formation at $\sim 0.8\text{V}$. Hence, a new SEI may be governing the surface charge transfer characteristic of the treated electrodes. EIS reveals the stability of the new SEI through a consistent and low charge transfer resistance ($R_{ct} \sim 50\Omega$) over 30 cycles, as illustrated in figure 3. In the case of GOT-Sn/G, we speculate that GO itself acts as a passivating layer that decreases R_{ct} and improves SEI stability.

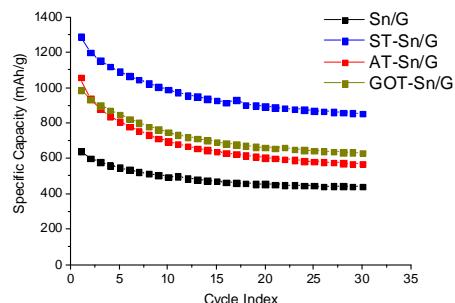


Figure 1: Cycling profiles of as-fabricated Sn/G anode and surface treated Sn/G anodes at 26mA/g.

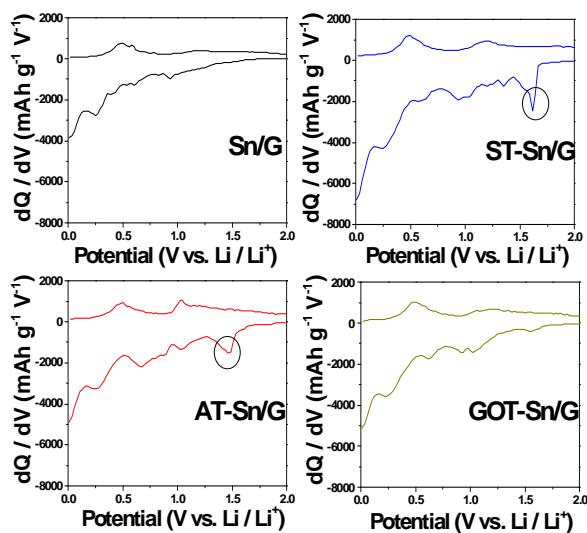


Figure 2: First cycle differential capacity plots for four Sn/G anodes. The circled region of ST-Sn/G and AT-Sn/G arises due to the formation of a new SEI.

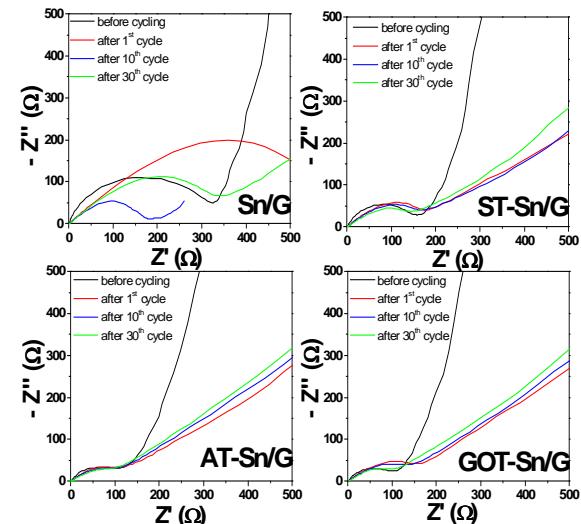


Figure 3: Nyquist plots of delithiated electrodes conducted from 1MHz to 0.02Hz showing a consistent impedance profile for surface treated anodes.

References:

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