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Gaining cycling stability of Si- and Ge-based negative Li-ion high areal capacity electrodes by using carbon nanowall scaffolds†

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We report an approach to stabilize the electrochemical performance of silicon- and germanium-based thin film anodes by using carbon nanowall matrices. Silicon and germanium layers were deposited onto vertically oriented carbon nanowall scaffolds and this procedure has been repeated multiple times producing multilayered structures with increased silicon and germanium areal mass loading. It was demonstrated that the areal specific capacity of multilayered anodes achieves up to 2 mA h cm^{-2} without sacrificing cycling stability. Based on post-mortem SEM analysis of the electrodes we speculate that the reason for the improved cycling stability of multilayered highly loaded silicon/graphene composites is the ability to relax the mechanical stresses in the films.

Introduction

Both silicon and germanium form lithium-rich alloys with the $Li_{22}X_5$ (X = Si and Ge) composition. Such alloys can be produced upon electrochemical lithium insertion in Si and Ge electrodes making them quite attractive as high capacity anode materials for lithium-ion batteries. In contrast to commercially used graphite (theoretical gravimetric capacity is 372 mA h g^{-1}), capacity exceeds 4000 for Si and ≈1600 mA h g^{-1} for Ge. Germanium, although showing lower specific capacity, has electronic conductivity and the Li diffusion coefficient almost two orders of magnitude higher than those of Si.[1] This allows Ge to be considered as an anode material suitable for high power batteries, although the cost of germanium is rather high.

As was demonstrated, Si[2–4] and Ge[5,6] alloying during the first Li insertion cycle typically proceeds with solid-state amorphization of the host material. This is accompanied by huge volume expansion reaching 300–400% (ref. 4, 7 and 8), unavoidably resulting in active particle fracture, pulverization and rapid capacity fade. As a solution to this problem, researchers suggested application of diverse nanostructured materials including nanowires and nanoparticles, which can withstand large material expansion/contraction during alloying/de-alloying thus enabling the mechanical stability of the electrodes during cycling.[5,6,9–12]

Here, we report an approach to prepare high areal capacity Si- and Ge-based electrodes by all-vacuum plasma deposition technology. Carbon nanowalls (CNWs) prepared by plasma-enhanced CVD (PECVD) as scaffolds were employed to fabricate multilayer composite Si- and Ge-based electrodes. We grow CNW layers, and then deposit Si or Ge layers and further repeat such a cycle multiple times producing a "multilayered" structure with increased active material mass loading. Finally, we show that by this way capacities up to 2 mA h cm^{-2} can be easily achieved without sacrificing cycling stability. Based on post-mortem SEM analysis of the electrodes we speculate that the improved cycling stability of "multilayered" highly loaded silicon/germanium/CNWs is enabled by effective mechanical stress relaxation inside these films. As both magnetron sputtering and PECVD are scalable industrial processes we believe that the proposed approach can be useful for producing advanced negative electrodes for lithium-ion batteries.

Experimental

The CNW layers were grown on nickel foil which is cut into discs of 1.5 cm diameter. All substrates were preliminarily ultrasonicated in a diamond powder suspension for 5 min to assist the carbon film nucleation. Further the substrates were washed in distilled water and dried. The CNW films were grown in the plasma of DC glow discharge in a mixture of hydrogen and methane. Details of the growth conditions are described in our previous work.[13]

After CNW growth substrates were transferred to another facility for deposition of silicon or germanium by means of

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