Lithium-Ion Battery Anodes

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Abstract

Artificial graphite as a commercial negative electrode (anode) material for lithium-ion batteries (LIBs) has reached its theoretical energy capacity. Electronic devices, power tools, and electric vehicles require electrode materials with higher energy and power densities. Comparing with graphite, several materials are promising to 2 to 11 times higher capacity. However, the volume change accompanied by lithiation (lithium goes into the host material) and delithiation (lithium leaves the host material) is as large as 300%. Thus, the durability and short cycling life are major problems for new electrode materials because of cracking as a result of large volume changes.

Two high capacity anode materials for LIBs, Sn and Si, are studied in this work. Thin-film electrodes show self-organized cracking patterns after cycling. The characteristics of cracking patterns are associated with film thickness, as well as the mechanical properties of electrode materials and substrates. Scaling behavior and fractal dimensions of cracking patterns are studied to understand the failure mechanisms of the electrode materials. This study provides guidelines for designing new electrodes with enhanced durability.

In addition, this work reveals an interesting phenomenon of lithiation-induced whisker formation in thin-film electrode materials. The whisker formation is believed to be the driving force for the observed whisker formation. Attention should therefore be paid to whisker formation in electrodes consisting of low melting point elements because metallic whiskers may penetrate through the battery separator, and short-circuit the electrochemical cell.

We modify the model so that the layer expands with lithiation, as well as contracts with delithiation. A constant strain condition is used in the modified model instead of constant dimensional change. Crack formation in thin-film electrodes, which may be a safety concern for LIBs.

The growing demands for electronic devices, portable tools, and hybrid- and all-electric vehicles require batteries with higher capacity and longer durability. Graphite as an anode material has already reached its theoretical capacity. New anode materials with higher capacity than the commercially available graphite are being intensively explored.

The most promising materials for the anodes of LIBs include Si, Sn, Ge, and their alloys. However, these materials usually show poor cycle life compared to graphite. The main cause for the poor cycling behavior is fracture which is the result of large volume change (280% for Si and 360% for Sn) and the large diffusion-induced stress.

In this work, we study the crack pattern formation in thin-film electrodes as a result of lithiation and delithiation cycles. We also present a modified spring-block model to simulate the crack pattern formation in thin film lithium-ion battery electrodes. Furthermore, whisker formation is observed on Sn thin-film electrodes, which may be a safety concern for LIBs.

Background

Analysis of Crack Patterns

The simulation results matches well with experimental data. For thick film, the crack has a “growth” behavior. For thin films, crack pattern appears as “diffusive”. A scaling behavior between the mean fractured area and film thickness is observed: $A \propto t^n$. The shape of cracks varies with film thickness:
- For different thicknesses, $d_2$ represents simple Euclidean shape; $d_2 = 2$ represents complicated fractal shape.
- There is a critical thickness $t_c$. For films with thickness $t < t_c$, the strain energy is not large enough to initiate any crack. $t_c$ is found to be between 100 and 200 nm. Once primary cracks form, the crack pattern does not change with further cycling. Surface roughness of film changes and peel off is observed.

Sn-Whisker Formation during Lithiation

- There is no internal stress in the Sn thin films (no intermetallic, and samples were annealed after deposition).
- Single-crystalline Sn-whisker formation is observed after lithiation. The driving force is lithium diffusion-induced stress.
- Single-crystalline Sn-whisker could penetrate through the thin (~15 μm) porous separator (polymer), and short-circuit the electrochemical cell.

Conclusions

1. A computer program is successfully used to simulate crack pattern formation in a-Si films as a result of electrochemical lithiation and delithiation. A scaling behavior between the mean fractured area $A$ and film thickness $t$ is observed: $A \propto t^n$. $n$ is found to be 2.16. For each specific condition, crack pattern shows self-similarity. Cracking behavior in thick films is “growth”, and cracks in thin films is “diffusive”.

2. There is a critical thickness below which cracking does not occur. The critical thickness is found to be between 100 and 200 nm. Electrodes of LIBs could be designed according to this criterion to prevent cracking.

3. A first observation of Sn whisker growth after lithiation of Sn thin film electrodes is made. The high compressive stress during lithiation is likely the driving force for the whisker growth. Since these whiskers may short-circuit the cells, whisker formation during electrochemical reactions could be a safety concern for LiIBs using low melting point elements as electrodes.

References: