

Dynamics of Al anode degradation in thin-film solid-state batteries

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Thin film solid state Li-ion batteries employing inorganic, non-flammable electrolytes (TFLIBs) are inherently safe, have negligible self-discharge rates and have demonstrated extremely long cycle life. Using TFLIBs to provide on-chip energy storage would enable concepts such as distributed power wherein components of an integrated circuit (e.g. memory elements) remain powered even upon disconnection from external power, providing one approach for hardware-level information security. Other emerging applications include autonomous MEMS, distributed sensor networks, and medical implants. Metallic Li is currently used as the anode in most commercial TFLIB. However, concerns over semiconductor device contamination and the relatively low melting point (180 °C) make metallic Li undesirable for on-chip integrated microbatteries. A potential alternative to elemental Li anodes is Al, which is highly conductive, compatible with semiconductor processing, inexpensive, and has high Li capacity of ~990 mAh/g. Furthermore, Al alloys with lithium producing the intermetallic compound, LiAl, resulting in a single plateau voltage profile. However, like other Li forming alloy compounds, Al suffers large volumetric expansion/contraction during lithiation/de-lithiation, which can lead to fracture and pulverization of the anode material.

Here, we use *in situ* real-time scanning electron microscopy (SEM) under ultra-high vacuum conditions combined with electrochemical cycling to quantify the dynamic degradation of an Al anode upon charging/discharging of all solid-state thin-film batteries with of a LiCoO₂ cathode and N-doped LiPO₄ (LiPON) electrolyte. Unlike earlier studies, we simultaneously record the electrochemical potential and the Al anode morphology during charging and discharging. Surprisingly, we find that the lithiation/delithiation process is restricted to the surface of the Al anode where highly porous LiAl (*Fd3m* phase) clusters nucleate and grow during charging, and shrink during discharging. The loss in capacity is directly related to the fraction of the Al surface covered with the highly porous LiAl clusters. Using *ex situ* transmission electron microscopy (TEM) we find that the LiAl clusters form only on the surface of the anode, suggesting that the bulk of the Al film remains essentially strain-free during lithiation/delithiation. The rapid loss in capacity, even at relatively low lithiation level (<10% of theoretical capacity) is in sharp contrast to similarly prepared TFLIBs with Si thin film anodes which exhibit excellent cycle life, as shown in Fig. 2. In our presentation we will discuss the underlying differences in Al and Si anodes which explain the distinct behavior.

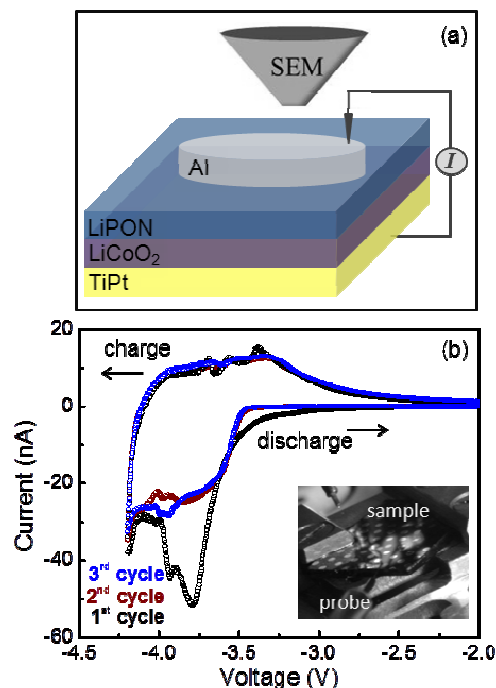


Figure 1: (a) Schematic illustration of *in situ* real-time measurements of electrochemical lithiation/delithiation cycling and morphology evolution of Al-Li alloys on solid state thin film batteries. Layers are represented out of scale for clarity. (b) Cyclic voltammogram from 2.0 V to 4.2 V versus Li/Li⁺ at a 0.15 mV.s⁻¹ scan rate for a representative battery. The first three cycles are shown. Inset: micrograph of sample and electrical probe inside UHV chamber.

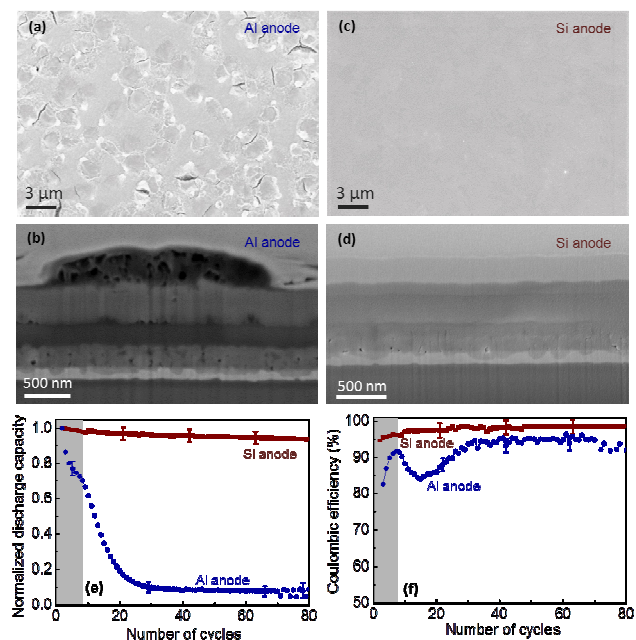


Fig. 2 a.) Plan view and 52° tilted SEM images of (a,b) Al anode and (c,d) Si anode batteries after 10 charging cycles. (e) Discharge capacity at 10 nA for Al anode and 30 nA for Si anode, and (f) Coulombic efficiency as a function of number of cycles.