

Surface/Interface Effects In All-Solid-State Li-Ion Batteries

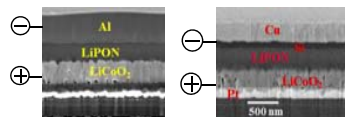
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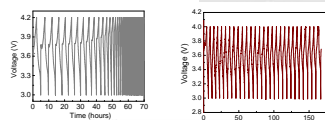
INTRODUCTION

- Thin film solid state Li-ion batteries are needed for autonomous microsystems, sensors, memory back up power.
- Li metal anode melts below solder reflow temperature, complicating on chip integration.
- Al and Si alloy with Li at potentials close to metallic Li, are inexpensive, have higher melting points, and have high capacities of ~990 mAh/g and ~3500 mAh/g, respectively.
- Solid state batteries with Al anodes degrade after a few cycles, while those with Si retain >90 % of their capacity after 100 cycles.
- We combine *in situ* cycling with surface conductivity and composition analysis to demonstrate how surface reactions on the Al negative electrode lead to loss of Li diffusion paths and loss of surface electronic conductivity, which together contribute to the rapid degradation of solid state Li-ion batteries with thin film Al anodes.

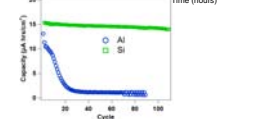
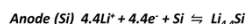
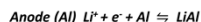
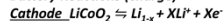
Batteries fabricated using PVD on Si/SiO₂ substrates



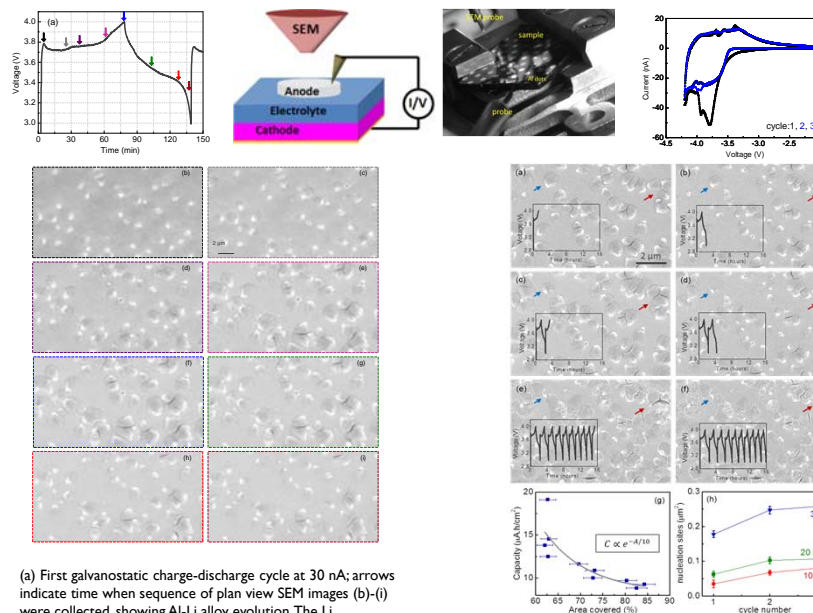
Galvanostatic charge/discharge cycles at 15 μ A/cm²



Battery Reactions (charge)



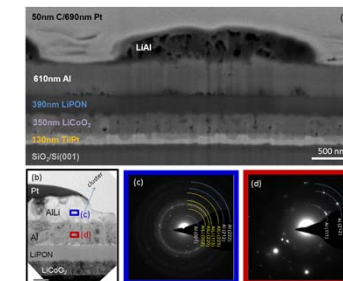
IN SITU SCANNING ELECTRON MICROSCOPY



(a) First galvanostatic charge-discharge cycle at 30 nA; arrows indicate time when sequence of plan view SEM images (b)-(i) were collected, showing Al-Li alloy evolution. The Li percentage shown in the top y-axis of (a) refers to the atomic concentration of Li that diffuses during the charging and discharging cycles, respectively.

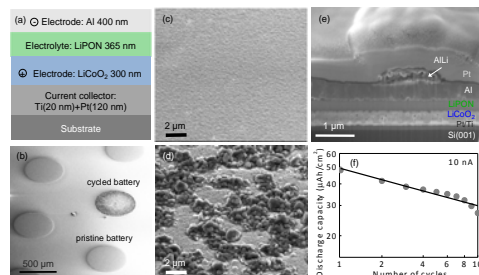
(a)-(f) Sequence of in situ SEM images showing Al-Li alloy morphology evolution at the Al anode surface using 30 nA. (g) Discharge capacity as a function of the percentage of the area covered by the cluster. (h) Nucleation sites as a function of cycle number for similar batteries charged at different current values.

TEM Analysis: LiAl only found in the mound



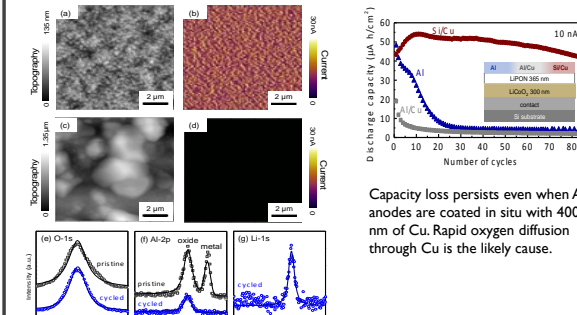
(a) Cross section SEM image of a battery after ten cycling sweeps showing an AlLi mound formed at the Al anode's surface. (b) TEM cross-section bright field. Scale bar is 250 nm. (c)-(d) SAED patterns from (a) collected at two different locations: (c) a mound on top of an Al layer containing the AlLi Fd3m phase, and (d) underneath it, showing pure Al.

RAPID CAPACITY LOSS, MORPHOLOGY CHANGE IN AL ANODES



(a) Schematic of all-solid-state batteries with Al negative electrodes. (b) SEM of micron-scale devices showing morphology changes upon cycling. SEM of Al surface for (c) pristine and (d) cycled devices shown in (b). (e) Cross-section SEM image of Al electrode after 10 charging cycles, tilt = 45°. The Pt layer is added uniquely to protect the surface of the battery during the ion milling process and is not an active layer of the device. (f) Discharge capacity as a function of the number of cycles for 10 nA.

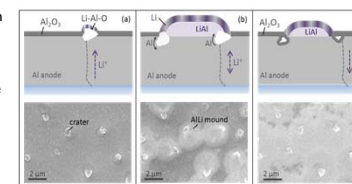
OXIDATION OF LITHIATED Al SURFACE AND LOSS OF CONDUCTIVITY



Topography and conductive atomic force microscopy scans for (a, b) pristine and (c, d) cycled Al-based batteries, respectively, showing complete loss in electronic conductivity upon cycling. XPS of Al negative electrode for pristine and cycled batteries showing (e) oxygen peaks, (f) Al metal and oxide peaks, and (g) Li peak for the cycled device.

MODEL FOR RAPID CAPACITY LOSS

Model (a) Li diffuses to the surface of the Al thin film to react with Al₂O₃ surface oxide. Expansion of the lithiated Al₂O₃ creates a void with an unoxidized Al surface. (b) The surface of voids in the Al film provides a path for Al and Li to diffuse to a growing AlLi mound. As long as the voids remain unreacted this process is reversible. (c) Oxidation of the surface of the voids removes the diffusion paths for Al that is required for the facile decay of the AlLi mound. Loss of electrical contact further contributes to capacity loss



References

1. M. S. Leite¹, D. Ruzmetov, Z. Li, L. A. Bendersky, N. C. Bartelt, A. A. Talin³, "New insights from in-situ electron microscopy into capacity loss mechanisms in Li-ion batteries with Al anodes", *J. Mat. Chem. A* 2, 20552, (2014)
2. C. Gong, D. Ruzmetov, A. Pearce, D. Ma, J. N. Munday, G. W. Rubloff, A. A. Talin³, and M. S. Leite¹, "Surface/Interface Effects on High-Performance Thin-Film All-Solid-State Li-Ion Batteries", *ACS App. Mat. & Interfaces* 7, 26007 (2015) (*corresponding authors).

Why is Si more stable than Al?

- Li is insoluble in Si and must react in the bulk. In Al the sparingly soluble Li diffuses to the surface to react with Al₂O₃ and decrease strain energy.
- Si surface diffusion at room temperature is negligible, and thus the formation of surface mounds and the associated trapped Li does not occur.