Advances in Battery Engineering, Interface Design, and Characterization Mini-Symposium
Room 319 - Session BT2+AS+CA+TF-ThM

Advanced Battery Electrodes

Moderators: Prof. Alexander Kozen, University of Vermont, **Dr. Tanguy Terlier**, Rice University, **Dr. Andrew Westover**, Oak Ridge National Laboratory

11:00am **BT2+AS+CA+TF-ThM-13 Understanding the Electrically-Limited Reaction Kinetics and Dynamics for Conversion Electrode Iron Fluoride**, ***Chuan-Fu Lin,*** Catholic University of America **INVITED**

To maintain efficient reaction kinetics in standard electrodes, fast and stable ionic and electronic conductive networks are required for long-term reversibility, and this poses the major challenges for conversion-type electrode materials. The phase separation reaction, CM + Li^+ + e^- -> M (reduced metal) + LiX (Li compounds), induced by the lithiation process deteriorates the structural integrity, which certainly destroys the original ionic and electronic pathways and reconstructs new ones. However, it is still unclear whether the transports of conversion electrode are benefited or hindered from the reconstruction of transport pathways due to phase separation, yet the dynamic evolution of electrical conductivity in these systems remains overlooked.

This work aims to investigate the electrically-limited reaction of conversion electrodes upon phase separation and recombination by studying the structural, electrical, and electrochemical properties of amorphous and crystalline iron (III) fluoride (FeF_x) thin films synthesized via sputtering deposition. Using a binder-free lateral device architecture and probing measurement, we dynamically mapped resistivity evolution during electrochemical cycling. While pristine crystalline films exhibit lower initial resistivity than amorphous films, deep lithiation triggers a dramatic drop in resistivity by over five orders of magnitude in both structural variants. Despite the massive volume fraction of the insulating LiF byproduct (1 : 4.17 for Fe : LiF ratio), the resistivity reduced to ~0.35 Ω·m, demonstrating a common conduction pathway formed by a metallic Fe network within the nanocomposite. Correlating this resistivity evolution with X-ray Photoelectron Spectroscopy (XPS) spectra reveals the electrically-controlled reaction dynamics of the thin-film conversion electrodes. Conversely, delithiation results in a resistivity increase of two orders of magnitude, driven by a rate-dependent electrochemical "trapping effect." Fast charging causes isolated Fe domains electronically stranded within the LiF matrix and driving irreversible capacity loss. These results elucidate the coupling between chemical quantifications, reaction dynamics, and electrical properties, providing understanding of the influence of the electrical conductivity for high-energy-density conversion cathodes.

11:30am **BT2+AS+CA+TF-ThM-15 Correlating Electrical Property Evolution and Reversibility in Sputtered ZnO Thin-Film Conversion Electrodes**, ***Sukanya Goswami,*** *Chuan-Fu Lin,* The Catholic University of America

During conversion reaction in Lithium-ion batteries, electrical properties shift as reaction kinetics vary with phase separation, state of charge, and evolving conductivity. Understanding how these dynamic electrical transitions govern reaction control is essential for optimizing conversion electrodes. This study probes the evolution of ZnO conversion electrodes during cycling, examining the electron transport, reversibility and capacity retention. Because the literature on ZnO remains limited, it provides a simple benchmark for testing broader conversion-mechanism concepts and for comparing phase separation and recombination process across conversion materials in LiBs. **Sputter-deposited ZnO thin films** were cycled in a lithium-ion half-cell configuration and their electrical transport properties tracked ex-situ using **two-probe resistivity measurements** after each set of cycles.

The resistivity data reveal a clear and progressive deterioration in electronic transport over cycling. Starting from values on the order of **10^{-4} Ω.m** in the early cycles, resistivity increases by several orders of magnitude, reaching **1-7 Ω.m** by **cycle 30**. This monotonic rise reflects a gradual breakdown of the conductive percolation network as the conversion reaction proceeds. Persistent differences in resistivity during early cycling reveal an asymmetry between lithiation and delithiation, likely caused by sluggish reconversion kinetics of the phase-separated products. These electrical changes correlate directly with coulombic efficiency. When the electrode maintains sufficient conductivity, capacity retention is upto **95%**. Conversely, as resistivity rises sharply with progressive cycling, coulombic efficiency becomes irregular and drops. This correlation implicates degradation of electronic transport, driven by delamination caused by the volume expansion during phase transformation, as the primary mechanism governing capacity fades.

To understand the structural and chemical origins of these changes, cycled electrodes were characterized by **XRD, XPS, and SEM**. XRD tracked phase separation and recombination between ZnO, metallic Zn and Li_2O. XPS provided insight into surface chemical states and irreversible interfacial species, while SEM captured morphological degradation including delamination. Together, these results establish a direct link between electronic conductivity, conversion reaction reversibility and coulombic efficiency, offering a framework for mitigating kinetic limitations in ZnO based thin film cathodes.

11:45am **BT2+AS+CA+TF-ThM-16 Molecular Mapping Investigations of Prelithiation Alloy Formation via Thermal Evaporation on Silicon Based Electrodes**, ***Gabriel Parker,*** *Amanda Musgrove, Gabriel Veith, Ivan Matyushov, Xiao-Ying Yu,* Oak Ridge National Laboratory, USA

Abstract: Silicon based composites have become increasingly popular as potential anodes for lithium-ion batteries due to their large storage capacity, relative abundance, and low cost. However, these anodes often see reduced initial columbic efficiency (ICE) due to disruptive volume expansion up to 300% and continuous unstable solid electrolyte interphase (SEI) layer formation. Prelithiation, the process of adding excess reservoir of Li to the electrode to compensate for irreversible SEI formation losses during their sample preparation, has proven to solve the issue of immediate capacity loss. Thermal evaporation is a prelithiation technique with limited studies on its effectiveness. In this study, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used to investigate the benefits of prelithiation via thermal evaporation. ToF-SIMS provides chemical mapping and spatial information in 2D and 3D visualizing the deposition of lithium, identifying Li_xSi_y alloy and $Li_xSi_yO_z$ silicate formation, and the distribution of lithium passivation into the electrodes. Passivation under different atmospheric conditions, such as inert Argon (Ar) and Ar/ carbon dioxide (CO_2), highlights the impact of the environment on the passivation effectiveness and formation of Li_xSi_y alloy and $Li_xSi_yO_z$ silicate. The ToF-SIMS molecular imaging and depth profiling results indicate that prelithiation via thermal evaporation effectively distributes lithium throughout the depth profile thickness of several hundred nanometers. It induces a greater degree of $Li_xSi_yO_z$ silicate formation over Li_xSi_y alloy. The results provided by the ToF-SIMS are corroborated by electrochemical measurement of the electrodes under inert Ar and Ar/CO_2 environments indicating that the Ar/CO_2 electrode retained a higher specific capacity over multiple cycles. Our ToF-SIMS characterization results show the effectiveness of thermal evaporation in producing a more stable electrode and an electrode with an effective lithium reserve that can preserve its capacity.

Keywords: Solid-state batteries, solid-electrolyte interface, ToF-SIMS, prelithiation, molecular imaging.

12:00pm **BT2+AS+CA+TF-ThM-17 Engineering Conformality of Lithium–Terephthalate Thin Films via Precursor Selection**, ***Anish Philip,*** *Joakim Jestilä, Milad Madadi,* Aalto University, Finland*; Jussi Kinnunen,* Chipmetrics Ltd, Finland*; Antti Karttunen, Maarit Karppinen,* Aalto University, Finland

Lithium-terephthalate (Li-TP) is recognized as a highly promising anode material for lithium-ion batteries.[1] The advantages of atomic/molecular layer deposition (ALD/MLD) technique have enabled the realization of Li-TP thin films in a highly controllable manner needed for its use in thin-film microbattery configuration.[2] However not much attention has been paid to understand the importance of selecting an appropriate lithium precursor for controlling the thin film properties and conformality, even though Li-TP materials are highly desirable from the battery application point of view. Given their potential application in 3D thin-film microbatteries, understanding both conformality and thin-film coverage (penetration depth) are also crucial. In this research, we investigated the impact of different lithium precursors on the Li-TP thin film properties, conformality and penetration depth (PD). The lithium precursors evaluated were: lithium tert-butoxide (LiO^tBu), lithium bis(trimethylsilyl)amide (Li-HMDS) and lithium 2,2,6,6-tetramethyl-3,5-heptanedionate (Li-THD); for the first two precursors the ALD/MLD process was developed/optimized as they had not been previously employed for the Li-TP thin film growth. For conformality measurements, we utilized lateral high-aspect-ratio (LHAR) PillarHall[3] structures and a novel imaging ellipsometry technique that enables film thickness determination even at Ångström level. To support the experimental work, a detailed computational survey of the precursors was conducted. Through DFT optimizations combined with highly accurate

DLPNO-CCSD(T) energy calculations the most prevalent oligomeric forms under typical ALD conditions were determined; the effective diameter (d_{eff}) and mean free path (MFP, λ) of the precursor's oligomeric form were found to play a major role in determining the conformality characteristics of the resultant Li-TP thin films (Figure 1). Among the three precursors investigated, Li-HMDS was found to result in Li-TP thin films with superior conformality characteristics. The current approach of using theoretical calculations to predict film conformality based on precursor molecular structure can significantly reduce the amount of experimental work required and streamline the screening process for precursors aimed at enhancing conformal coating.

References

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