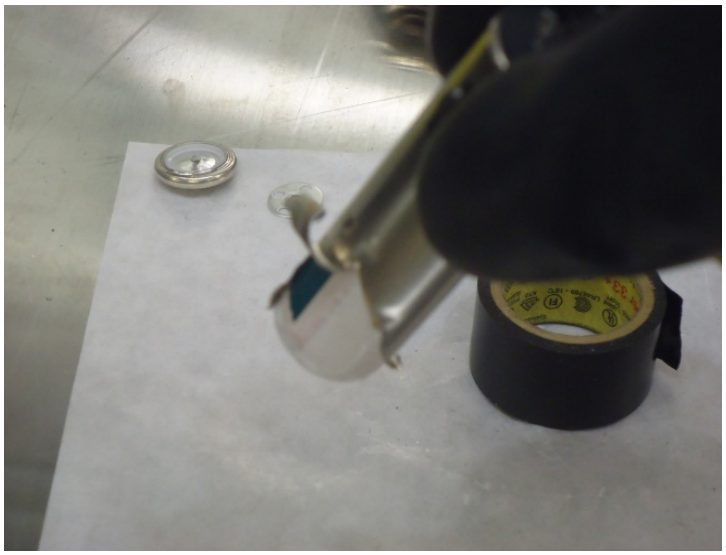
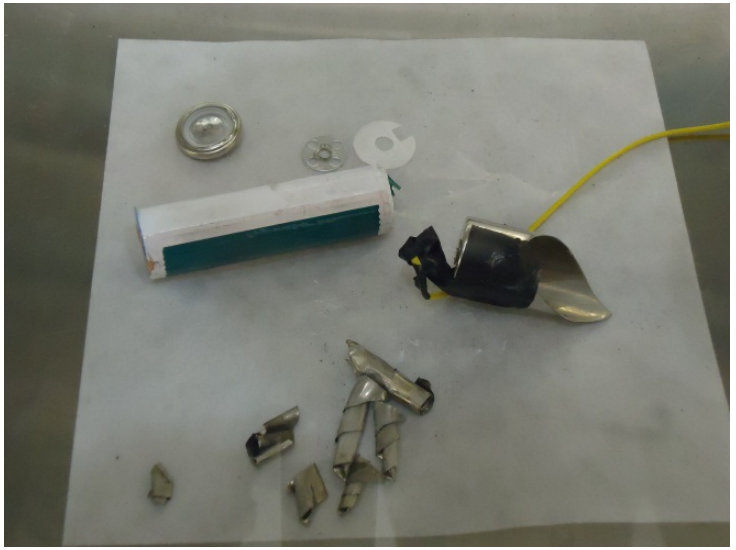
Post-Test Analysis of Lithium-Ion Battery Materials at Argonne National Laboratory





J. Bareño, N. Dietz Rago, I. Bloom

DOE Annual Merit Review

Washington, DC, June 18, 2014

Project ID: ES166

Post-test Analysis of Lithium-Ion Battery Materials at Argonne National Laboratory

Overview

Timeline

- Facility Planning: 2010
- Facility Commissioned: 2011
- End: Open – this is an ongoing activity to provide information which is complementary to that obtained during battery testing

Budget

- FY14: $ 700k
- FY13: $ 300k
- FY12: $ 350k
- Status: Ongoing

Objectives

- To provide DOE and its contractors with an independent assessment of state-of-the-art battery technology
- To help elucidate causes of battery performance decline
- To develop analysis procedures, which could be used as part of a standard or accepted practices

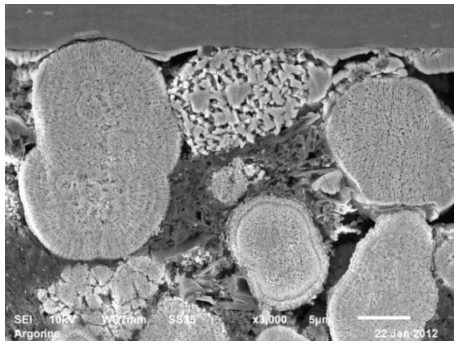
Collaborations

- CAMP (Argonne)
- JCI
- Maxwell
- ARL
- JPL
- ABR
- U. Hawaii
- Penn State
- CIC Energigune (Spain)
- U. Dalhousie (Canada)

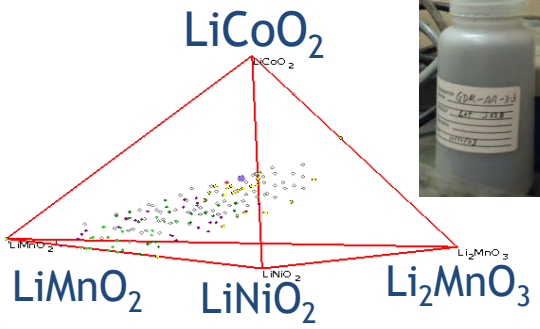
Post-Test Facility at Argonne -- Relevance

- Battery performance and life testing is an on-going program at Argonne. Here, batteries from USABC and DOE projects are objectively evaluated according to a given set of protocols
- Testing provides a lot of information about how battery performance changes with time under a given set of conditions
- Post-test diagnostics of aged batteries can provide additional information regarding the cause of performance degradation, which, previously, could be only inferred
- Here, the results from physical, spectroscopic, metallographic, electrochemical tests will be used to aid in the further improvement of a given technology
- The experience and techniques developed in DOE's applied battery R&D program will be used in a standardized fashion, similar to the performance test protocols. This will make comparisons of failure modes within a given technology and, perhaps, across technologies easier
- Facility is available to help DOE's ABR, BATT and USABC Programs and to help industrial battery developers better understand life-limiting mechanisms specific to their technology

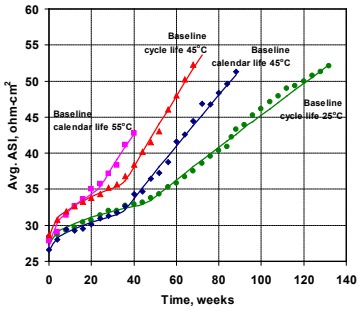
Post-Test Facility at Argonne -- Relevance



Materials Development



Prototyping and Standardized Testing



Post-Test Analysis

- Post-test analysis of aged batteries provides materials-level insight into the root causes and mechanisms of performance degradation
- Facility is available to support DOE's ABR, BATT and USABC Programs and to help industrial battery developers better understand life-limiting mechanisms specific to their technology

Post-Test Facility at Argonne Supports US Industry and Research Communities

Argonne National Laboratory is a long-time research and development collaborator with Johnson Controls. We work together with their expert staff and cutting-edge equipment to assess Lithium-ion prototype cells. Argonne National Lab consistently provides Johnson Controls with excellent customer service and expert analysis, and we highly value our relationship.

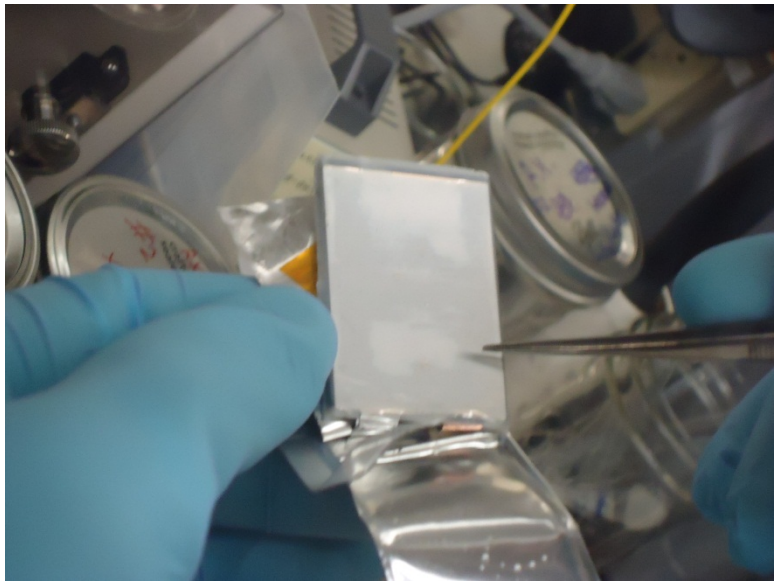
-- Yongkyu Son

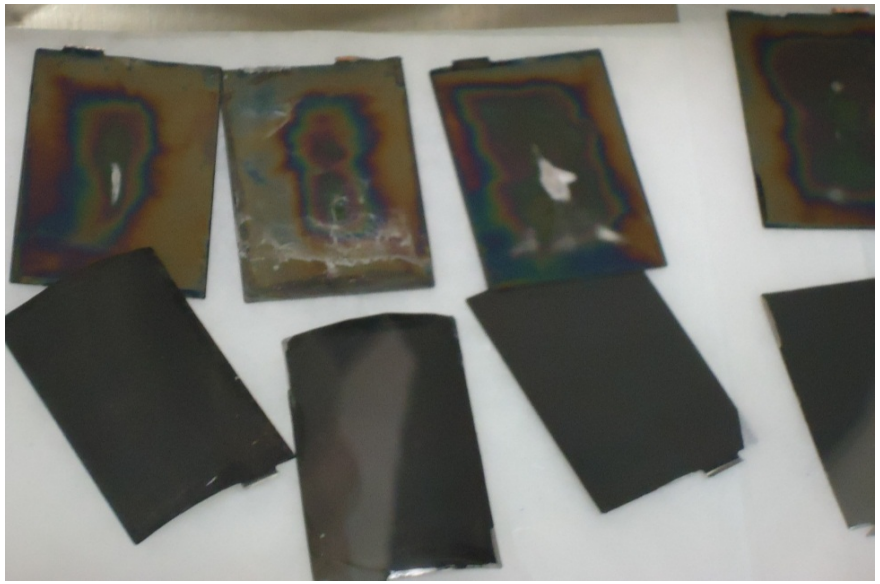
Principle Investigator and Scientist

Johnson Controls Power Solutions

Technical Progress - Case Study
Post-test characterization of Build 9 cells from Argonne CAMP facility

- The objective of the work is to develop standard electrochemical couples, and characterize their electrochemical and physicochemical properties.
- These materials and data are made available to BATT and ABR projects, as part of the CAMP Electrode Library, to test variants (e.g. new electrode materials, electrolytes, additives) and compare electrochemical and physicochemical properties to an established baseline.

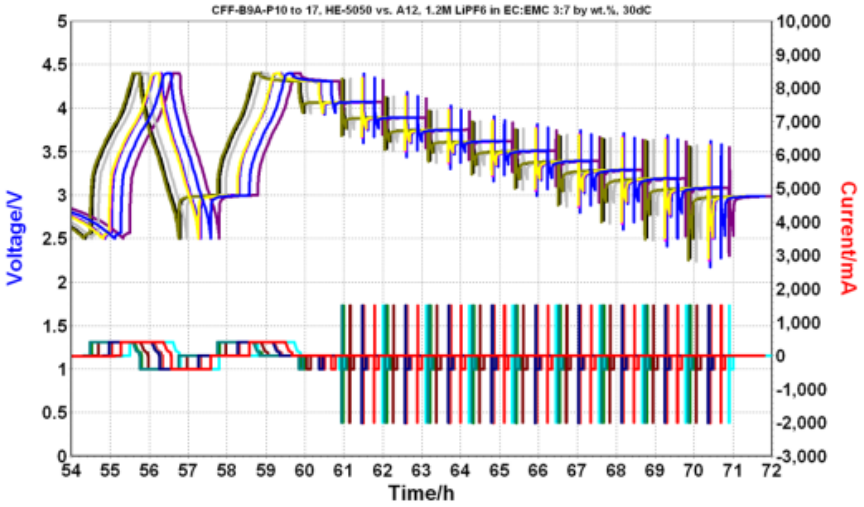




CAMP Build 9A: Technical Data

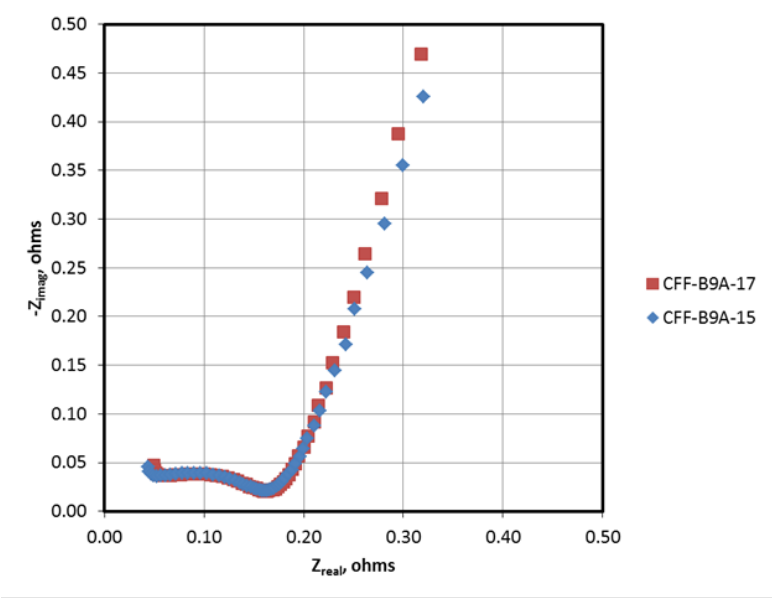
- **Anode Formulation (Dry Composition)**
  - 91.8 wt% Conoco Phillips: CGP-A12 Graphite
  - 2 wt% Timcal C45 Carbon Black
  - 6 wt% Kureha KF-9300 PVDF Binder
  - 0.17 wt% Oxalic Acid
- **Anode Electrode Properties**
  - Copper Foil Thickness: 10 microns
  - Total Electrode Thickness: ~169 microns (DS)
  - Anode Coating Thickness: ~159 microns (DS)
  - Anode Coating: 11.4 mg/cm² (SS)
    (Total Material wt; No Foil)
  - Capacity: 3.47-3.62 mAh/cm²
  - Target Porosity: 33.6%
  - Coating Density: 1.44 g/cm^3
- **Cathode Formulation (Dry Composition)**
  - 92 wt% Toda HE5050: $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$
  - 4 wt% Timcal C45 Carbon Black
  - 4 wt% Solvay 5130 PVDF Binder
- **Cathode Electrode Properties**
  - Aluminum Foil Thickness: 20 microns
  - Total Electrode Thickness: ~129 microns (DS)
  - Cathode Coating Thickness: ~109 microns (DS)
  - Cathode Coating: 13.4 mg/cm² (SS)
    (Total Material wt; No Foil)
  - Capacity: 2.58-3.06 mAh/cm²
  - Target Porosity: 36.4%
  - Coating Density: 2.45 g/cm^3
- **n:p Ratio: 1.04-1.18**

All Cells Went Through:
1: Formation
2: Rate Study
3: RPT
4: Life Cycle (C/2)
Tested at:
30°C and 55°C

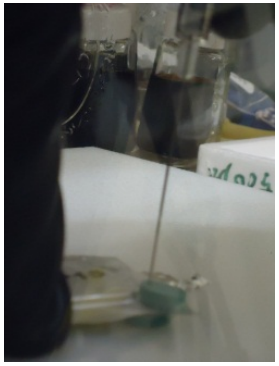


xx3450 Pouch Cell
13 Total Layers:
6 DS Anodes
5 DS Cathodes
2 SS Cathodes
Electrolyte:
1.2 M $LiPF_6$ in EC:EMC (3:7 wt%)

Initial characterization

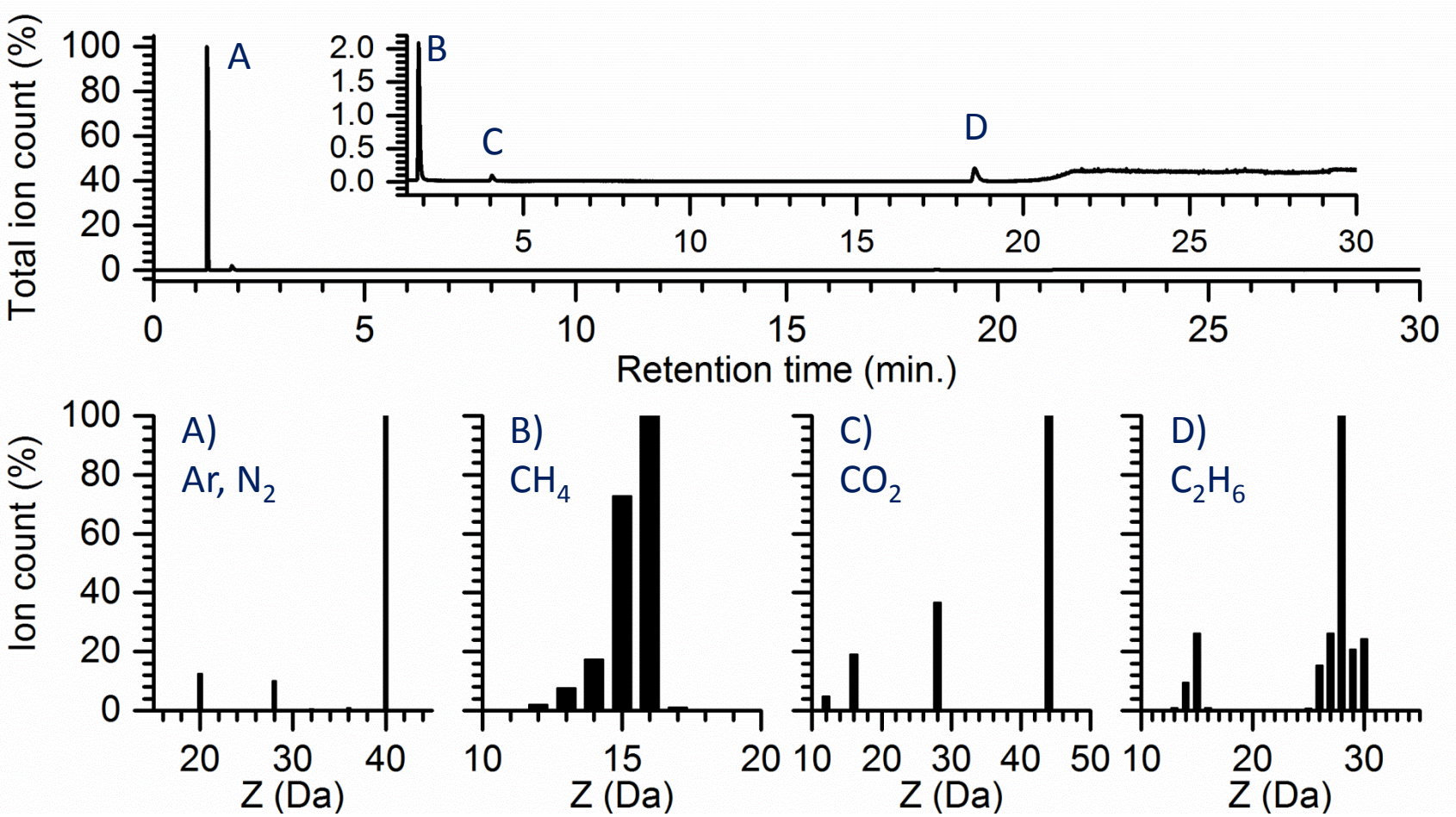


- Cells visually inspected upon receipt. No signs of leaks or damage
- E.I.S. reveals no noticeable differences between cells
- Headspace gasses evolved during cycling are sampled in glove box and transferred to GCMS for analysis using capped gas-tight syringe



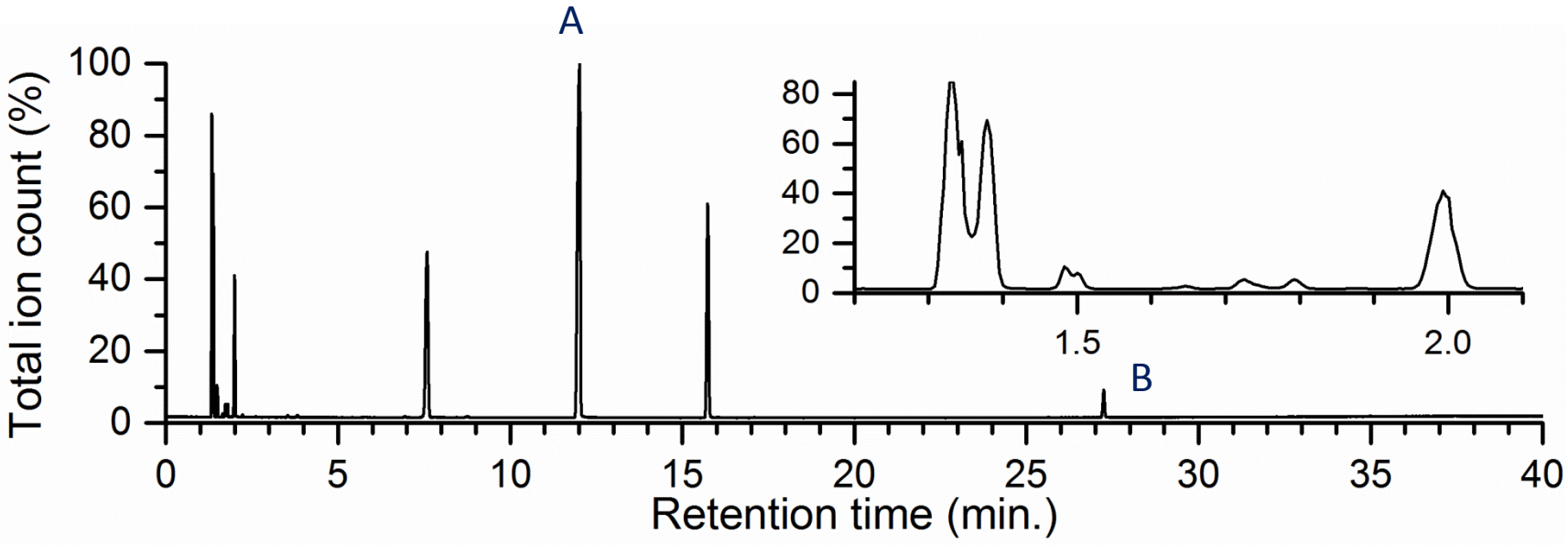
Gas Analysis: electrolyte degradation

- MS identification of peaks in chromatogram
- Big Ar peak is a sampling artifact
- Diffusion column separates CH_4 , C_2H_6 , and CO_2 -> oxygen evolution from cathode



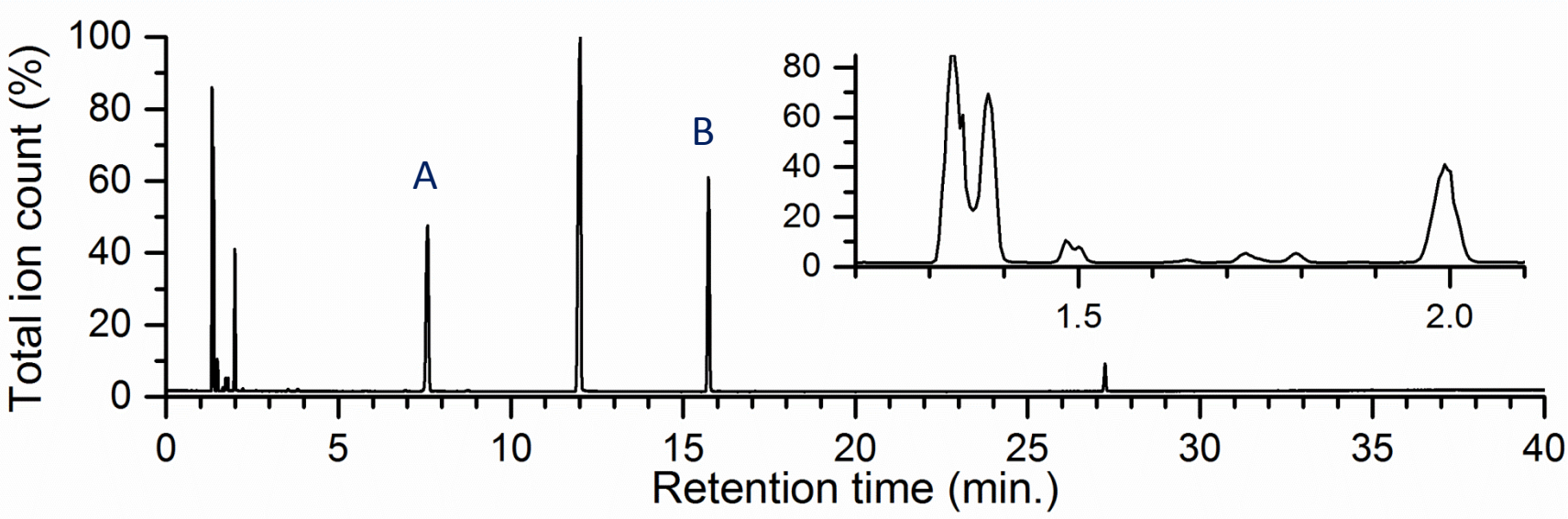
Gas Analysis: electrolyte degradation

- Polar column reveals
  - Electrolyte solvents: A) EMC, B) EC



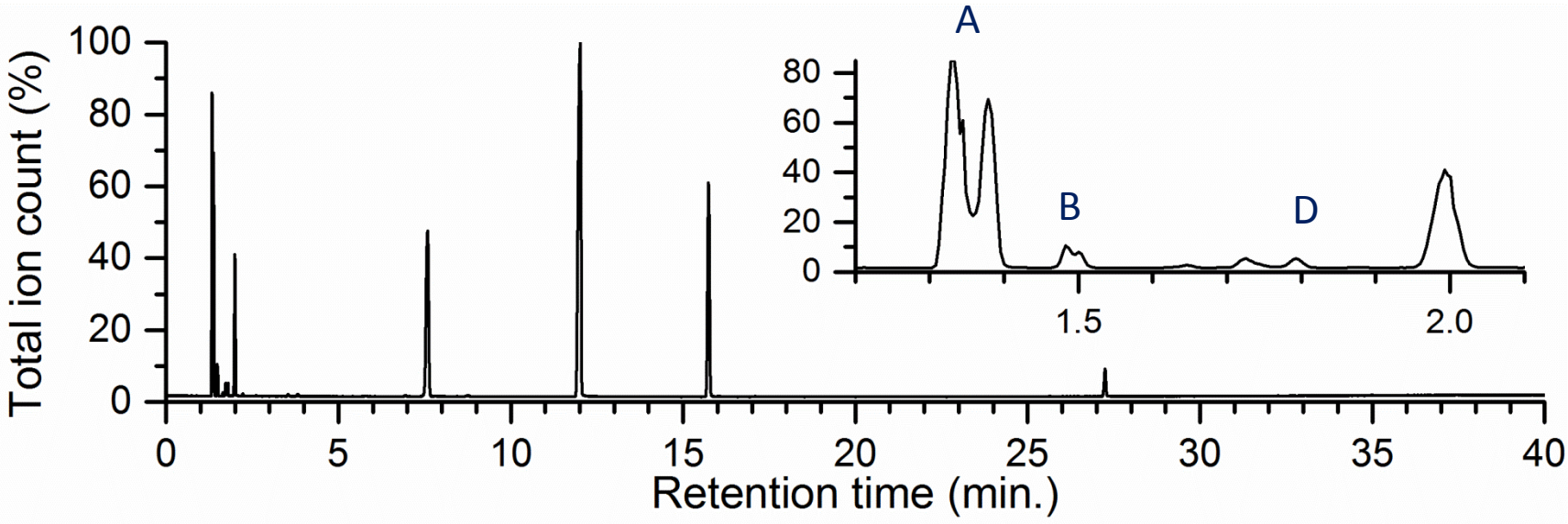
Gas Analysis: electrolyte degradation

- Polar column reveals
  - Electrolyte solvents
  - Transesterification products: A) DMC, B) DEC

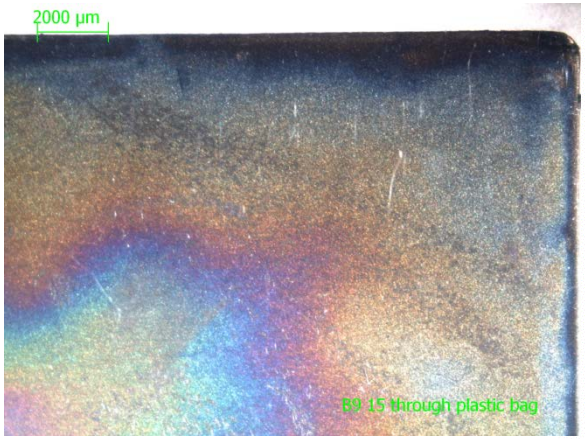


Gas Analysis: electrolyte degradation

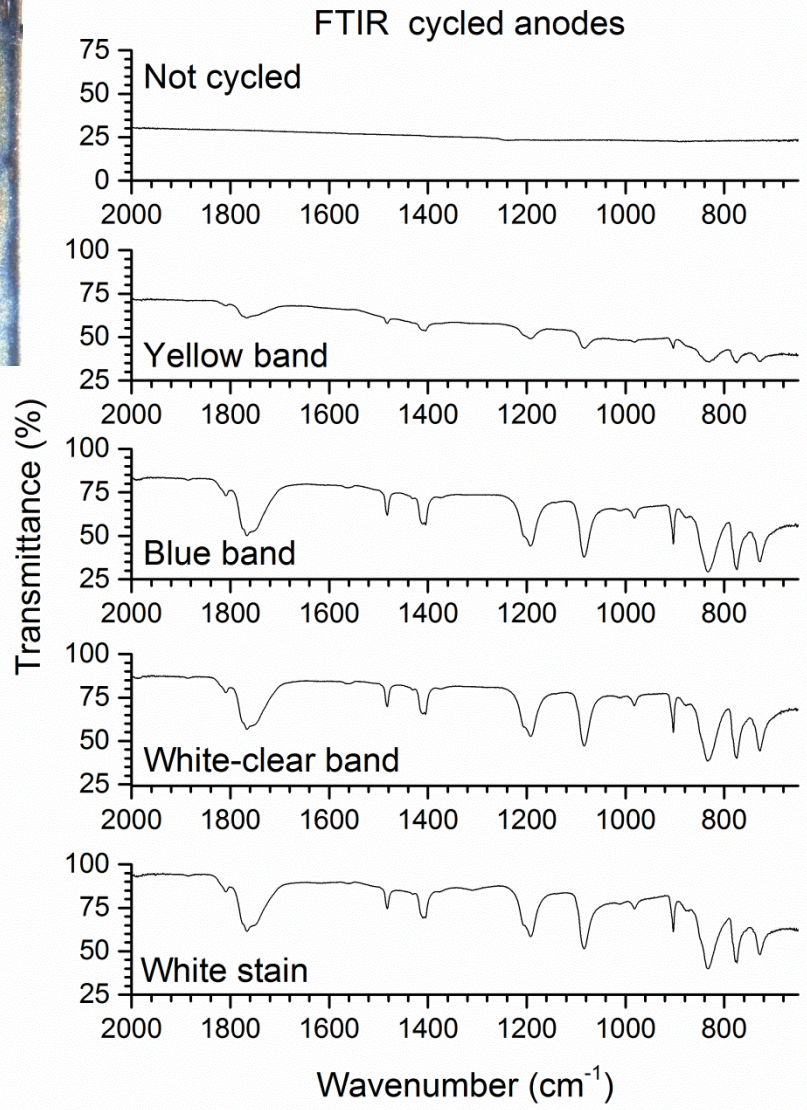
- Polar column reveals
  - Electrolyte solvents
  - Transesterification products
  - Short alkanes and fluoroalkanes: A) CH_4 + C_2H_6 , B) C_3H_8 + C_2H_5F , D) C_4H_{10}



Cell disassembly and FTIR: anode surface films

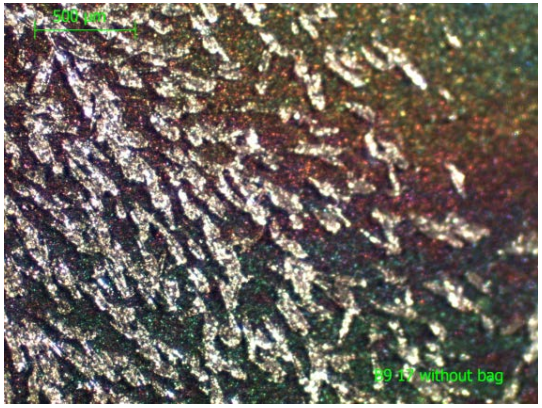


- Anodes present color bands reminiscent of thin-film interference patterns; e.g., oil films on water and surface oxide films
- FTIR shows that the intensity of some absorption bands depends on color of region, consistent with discoloration being caused by varying thickness of deposited film resulting from electrolyte decomposition
- This was not evident on the cathodes

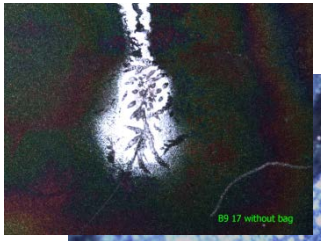


Optical Microscopy: precipitates on anode surface

White precipitates with silver metallic particles are seen on the surface. These particles are likely metallic lithium in a white salt deposit.



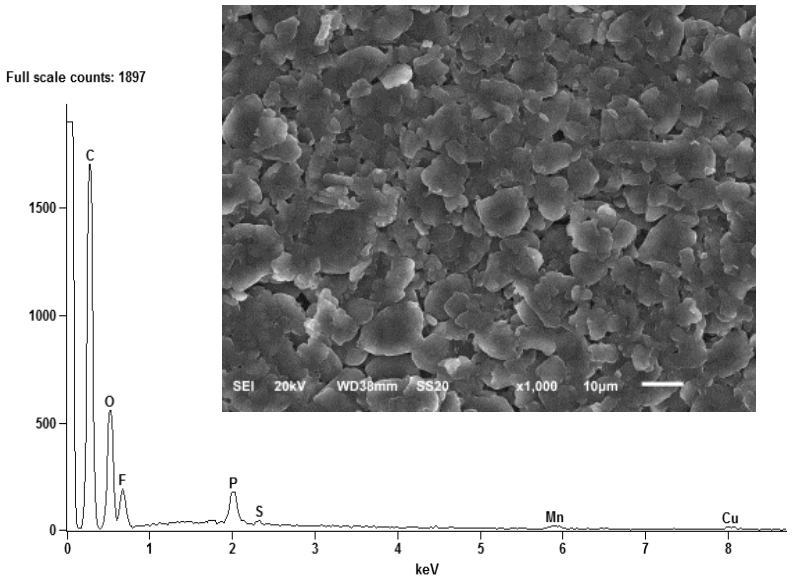
Small shiny dendrites are seen along the surface. These became wet upon air exposure and could be metallic lithium or deliquescent salts.



A white surface precipitate with a large-scale shiny gray dendritic structure is likely composed of metallic lithium. Upon exposure to air the dendritic structure started to foam.

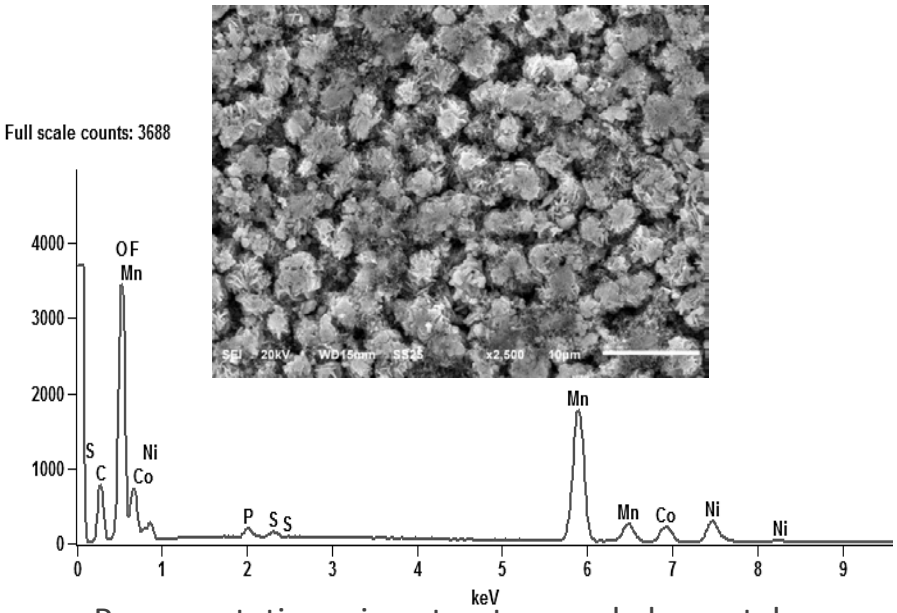
SEM/EDS: TM migration to anode

Anode



Representative microstructure and elemental composition of CAMP B9A anode.

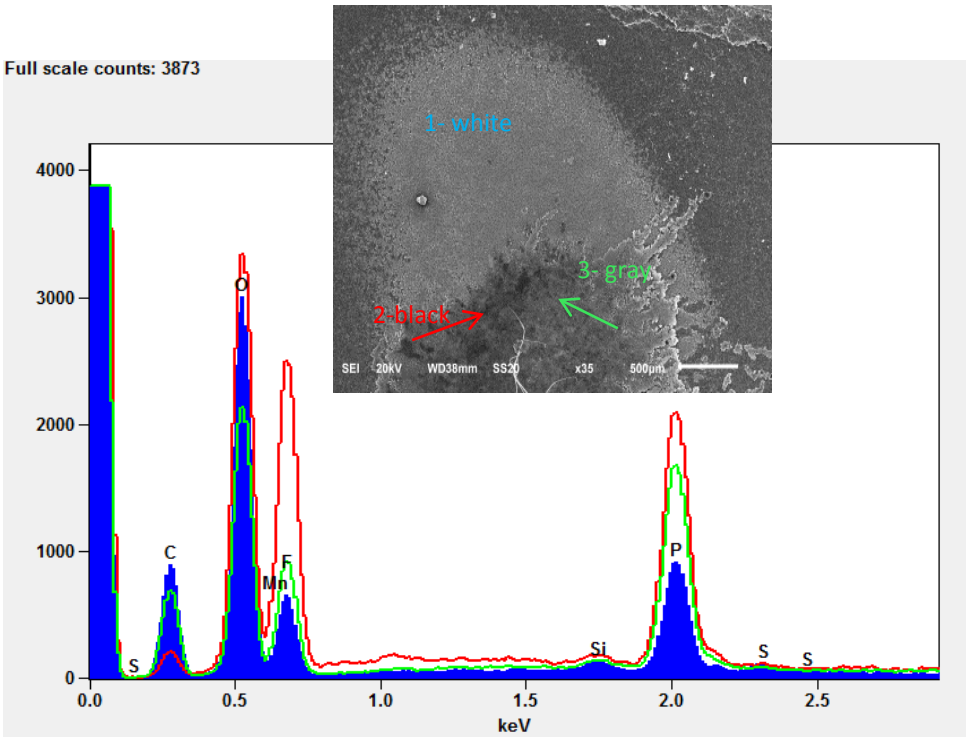
Cathode



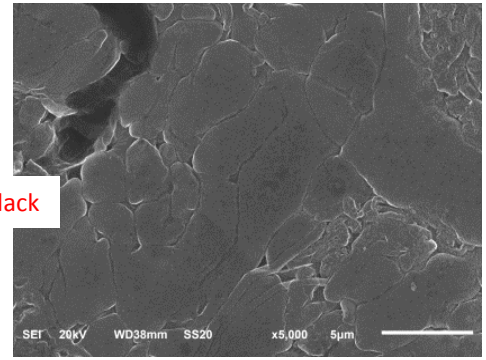
Representative microstructure and elemental composition of CAMP B9A cathode.

- Cu, Mn and Ni presence in the anode, due to migration from cathode and current collector

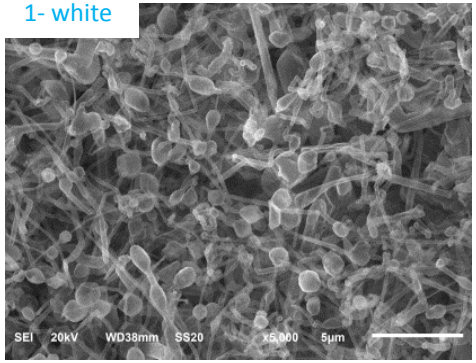
SEM/EDS: Inhomogeneous anode surfaces



2 - black



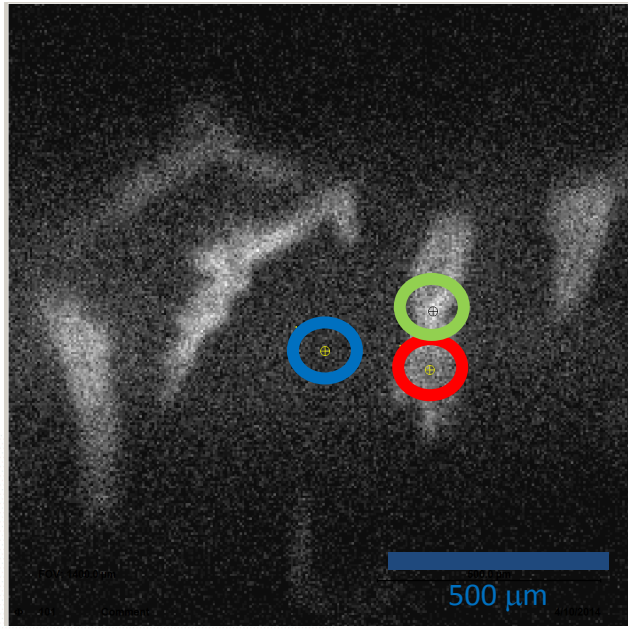
1- white

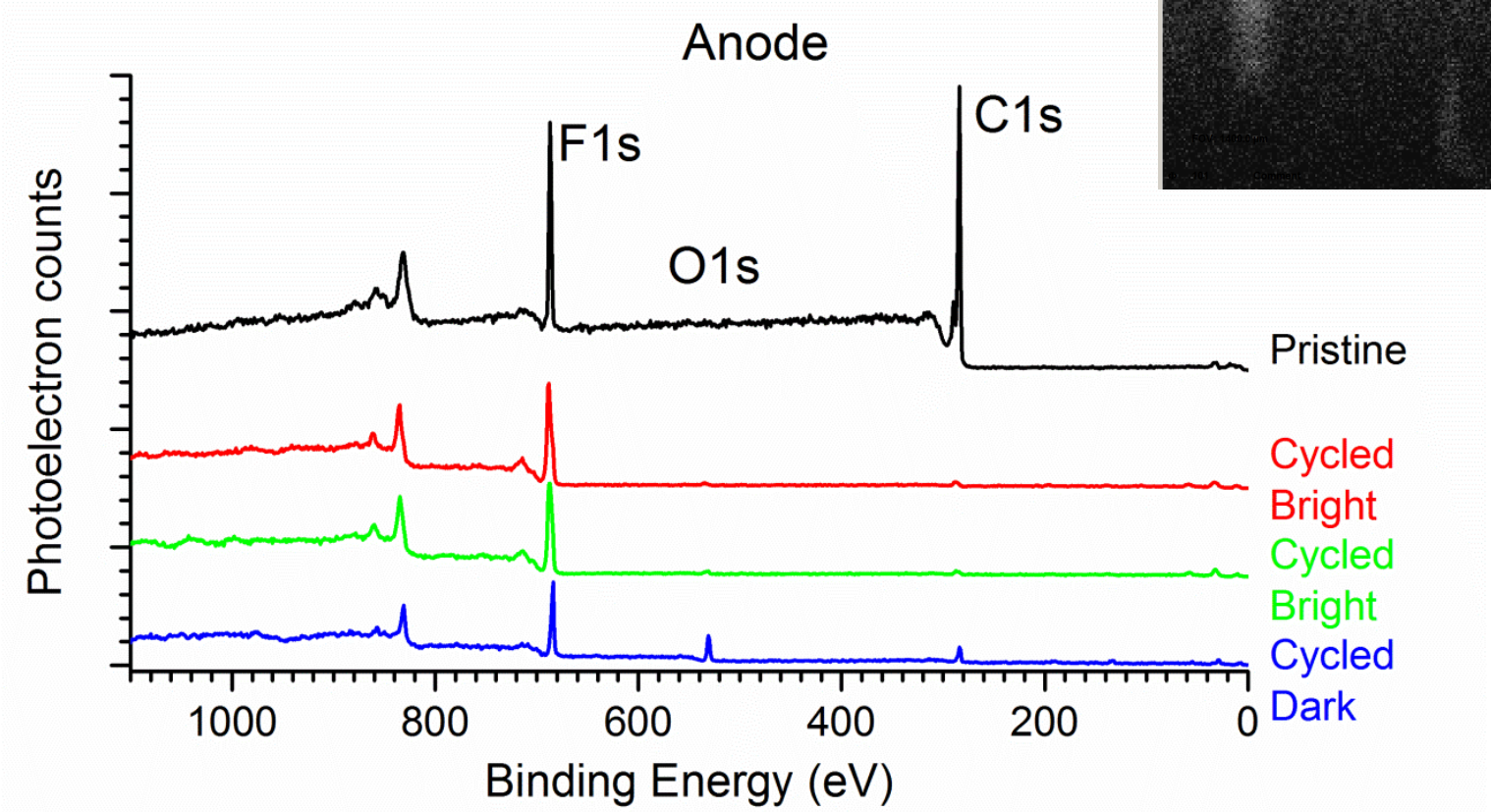


- Three different areas: White, gray and black
- Black areas are relatively flat, reminiscent of pristine anode topography. High F, P content relative to C and high variability
- White areas present fiber-like structure

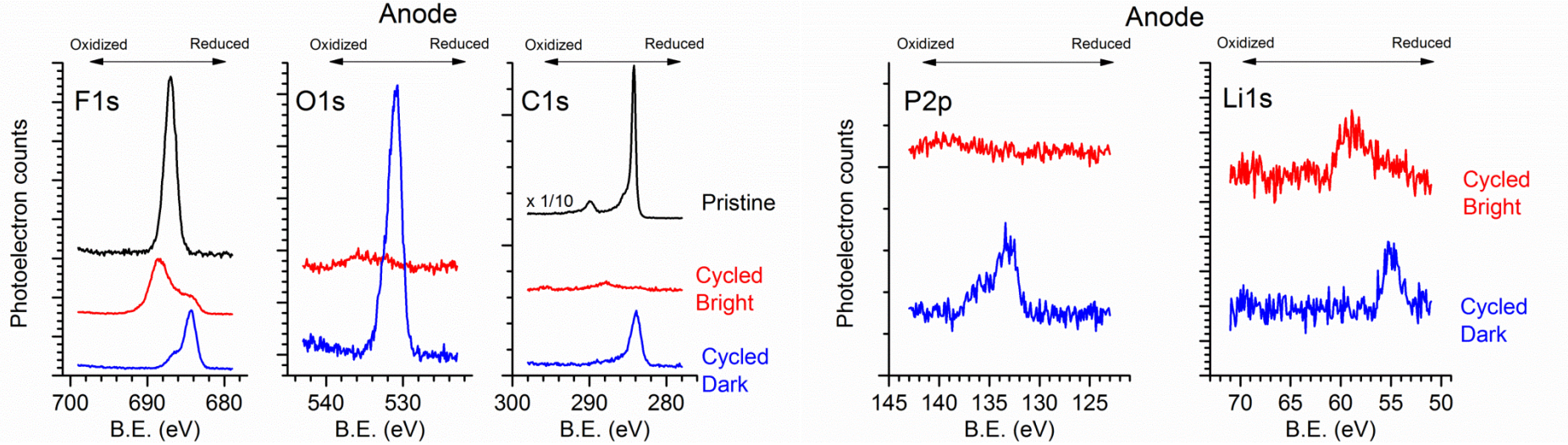
XPS: inhomogeneous anode surface

- SXI imaging in XPS: bright precipitates on cycled anode
- Bright regions have higher F content relative to O and C





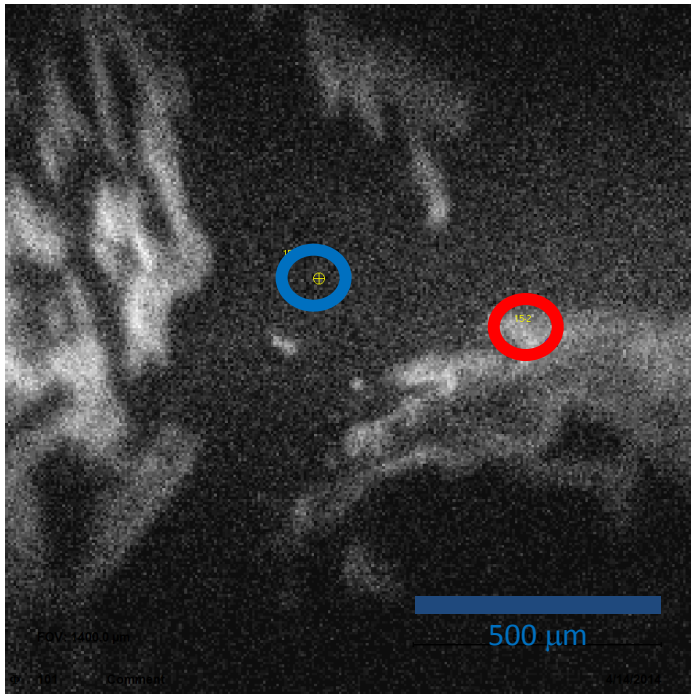
XPS: inhomogeneous anode surface

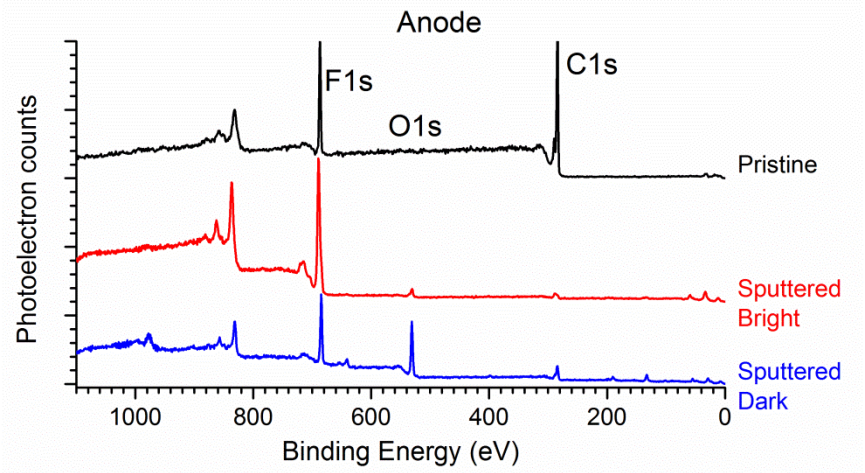


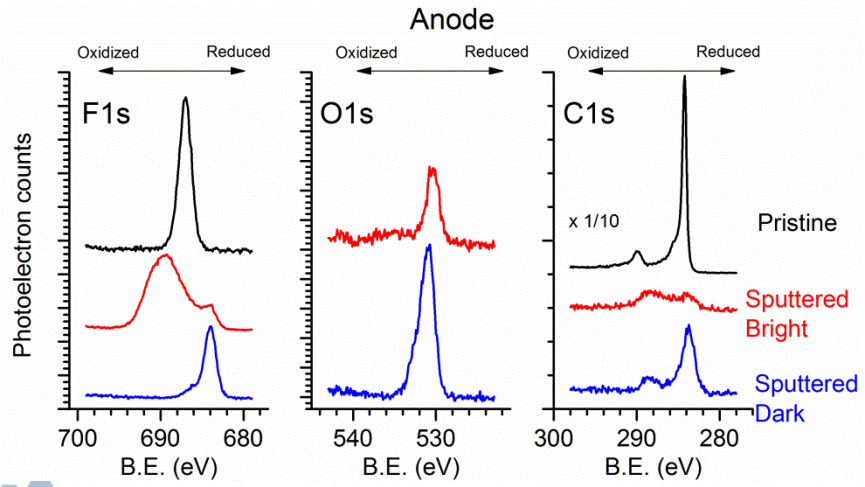
- XPS shifts point to different F environments at bright and dark regions, not just different concentration
- Li environment also different in bright and dark areas
- P correlated to C and O. Neither is prominent in bright areas
- Probably LiF precipitates on top of P-containing electrolyte decomposition products

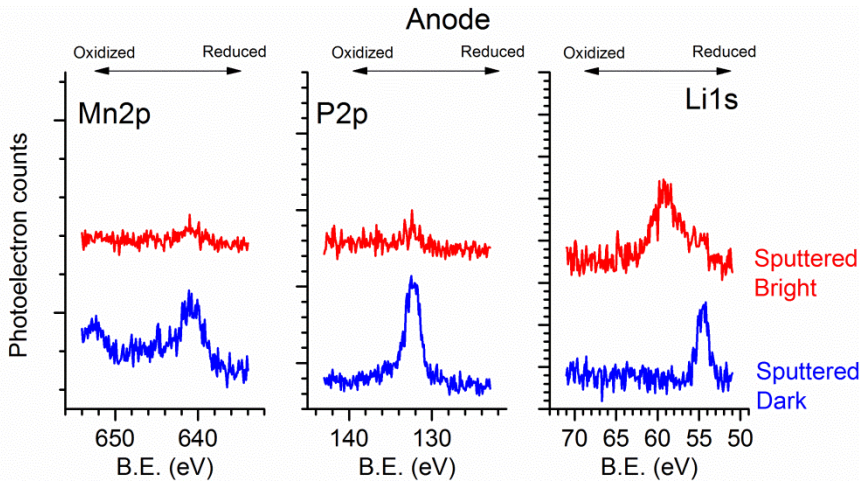
XPS: inhomogeneous anode surface

- After sputtering, bright and dark regions still present
- Same correlations between elements
- Mn detected on dark areas









Summary

- Performed post-test analysis of ~350 mAh LMRNMC/Graphite pouch cells produced by CAMP facility
- Initial inspection revealed no obvious defects and similar *end of test* performance across cells
- Gas analysis revealed O evolution from cathode and electrolyte degradation, including likely reaction products between electrolyte solvents and salt or binder
- Anode surface was highly inhomogeneous comprising: a surface film of varying thickness, white precipitates and dendritic growth of metallic Li and/or deliquescent salts, TM and Cu incorporation into the anode, preferential incorporation of P, C and O in some areas of the anode surface.
- Electrodes are part of CAMP's electrode library, available to DOE programs as baseline materials to test electrochemical performance and physicochemical changes in modified configurations (e.g. additives, novel electrodes and electrolytes)
- Post-test characterization facility is available for collaboration with researchers working on DOE programs and industrial partners.

Acknowledgments

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- We are thankful for helpful discussions and samples provider by Argonne CAMP facility:
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