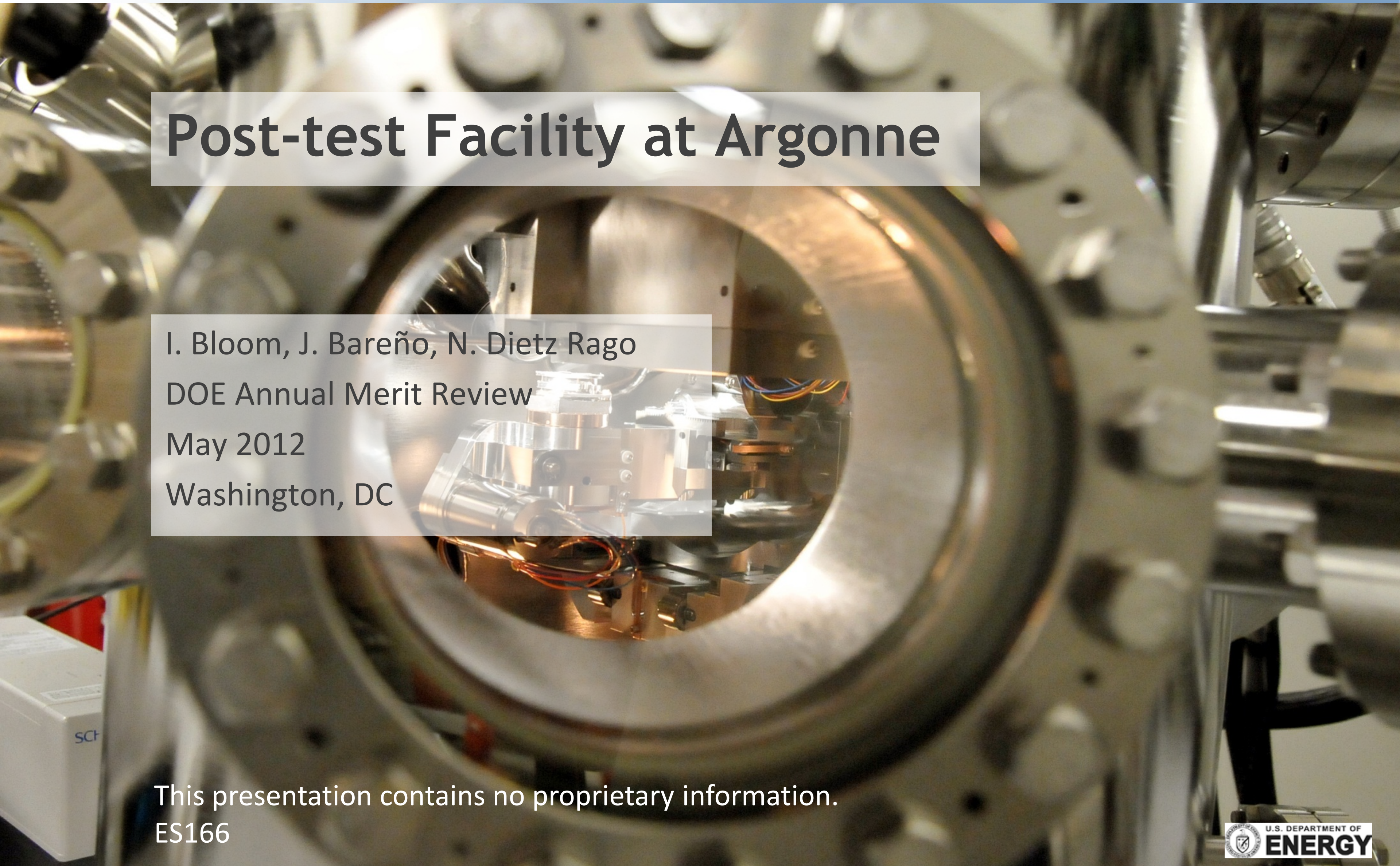
Argonne NATIONAL LABORATORY



Post-test Facility at Argonne

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DOE Annual Merit Review

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This presentation contains no proprietary information.
ES166

U.S. DEPARTMENT OF ENERGY

Post-test Facility at Argonne 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 aging

Budget

- FY10-11: 18-month project funding -- $2.0M (ARRA)
- Status: Construction is complete; facility is open and in operation

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

- Lawrence Berkeley National Laboratory: Li/air
- Argonne: Li/air, Li/S, Li-ion research groups; cell fabrication facility
- Dalhousie University (Canada) – in discussion
- Bar Ilan University (Israel) – in discussion

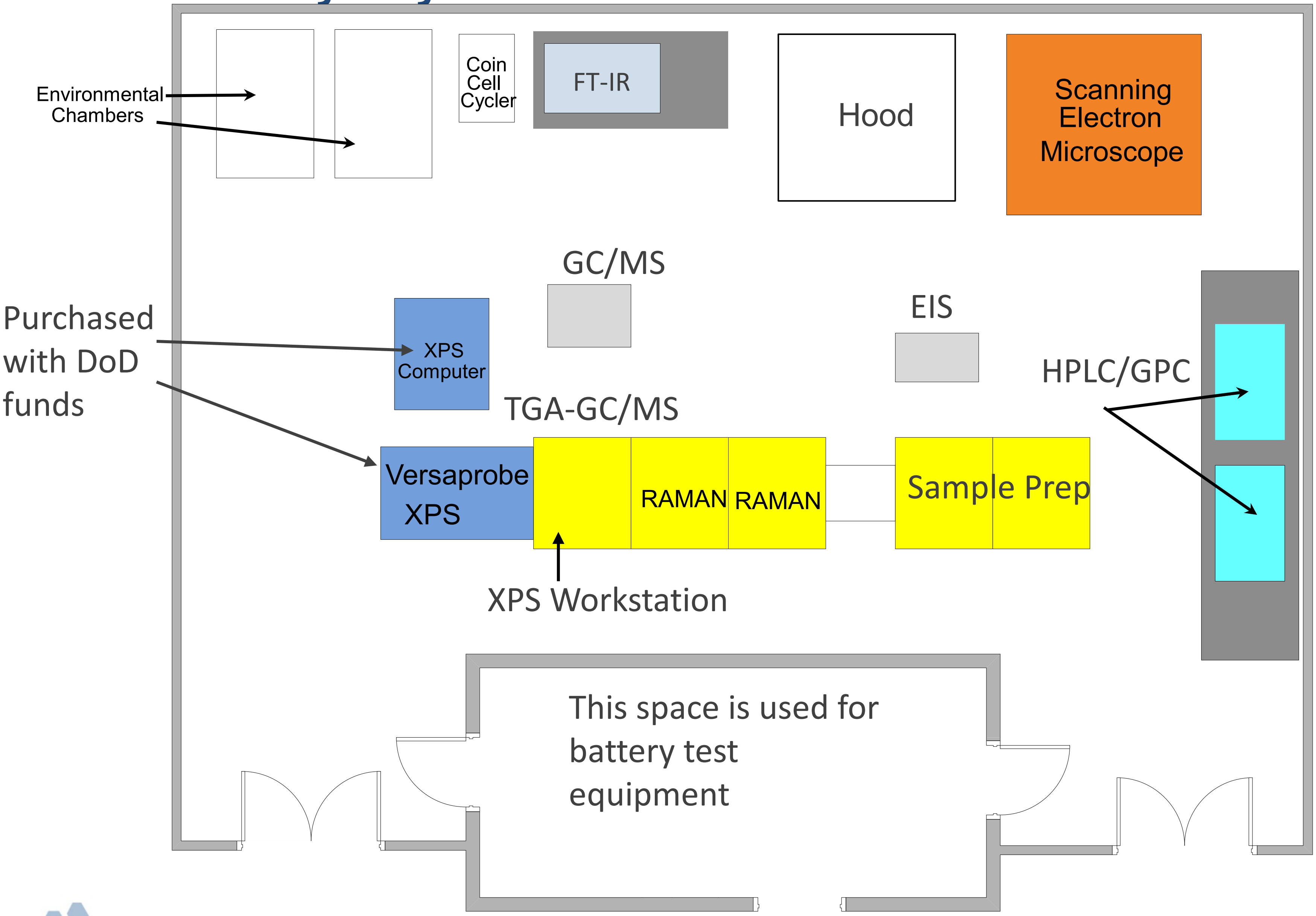
Post-Test Facility at Argonne

- 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

Equipment Needs For the Facility

- Identifying degradation modes in batteries, especially lithium-ion batteries, relies on both bulk- and surface-characterization techniques
- Thus, the needed equipment for the facility includes spectroscopy and surface-science instruments
  - FT-IR spectroscopy
  - Raman spectroscopy
  - Optical and scanning-electron microscopy
  - Electrochemical impedance spectroscopy
  - X-ray photoelectron spectroscopy
  - High Pressure Liquid Chromatography/Gel Permeation Chromatography
  - TGA-GC/MS
  - Half-cell fabrication and test equipment
- Since the battery materials may be air-sensitive, they will be handled and characterized in a controlled-atmosphere glove box to the greatest extent possible

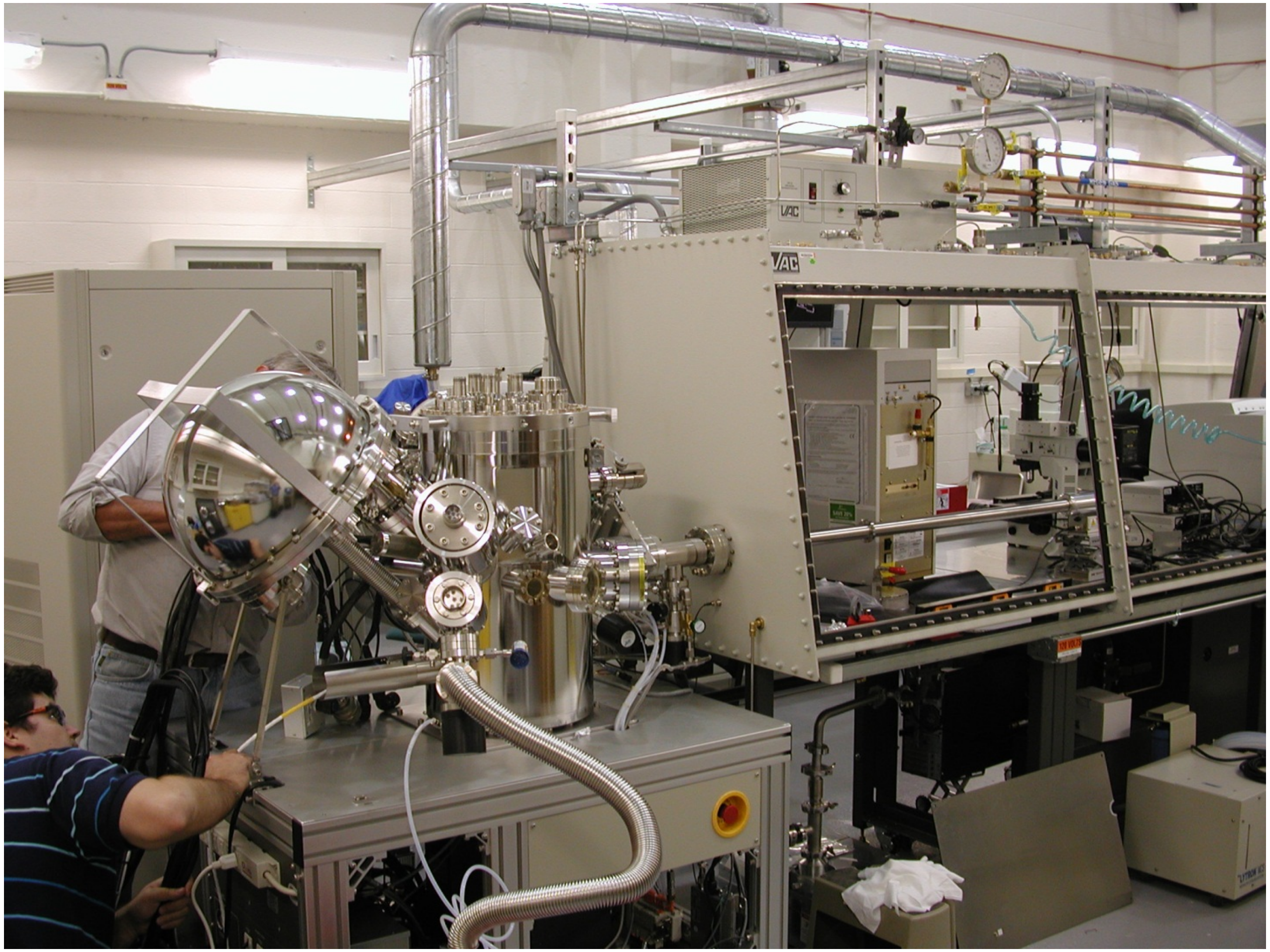
Laboratory Layout



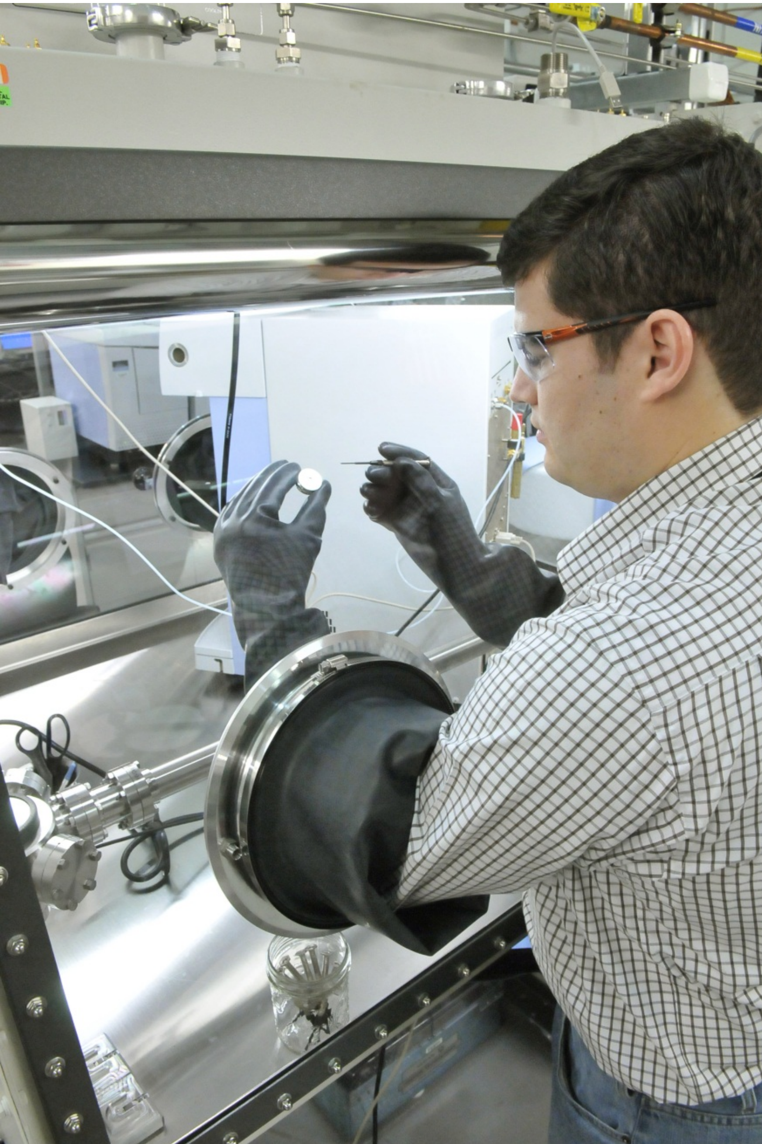
Facility Development Progress

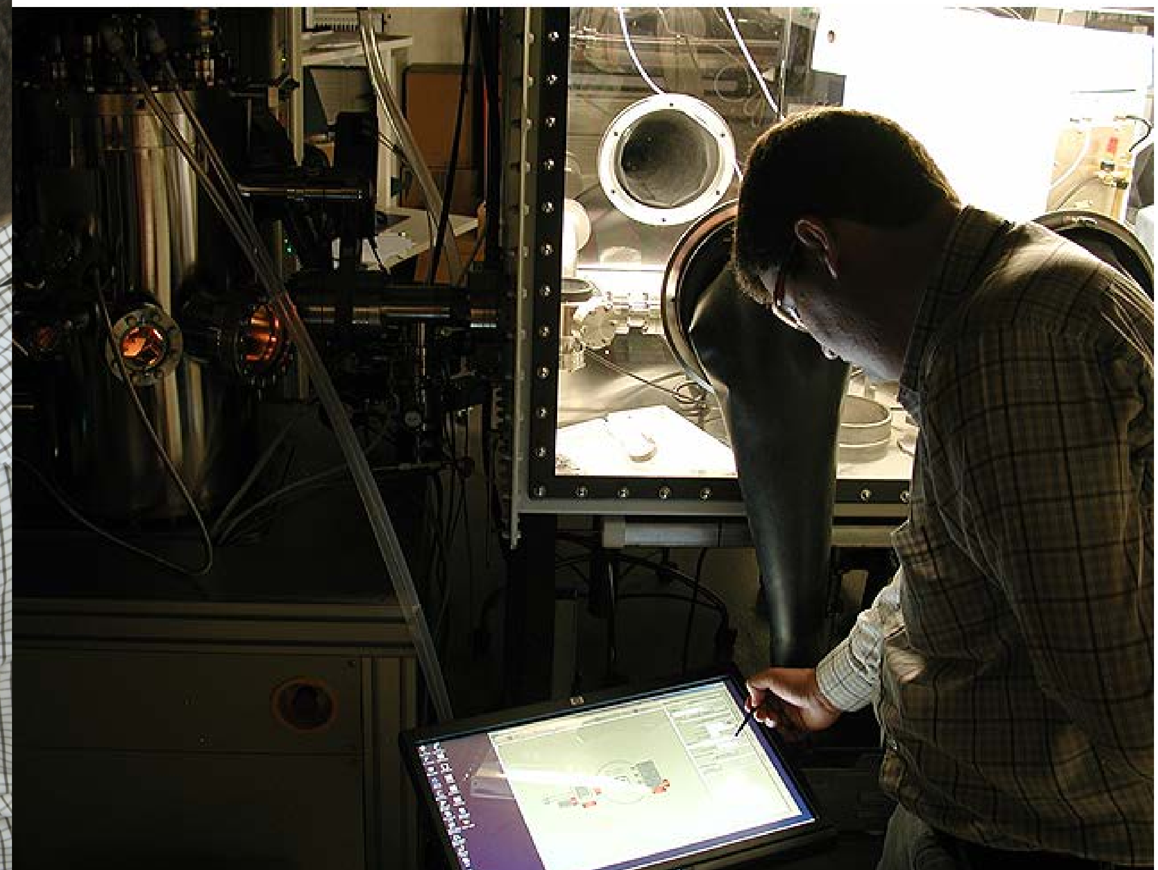
Renovation of the existing laboratory space

An XPS is Attached to Glove Box; Samples are Introduced to XPS Without Exposure to Air



XPS Sample Being Prepared for Characterization

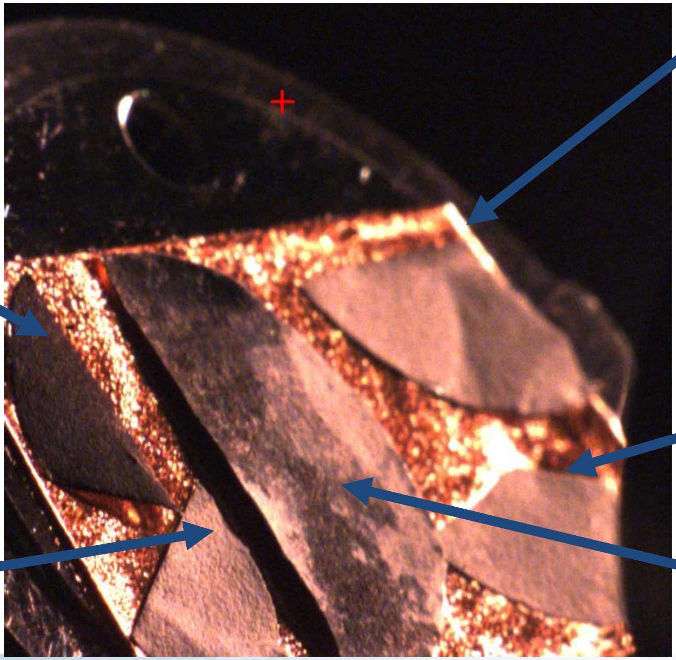




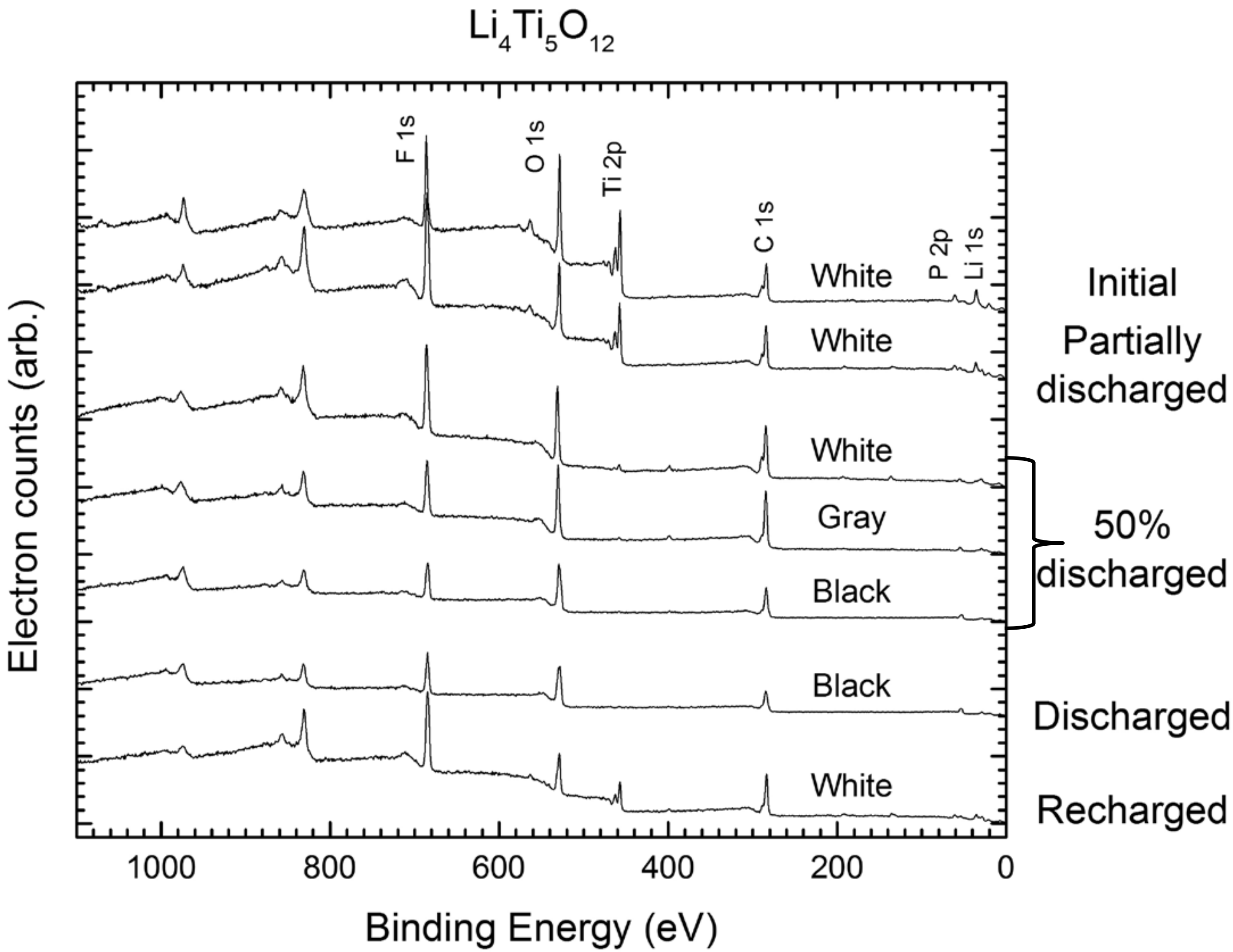
Facility Is Open and Operational

Post-test Facility Collaborates with Many Projects/Organizations

- LBNL: Conductive-additive-free $Li_4Ti_5O_{12}$ (LTO) anodes for Li-ion batteries
- ANL: Li-ion, Li/Air, and Li/S and ABR battery projects
- Samples representing different states of charge/discharge were received from LBNL and analyzed by XPS
  - Samples consisted of white, gray and black regions

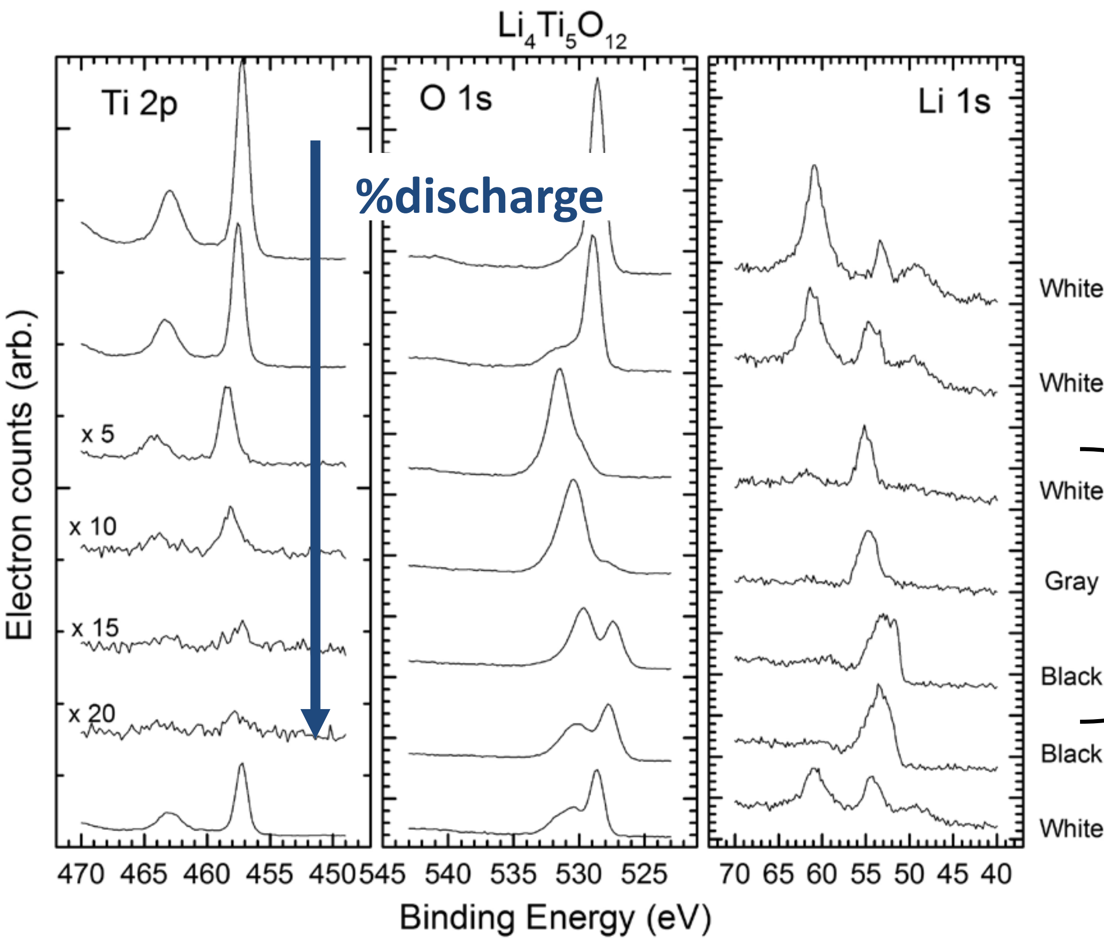


XPS Results from LTO Anodes



- Ti 2p peak disappears as material is discharged; it emerges upon recharge
- May indicate presence of an SEI layer which forms and dissolves with discharge and charge

XPS Results: Ti 2p Intensity Correlates with %DOD



Initial

Partial discharge

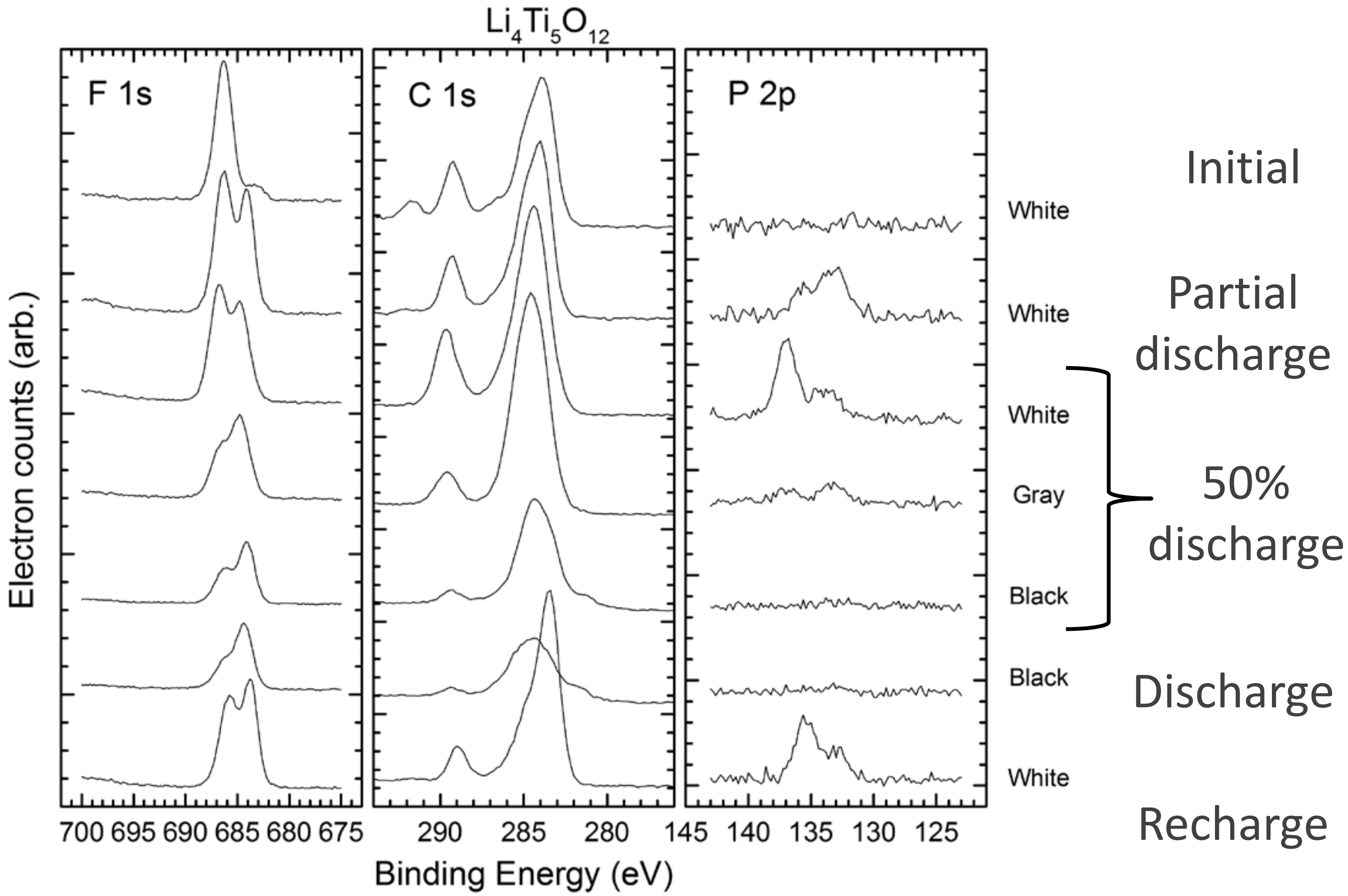
50% discharge

Discharge

Recharge

- Low energy component in O1s peak, which stays after recharge.
- The state of discharge (amount of additional lithium) increases downwards, except for the last curve which is the re-charged sample. The intensity of the Ti 2p peak is inversely correlated with the state of discharge, consistent with formation of SEI layer that dissolves upon recharge.

Other Changes Are Seen in XPS Results



ABR Deliverable – ACFF-B1A-PX
Integration of Testing and Post-Test Facilities

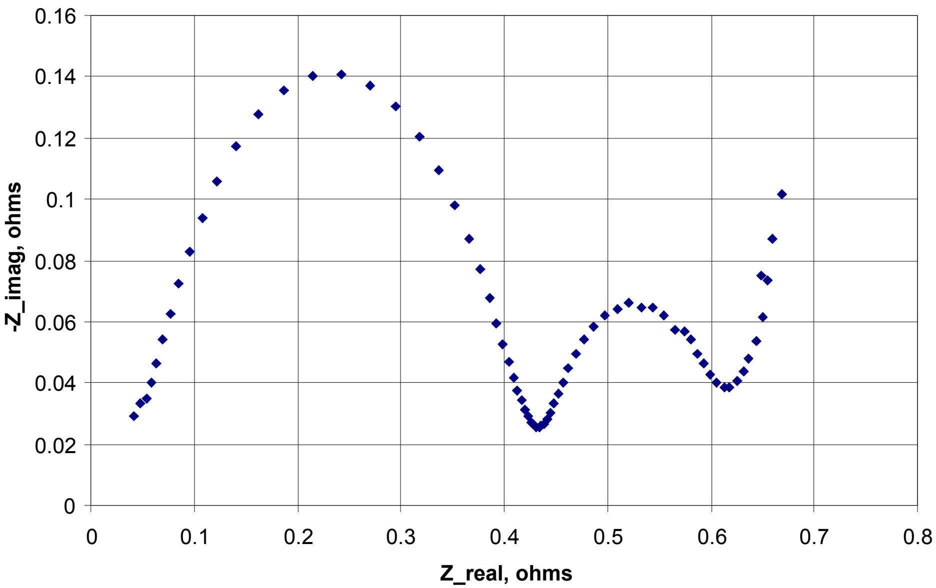
- Six, 250-mAh, Li-ion pouch cells were received on 3/31/11 for independent evaluation
- Cell chemistry:
  - Cathode
    - 86 wt% Toda HE-5050 NCM
    - 4 wt% Timcal SFG-6 Graphite
    - 2 wt% Timcal Super P
    - 8 wt% Solvay 5130 PVDF Binder
  - Anode:
    - 89.8 wt% Conoco Phillips: CGP-A12 Graphite
    - 4 wt% Timcal Super P
    - 6 wt% Kureha KF-9300 PVDF Binder
    - 0.17 wt% Oxalic Acid
- Testing started on 4/1/11
- Test plan: PHEV CD cycling at 30^{o}C
- Status: Testing is complete

Test Results (1)

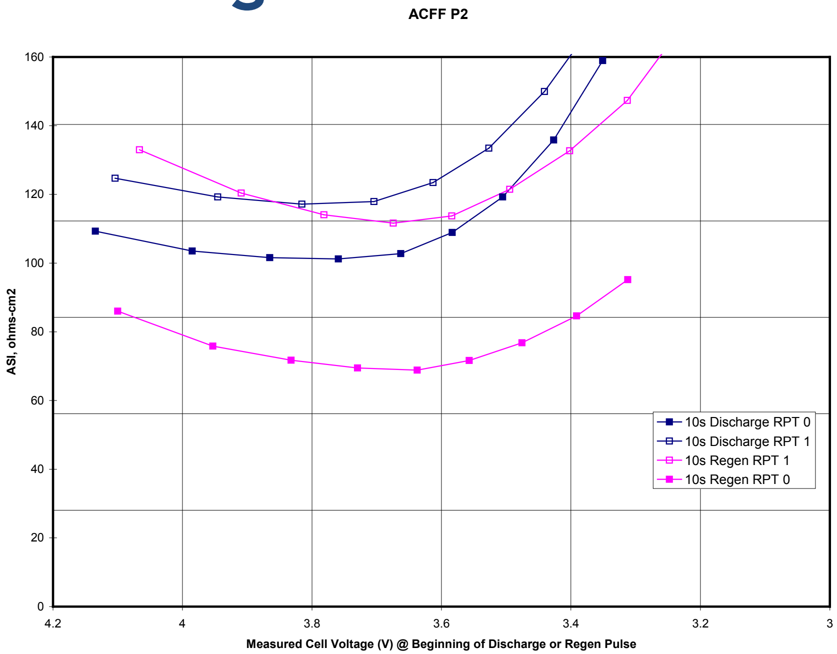
Gap table

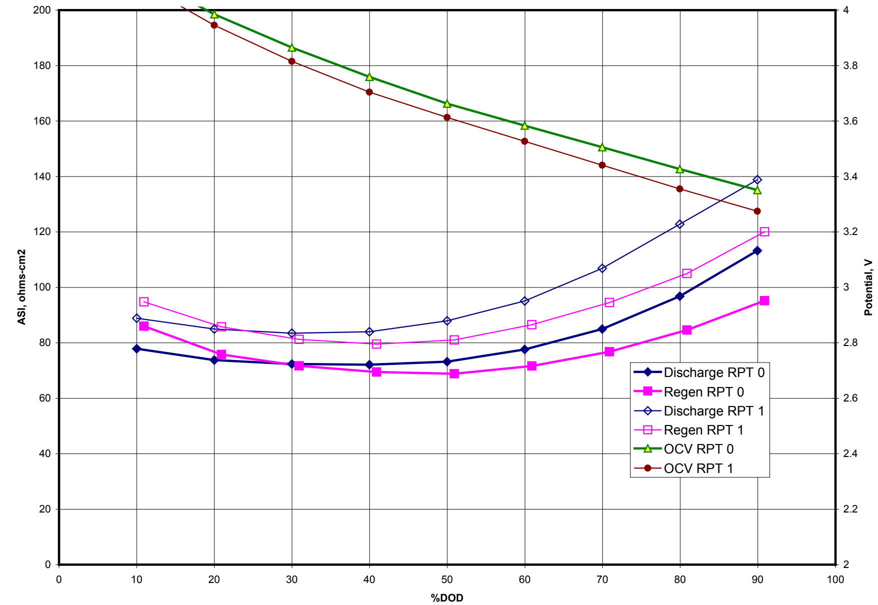
Unit	Goal	P1 RPT0	P1 RPT1	P2 RPT0	P2 RPT1	P3 RPT0	P3 RPT1
Ah		0.353	0.329	0.363	0.337	0.356	0.343
milliohms		122.51	135.54	73.21	87.95	72.89	77.38
Wh	3400	6396.67	Failed	4649.55	5718.46	5701.20	5427.19
Wh	500	2999.67	Failed	2318.47	1054.10	2301.20	2027.19
W	45000	56389.33	Failed	61305.29	49458.54	61513.32	57797.54
W	30000	37592.89	Failed	40870.19	32972.36	41008.88	38531.69
kg	60						
Liter	40						
Vdc	400						
Vdc	>0.55 x Vmax						
# of CD cycles	5000		100		100		100
# of CS cycles	300000						
BSF		12620	9200	9201	9200	9201	9200

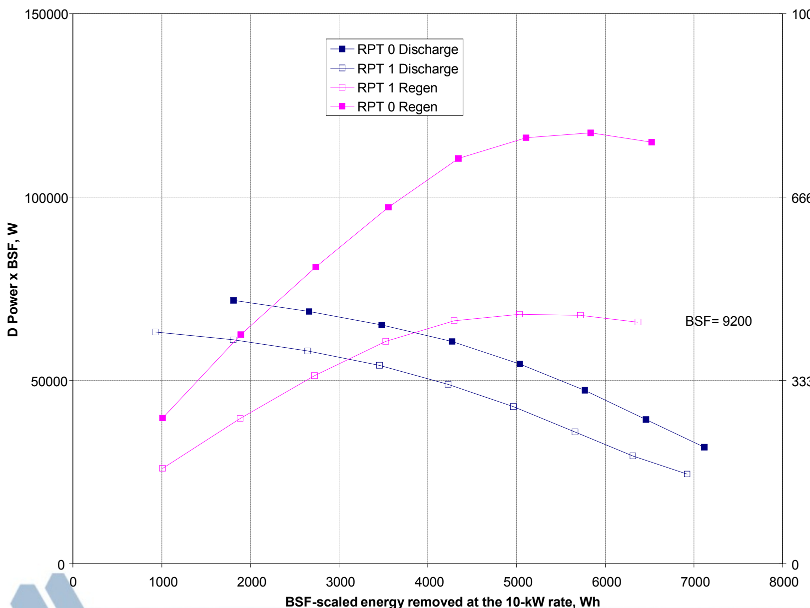
Unit	Goal	P4 RPT0	P4 RPT1	P5 RPT0	P5 RPT1	P6 RPT0	P6 RPT1
Ah		0.338	0.326	0.367	0.352	0.358	0.346
milliohms		77.66	82.64	73.67	80.45	69.21	72.98
Wh	3400	6399.67	4990.37	5833.59	5266.60	5271.50	4964.70
Wh	500	2999.67	1590.36	2433.59	1866.60	1871.50	1564.70
W	45000	56203.14	53743.25	61585.13	55784.00	57167	53916.76
W	30000	37468.76	35828.83	41056.75	37189.33	38111.33	35944.51
kg	60						
Liter	40						
Vdc	400						
Vdc	>0.55 x Vmax						
# of CD cycles	5000		100		100		100
# of CS cycles	300000						
BSF		9315	9200	9201	9200	9200	9200

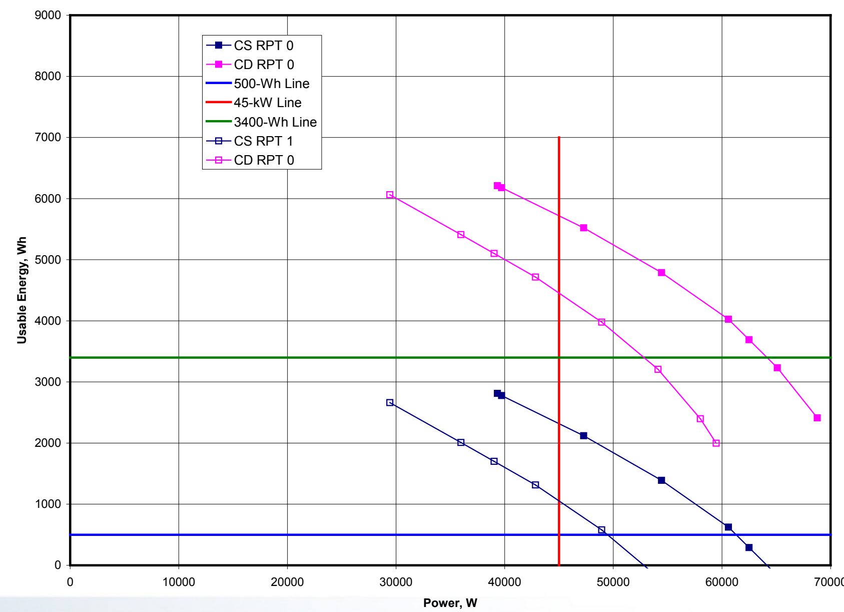


Changes in Cell Performance Are Seen With Cycling

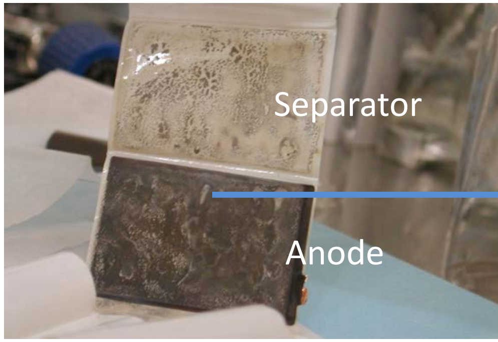


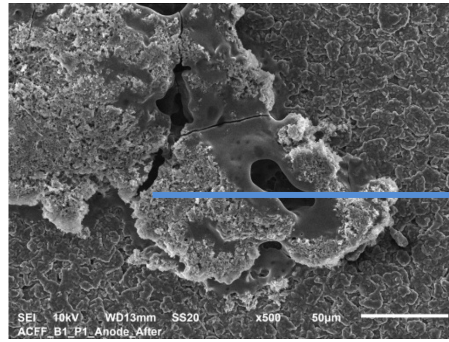


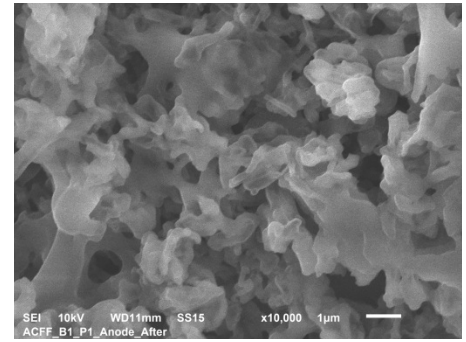




Analysis of ABR Cell
CGP-A12 Anode - Precipitates Are Seen in SEM Images



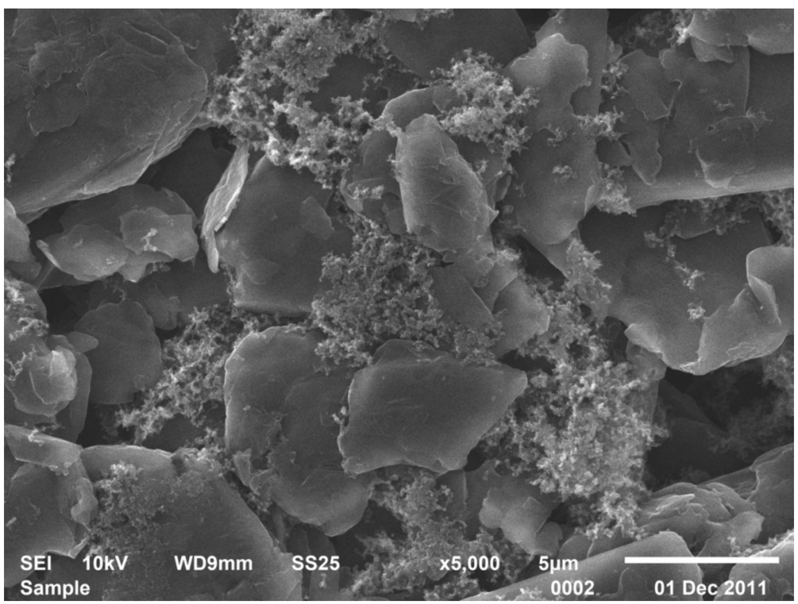




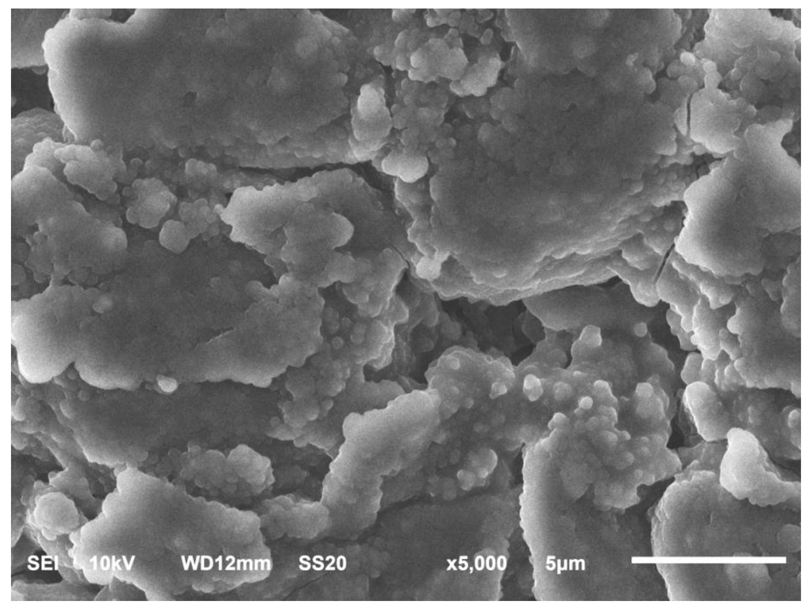
Unraveled cell pouch showing separator and anode.

After rinsing with EMC, SEM images of anode surface showing extensive surface precipitates.

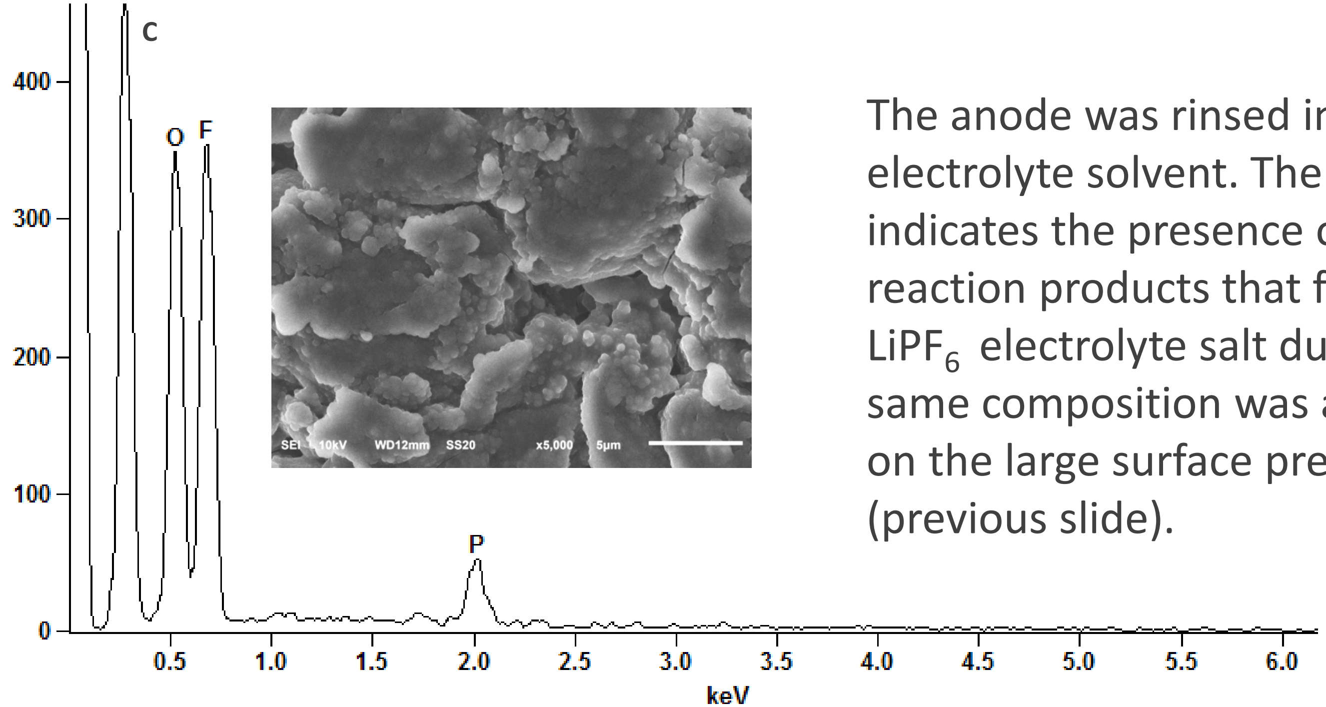
Surface - *Before Cycling*



Surface – *After Cycling and Rinsing*



EDS Analysis of Rinsed Anode Shows Presence of Insoluble Deposits



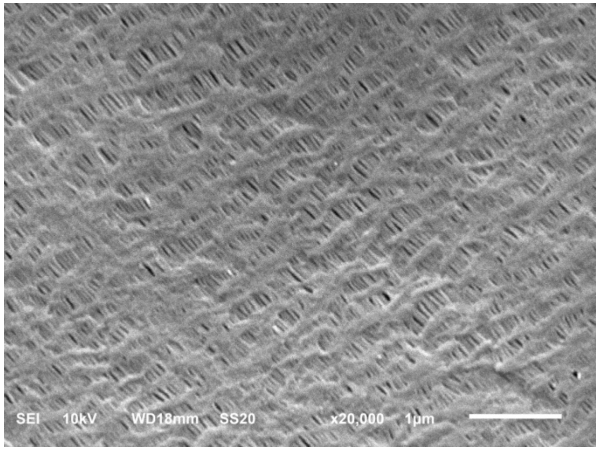
The anode was rinsed in EMC, the electrolyte solvent. The EDS spectrum indicates the presence of insoluble reaction products that formed with the $LiPF_6$ electrolyte salt during cycling. The same composition was also detected on the large surface precipitates (previous slide).

Element Line	*Net Counts*	*Weight %*	*Weight % Error*	*Atom %*
C K	3069	21.73	+/- 0.45	29.66
O K	2413	30.43	+/- 1.20	31.18
F K	2724	41.53	+/- 1.19	35.83
P K	554	6.31	+/- 0.42	3.34
Total		100.00		100.00

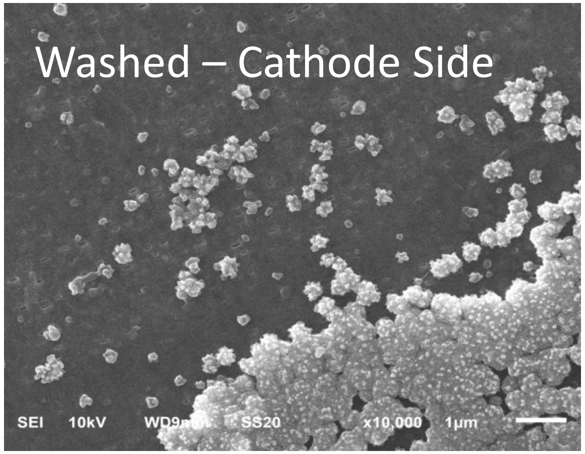
Note: Li is not detected by EDS

SEM/EDS Analysis of Separator Membrane Also Shows Presence of Insoluble Precipitates

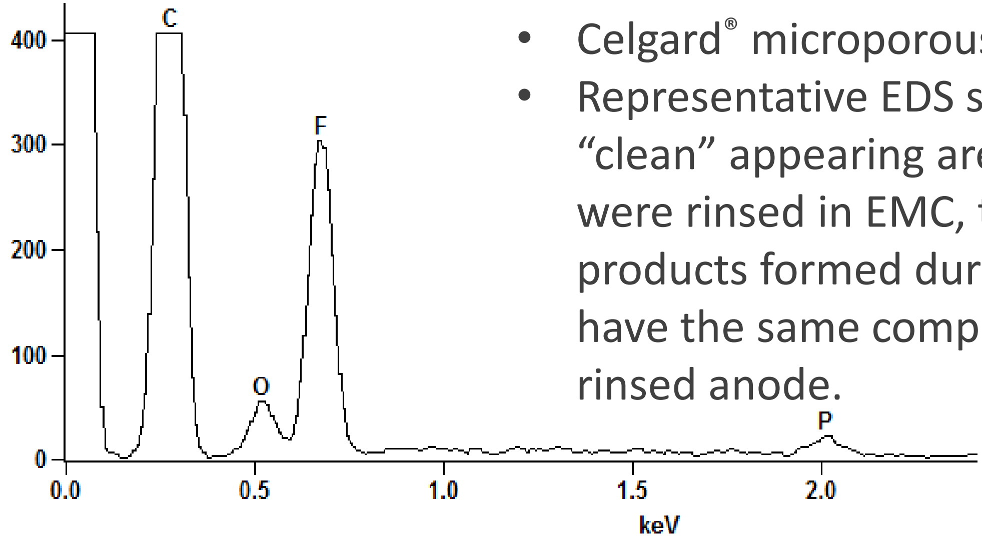
Before Cycling



After Cycling



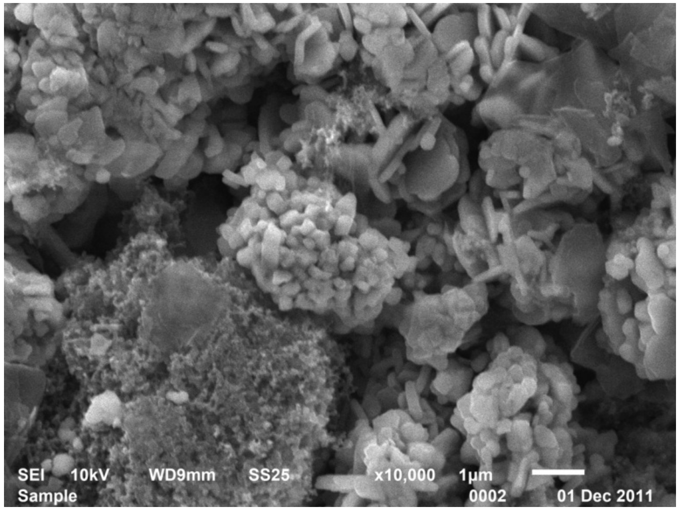
After Cycling



- Celgard® microporous, 25 µm tri-layer (PP-PE-PP)
- Representative EDS spectrum from surface precipitates and “clean” appearing areas on the membrane. The membranes were rinsed in EMC, the electrolyte solvent. The reaction products formed during cycling are insoluble in EMC and have the same composition as the precipitates on the rinsed anode.

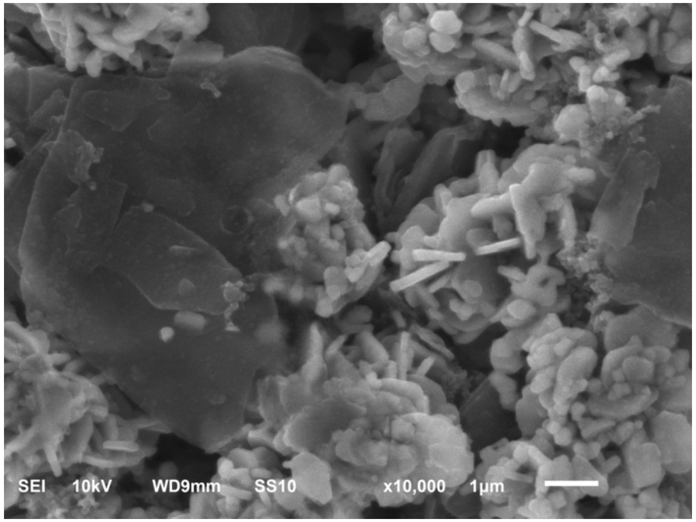
Analysis of ABR Cell
HE5050 NCM Cathode – No Obvious Changes

Surface *Before Cycling*

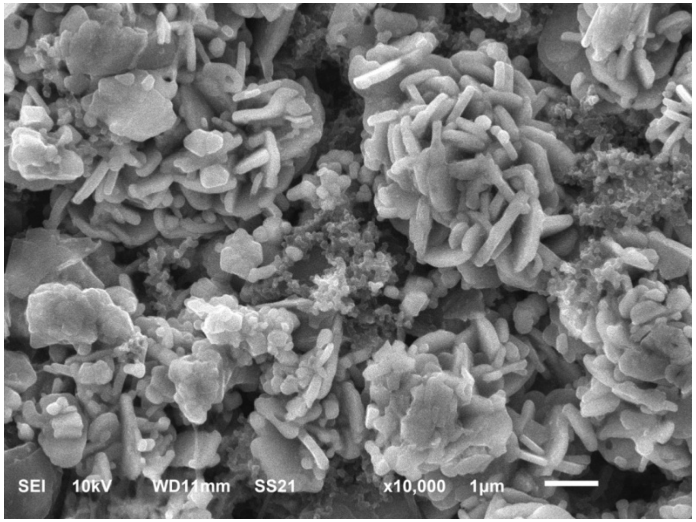


Surface images of the cathode show that there were no obvious microstructural changes due to cycling

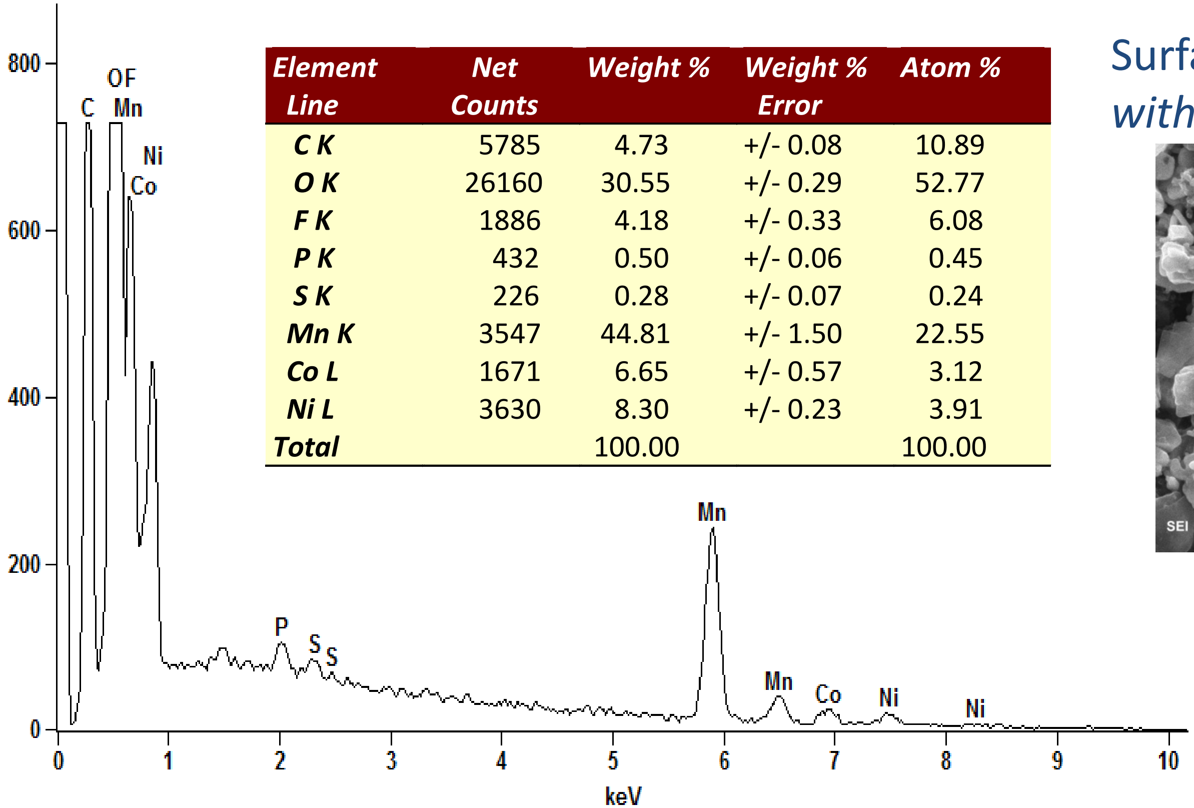
Surface - *After Cycling*



Surface - *After Cycling and Rinsing with EMC*

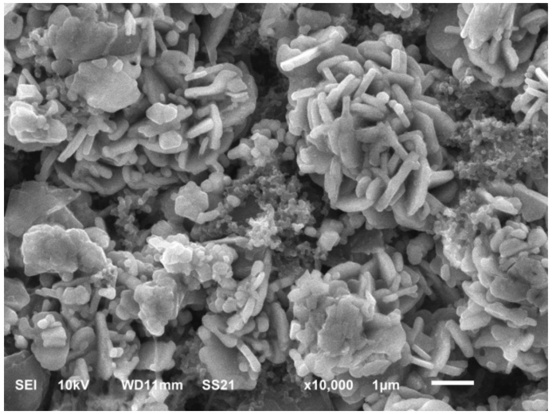


SEM/EDS of Rinsed Cathode Shows Presence of Insoluble Deposits



Element Line	*Net Counts*	*Weight %*	*Weight % Error*	*Atom %*
C K	5785	4.73	+/- 0.08	10.89
O K	26160	30.55	+/- 0.29	52.77
F K	1886	4.18	+/- 0.33	6.08
P K	432	0.50	+/- 0.06	0.45
S K	226	0.28	+/- 0.07	0.24
Mn K	3547	44.81	+/- 1.50	22.55
Co L	1671	6.65	+/- 0.57	3.12
Ni L	3630	8.30	+/- 0.23	3.91
Total		100.00		100.00

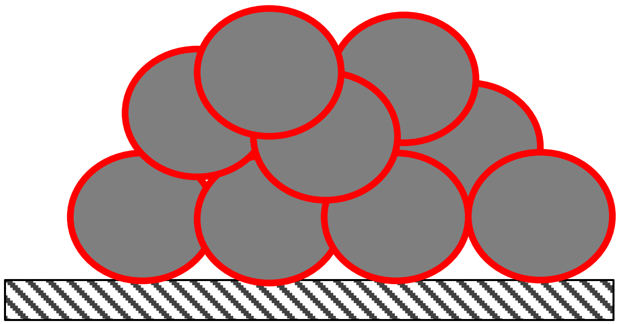
Surface - *After Cycling and Rinsing with EMC*



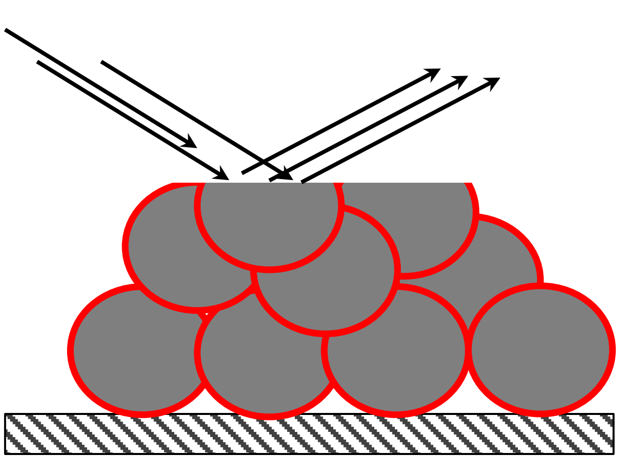
Representative EDS data indicates the presence of insoluble reaction products that formed with the $LiPF_6$ electrolyte salt during cycling. The oxide particles are produced in a sulfuric acid environment and, thus, is the most probable source for S.

XPS Analyses of ABR Electrodes

- Sections of the electrodes were removed from the cell and some were rinsed with EMC
- Photoelectron spectra were recorded of the rinsed and dried surface
- Where needed, sputtering was used to remove surface material to observe changes in the materials below. Spectra also reflect surface topography; may also include SEI



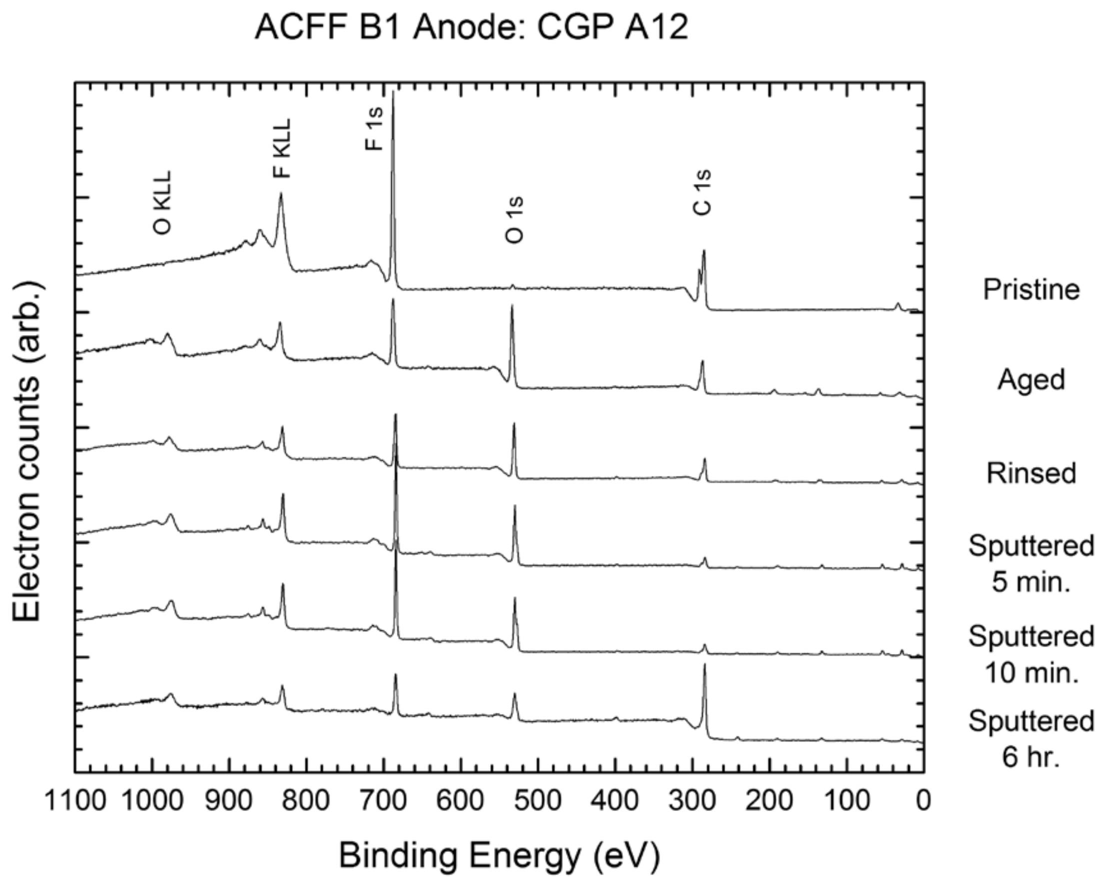
Before sputtering – see native surface materials. The red outline represents a surface layers, such as an SEI



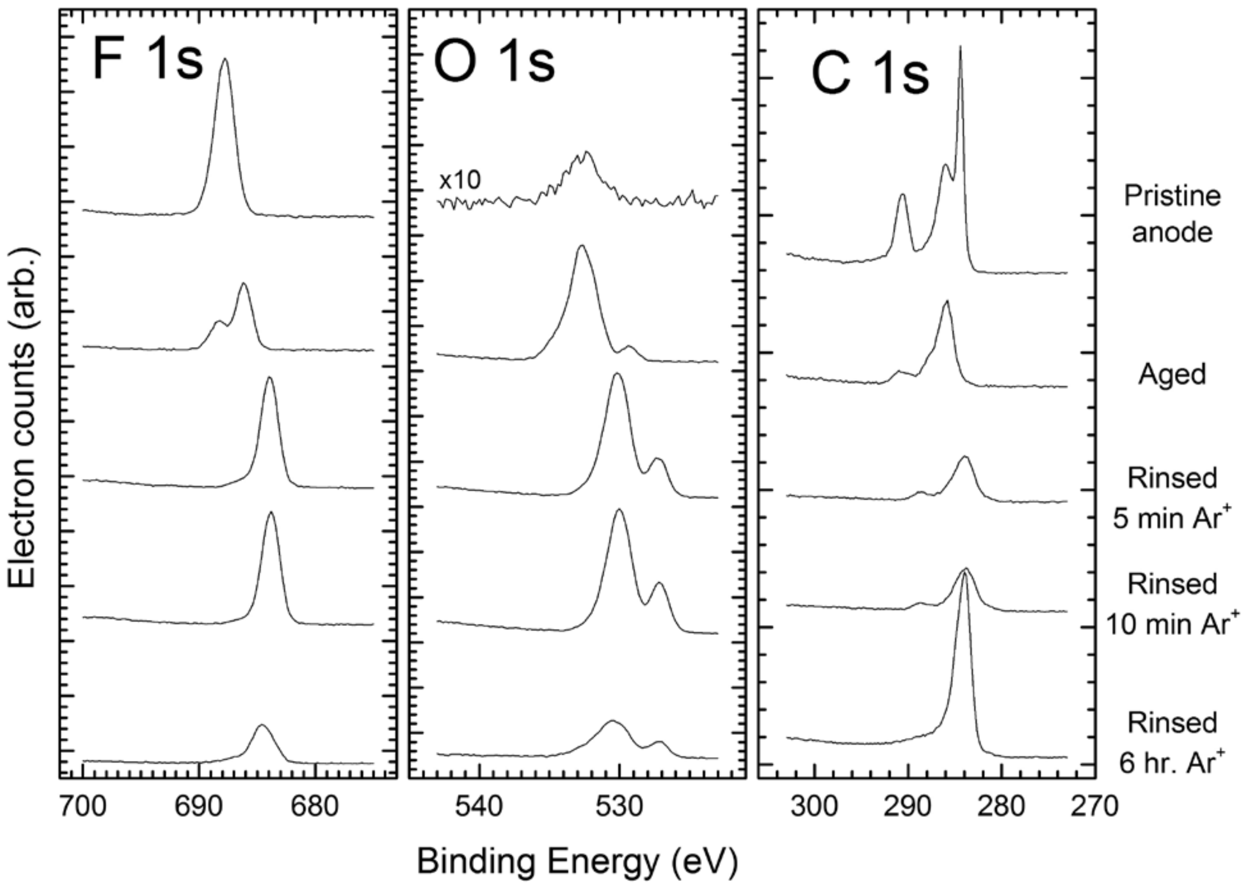
After sputtering – can see both surface and bulk materials and the changes in composition in them with depth (sputtering time)

XPS Analysis of Anode Harvested from ACFF 1st Cell Build

- Intense F1s peak decreases upon aging and rinsing and drying; recovers upon sputtering
- Continuous decrease of C1s peak

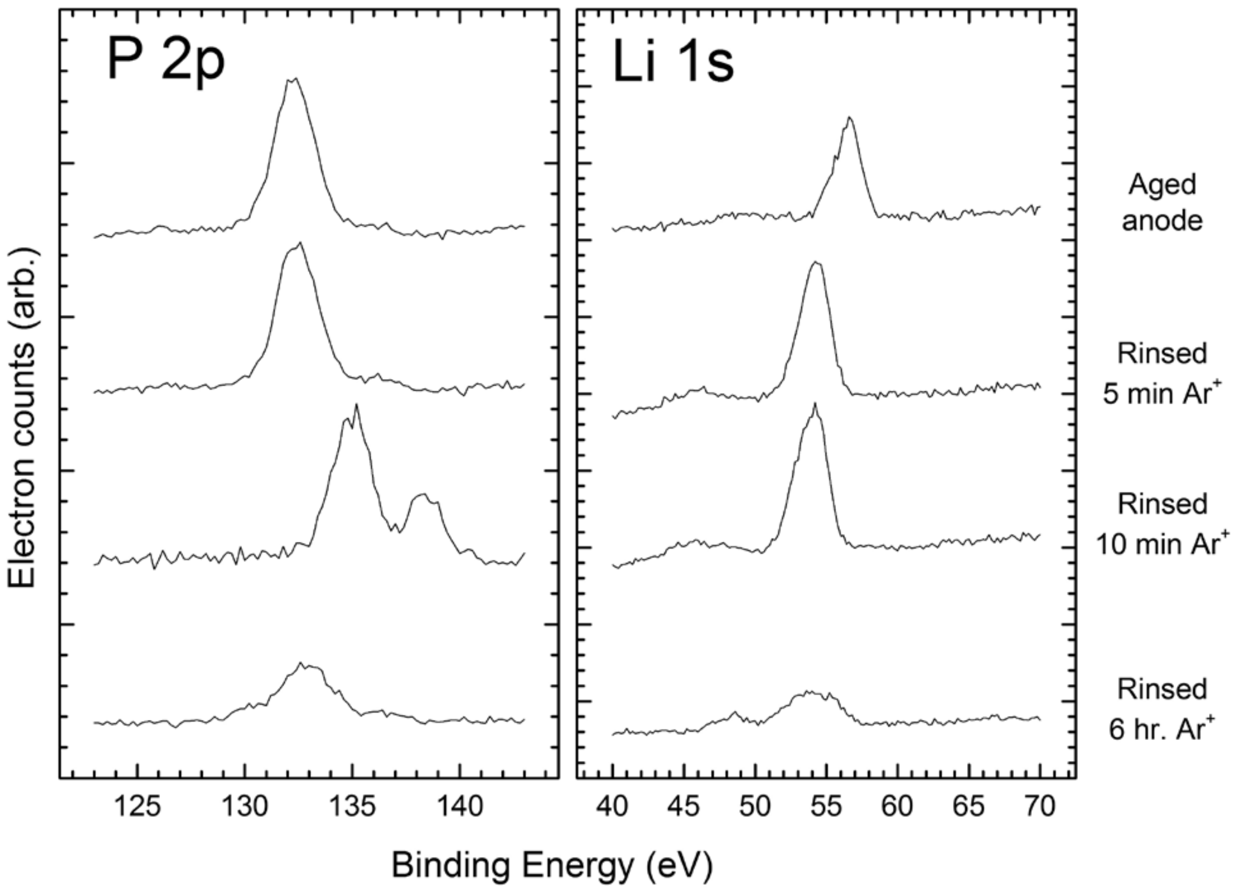


Changes Most Likely Due to SEI Growth Are Seen With Aging

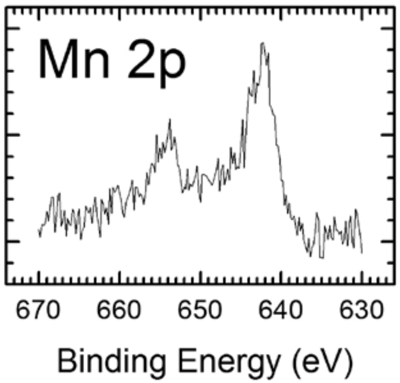


- Mn is present in sputtered sample
- Hard shift to higher B.E. of all regions in sputtered sample due to sample charging
- C1s looses sharp low B.E. component and broadens. Potential ion mixing
- High B.E. component of F1s forms upon aging; removed by sputtering
- Continuous development of low B.E. O1s component

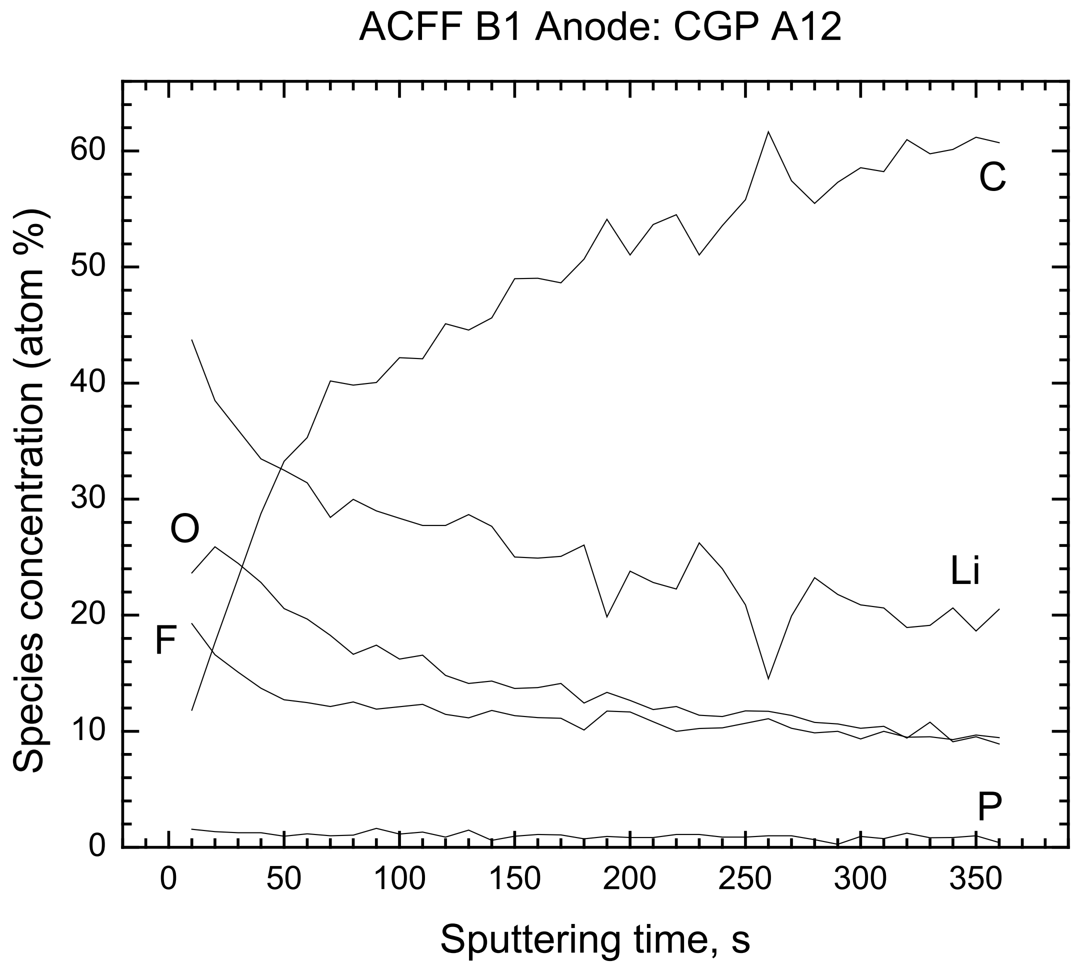
XPS analysis of CGP-A12 anode harvested from ACFF 1st cell build.



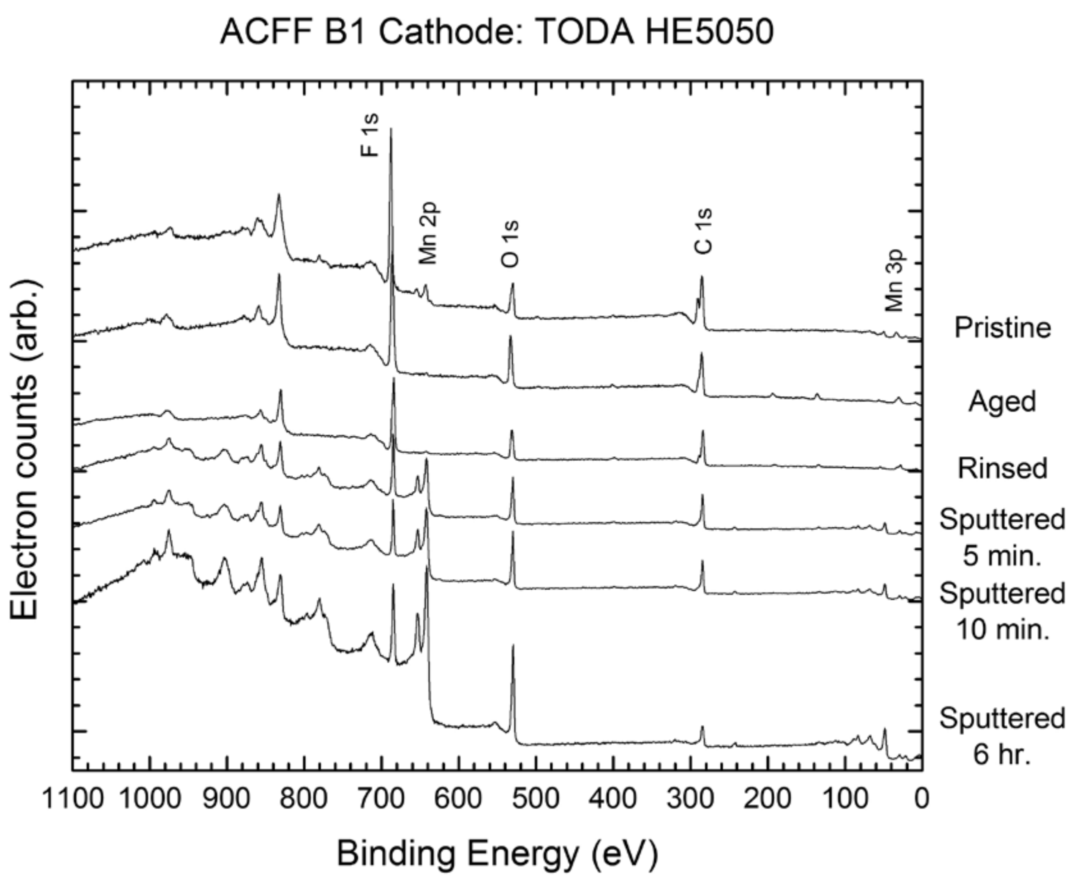
- No Li or P in pristine anode
- Li1s shifts to lower B.E. Less oxidized
- A high B.E. component appears in P2p



Sputtering with 3-kV Ar⁺ Reveals Composition Gradients on Electrode Surface

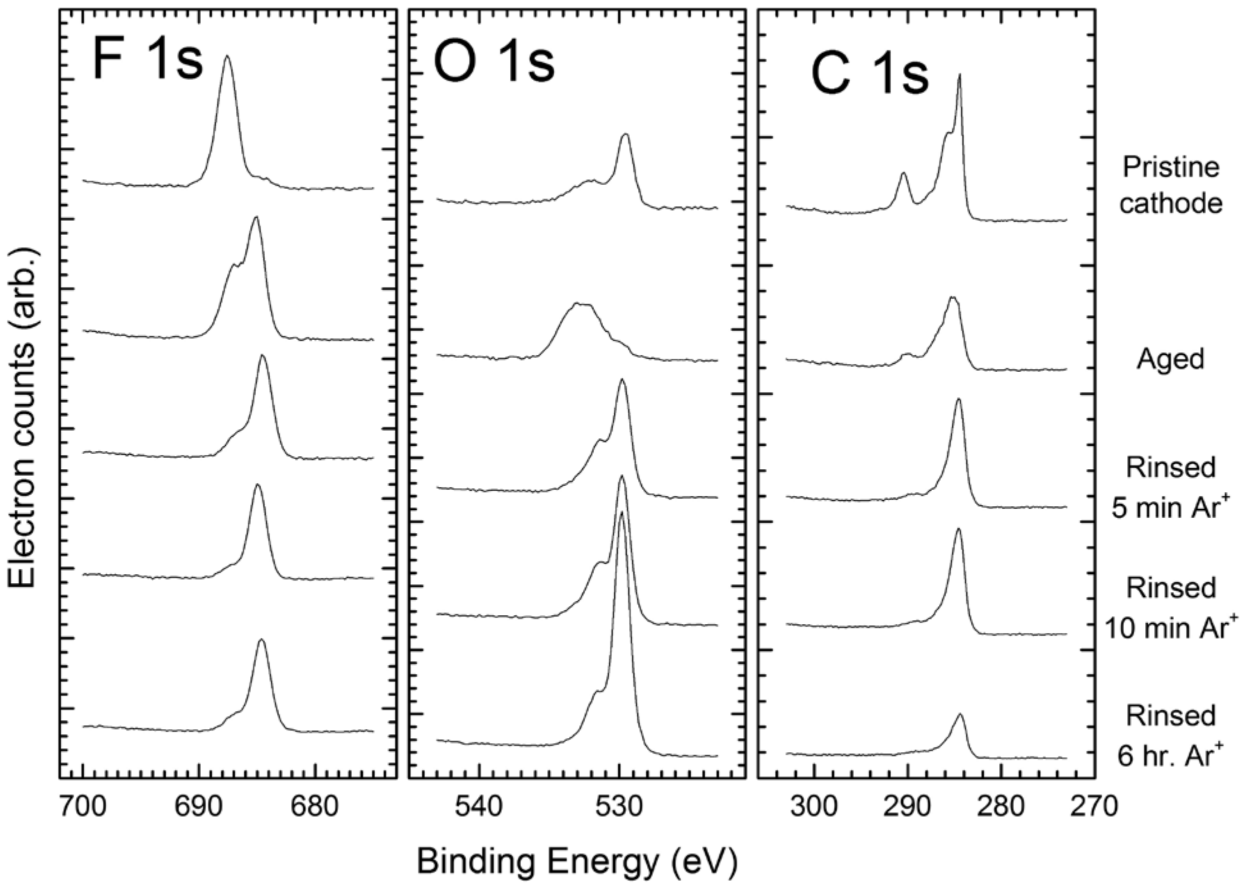


XPS Analysis of Cathode: Mn2p Signal Disappears With Aging and Reappears With Sputtering



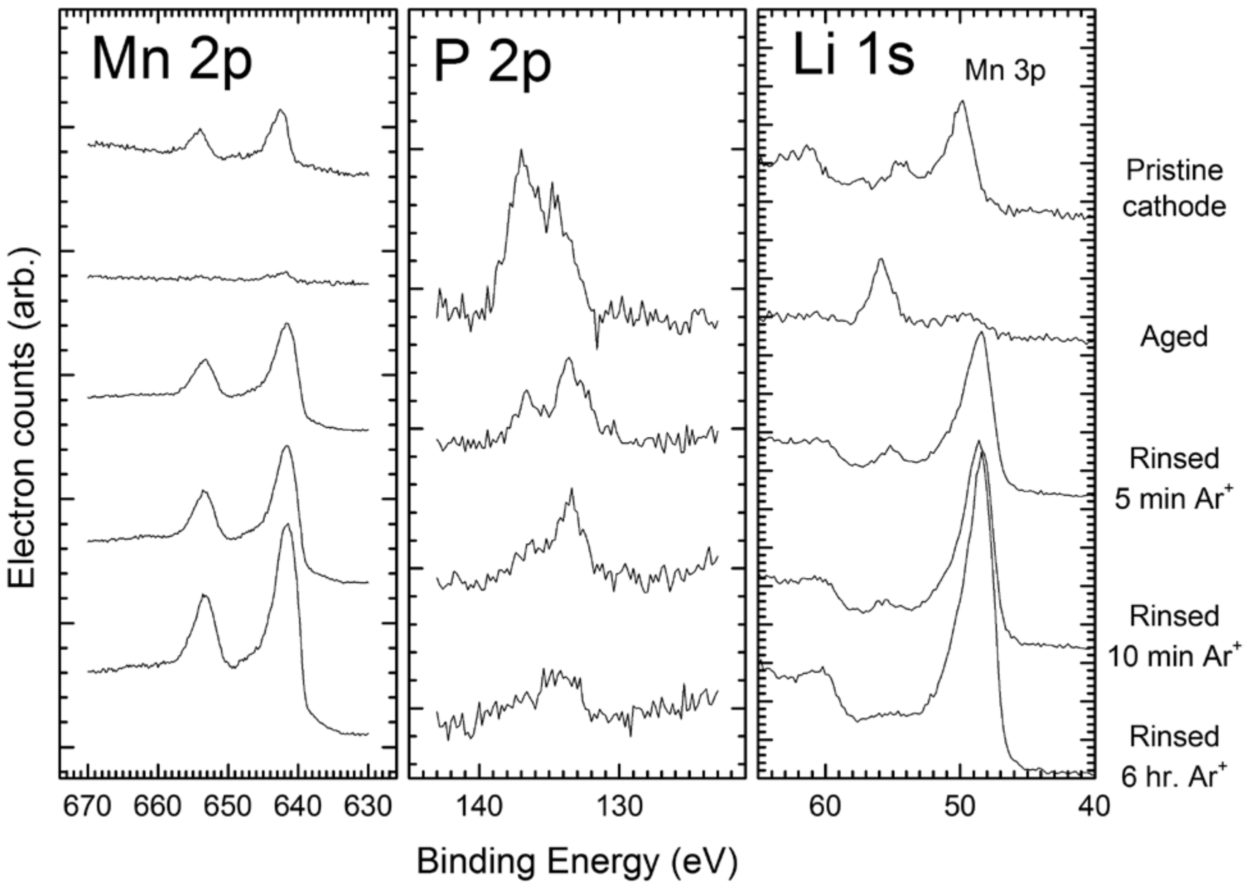
- Mn2p signal is lost upon exposure to electrolyte. Recovered after sputtering
- Consistent with presence of SEI or residue in aged sample
- Higher Mn2p and lower C1s signals in pristine than in sputtered sample indicate good conductive carbon coverage of active particles

Changes in F, O and C Regions Are Seen With Aging



- F1s develops high B.E. component, diminished by sputtering
- O1s high B.E. component dominant upon aging and decreases with sputtering
- Lower Mn2p and higher C1s signals in pristine than in sputtered sample indicate good conductive carbon coverage of active particles

Changes in Mn, P and Li Regions Are Seen With Aging

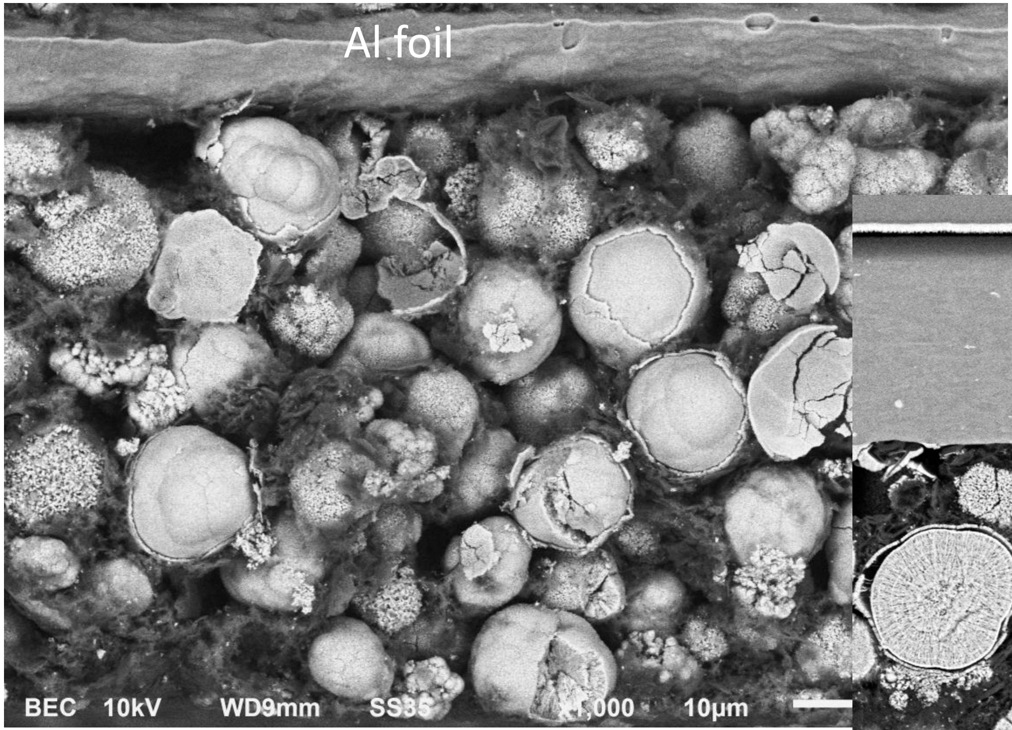


- Mn3p overlaps with Li1s
- High B.E. Li1s seems related to S.E.I. or deposit
- May indicate surface depletion of Li in active particles

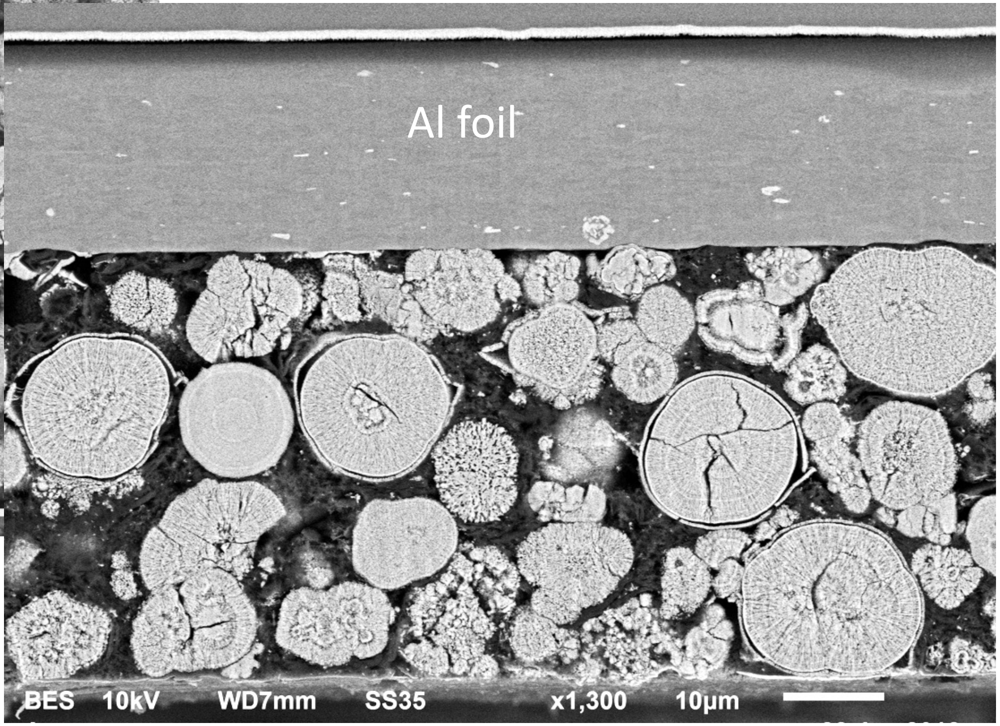
Advance Preparation Techniques Reveal Detailed Microstructures

Cathode: 84 wt.% $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$,4% SFG-6, 4% Super P, 8% PVDF binder (CFF cell builds)

Common: Fractured cross section

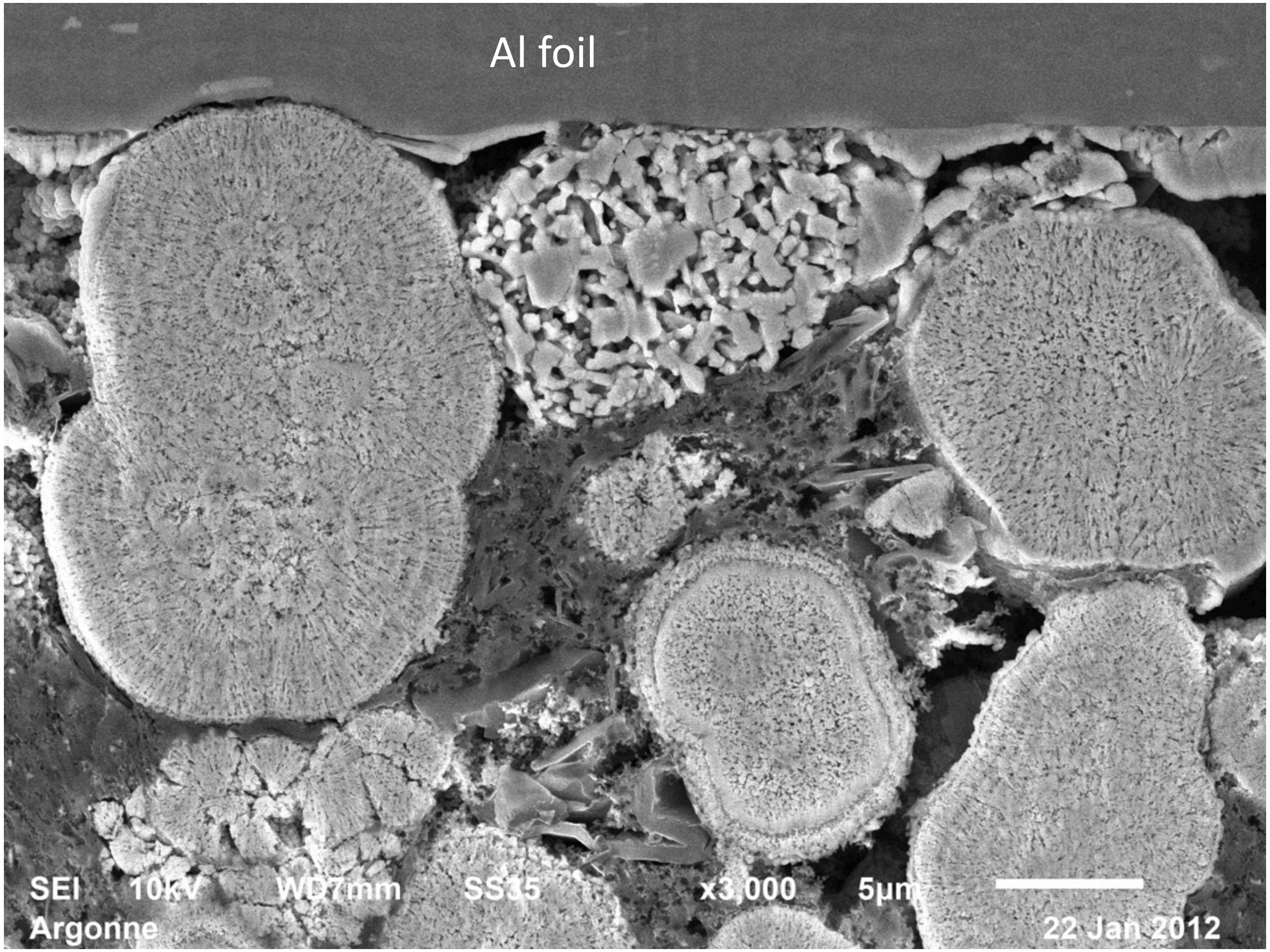


Advanced: Slope-cut cross section



Uses an argon-ion beam to sputter material on one plane, thus providing a flat un-altered cross section of the sample.

Characterization of Li-Mn-O-rich NMC Cathode Laminate on Al



An ion-milled slope cut cross sections each particle and produces a planar surface that enhances interpretation of microstructure by preserving material topology and providing for better EDS statistics. No mechanical deformation is introduced as in fracturing.

Summary

- A post-test facility has been established at Argonne to support DOE and USABC projects
- The facility is operating and collaborating with many groups
  - LTO anode with LBNL
  - Li/Air cells with ANL
  - Li/S and Li-ion with ANL
- The Post-test Facility is integrated with the Battery Testing and Cell Fabrication Facilities
- Next steps
  - Examine old (~13 y) cells from the ATD program to characterize the long-term changes present in the cells
  - Continue to collaborate with ABR, BATT and USABC programs
  - Open for collaborations with US battery developers and international battery research groups

Acknowledgment
This work was performed under the auspices of the US Department of Energy, Office of Vehicle Technologies, Hybrid and Electric Systems, under Contract No. DE-AC02-06CH11357.