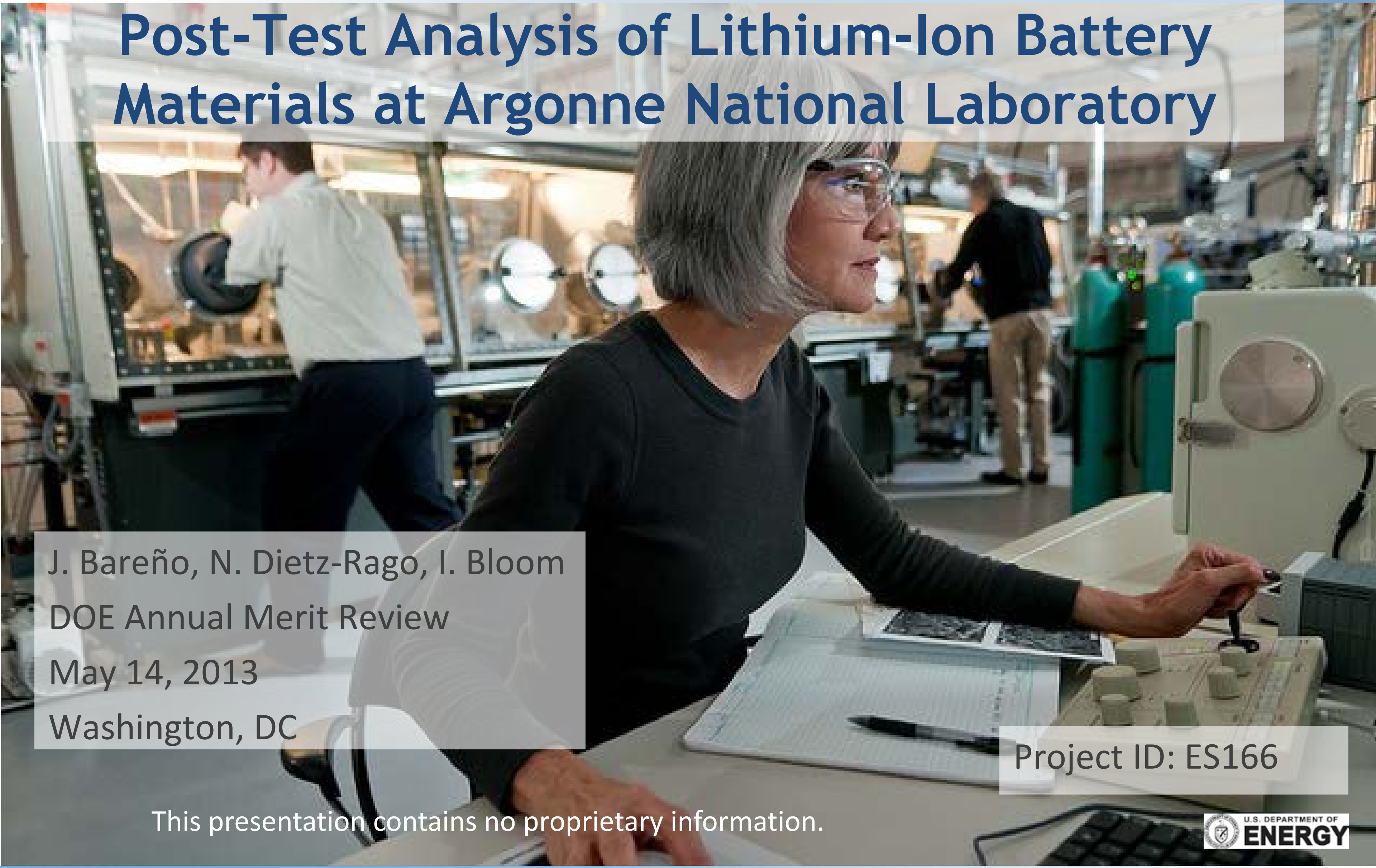
Post-Test Analysis of Lithium-Ion Battery Materials at Argonne National Laboratory



J. Bareño, N. Dietz-Rago, I. Bloom

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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

- FY13: part of $2.3M
- 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

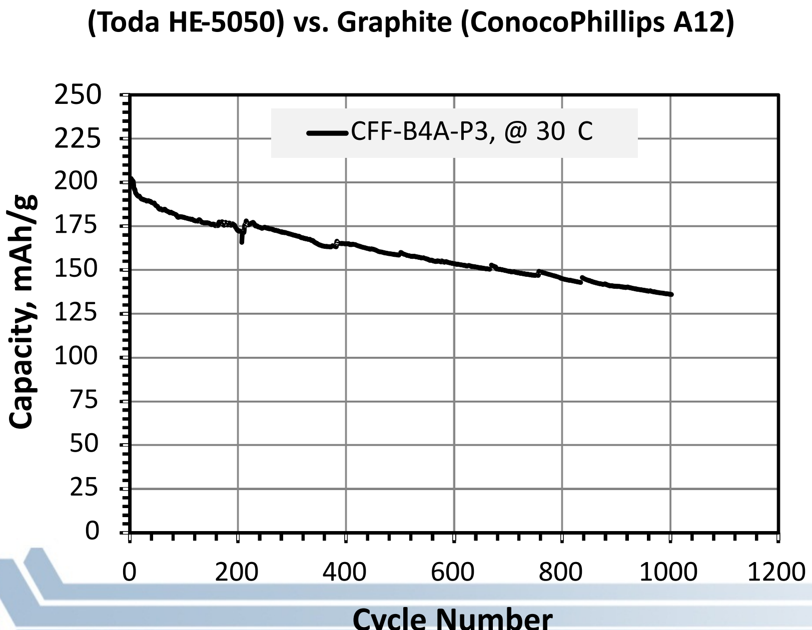
- Argonne: Li/air, Li/S, Li-ion research groups; cell fabrication facility
- Dalhousie University (Canada)
- Johnson Controls, Inc.

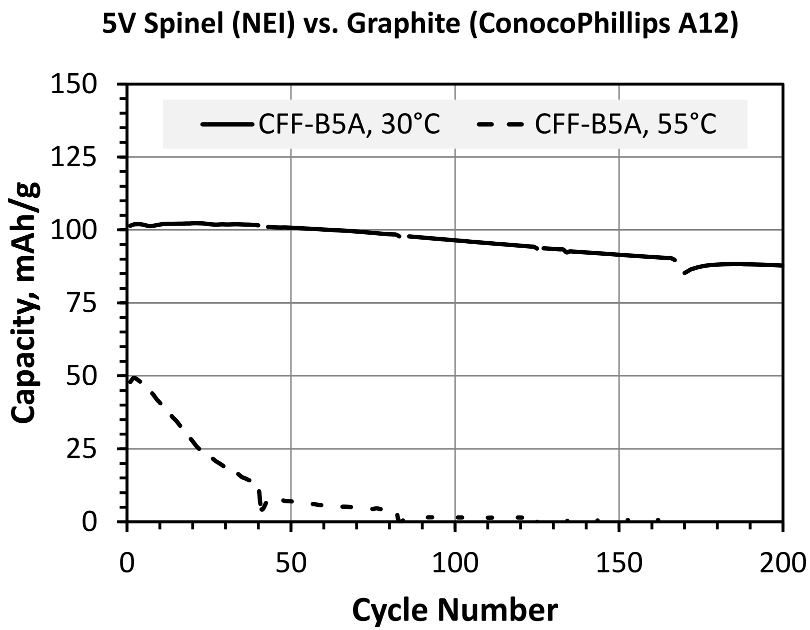
Post-Test Facility at Argonne -- Relevance

- 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

Technical Progress
Case Study: Aging of Cells Containing Toda HE5050 and 5-V Spinel Electrodes

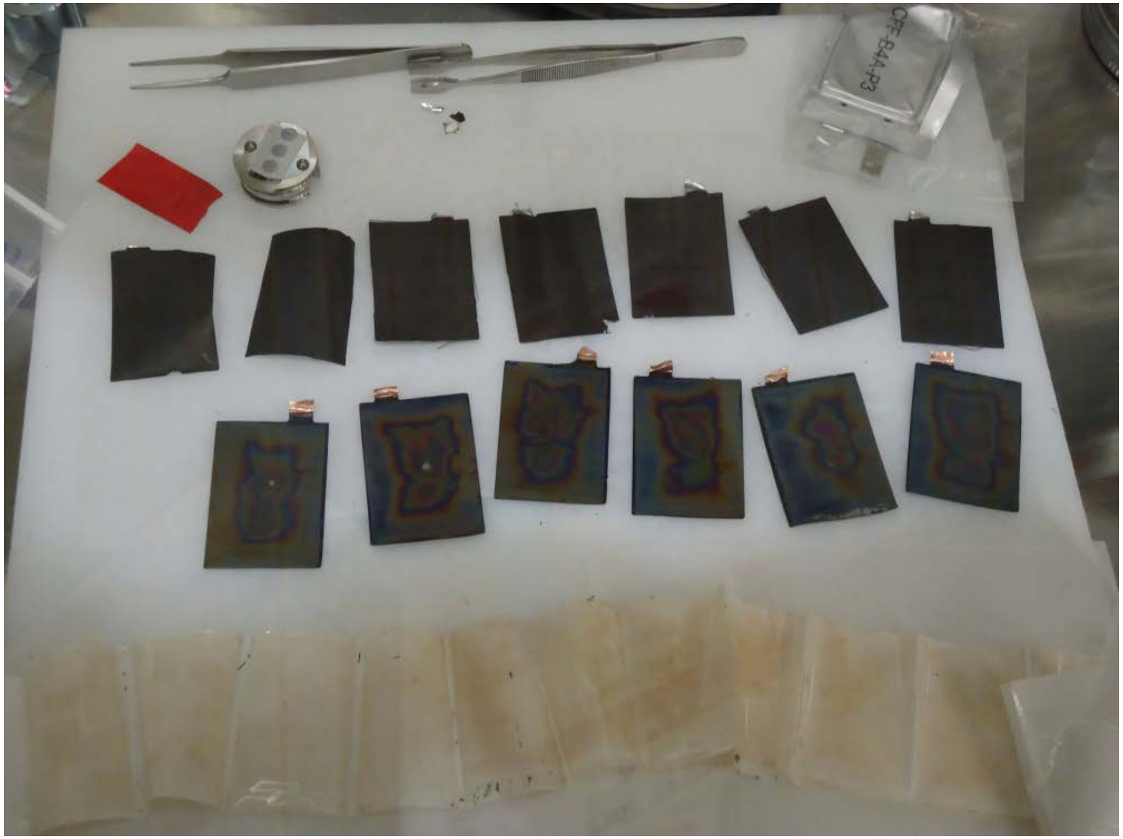
- Cells were made and tested in ANL's Cell Fabrication Facility
- Cell chemistries
  - Toda HE5050: $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ positive; 1.2 M $LiPF_6$ in EC:EMC (3:7 by wt); and graphite negative
  - 5-V Spinel: $LiNi_{0.5}Mn_{1.5}O_4$ positive; 1.2 M $LiPF_6$ in EC:EMC (3:7 by wt); and graphite negative
- Cells were cycled at C/2 rates at different temperatures





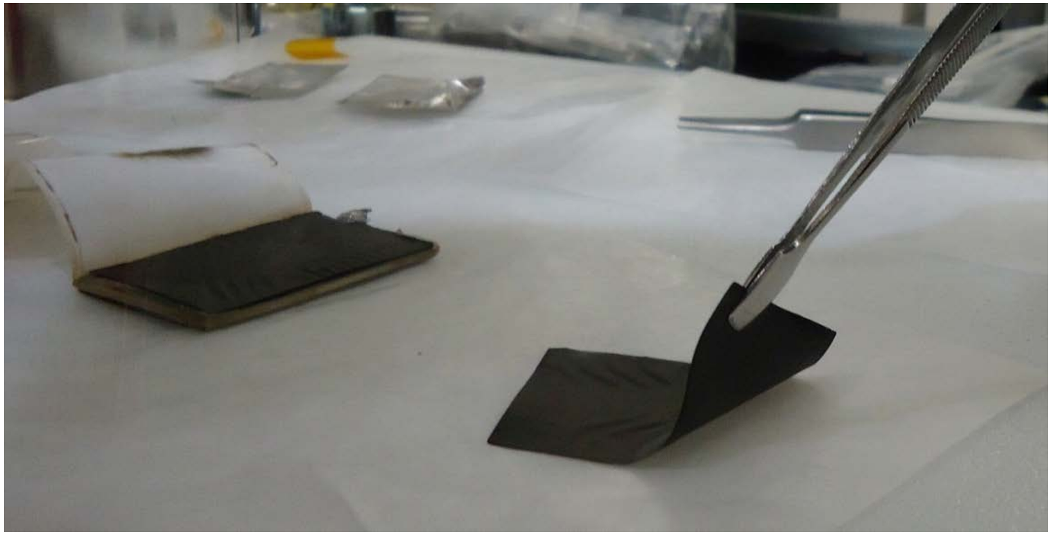
Case Study: Aging of HE5050 and 5-V Spinel Electrodes

- Initial disassembly in Ar-filled glove box
- HE5050: Gross observations: some staining on the separator; well-adhered laminates; staining pattern on the surfaces of both electrodes



Case Study: Aging of HE5050 and 5-V Spinel Electrodes

- Cell containing 5-V spinel
  - After cycling at 55°C, pouches were inflated; disassembly in a glove box shows poor adhesion of laminates to foil. The laminates possessed good mechanical strength

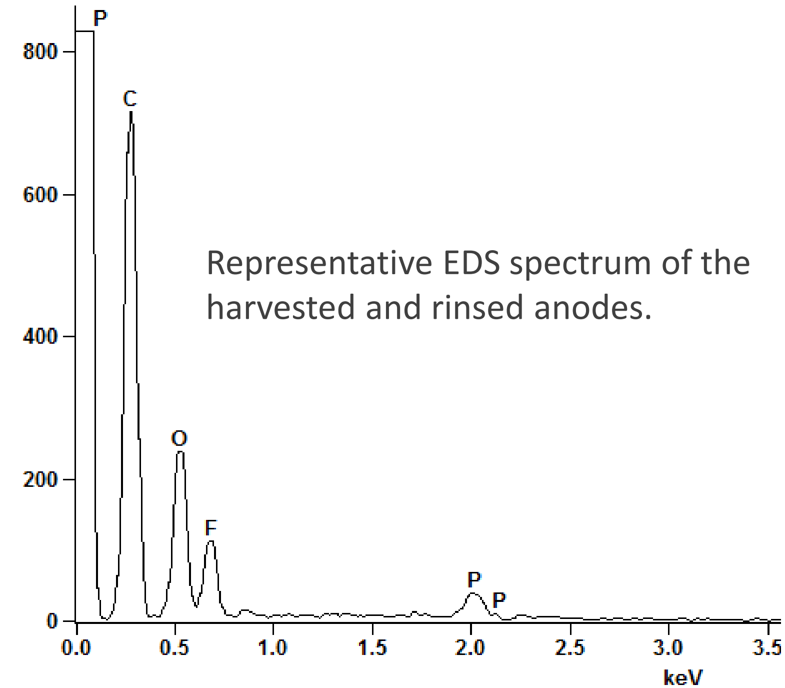



Case study: Aging of HE5050 and 5-V Spinel Electrodes

- Further disassembly of spinel-containing cell shows unusual “Zebra” staining pattern on separator and anode

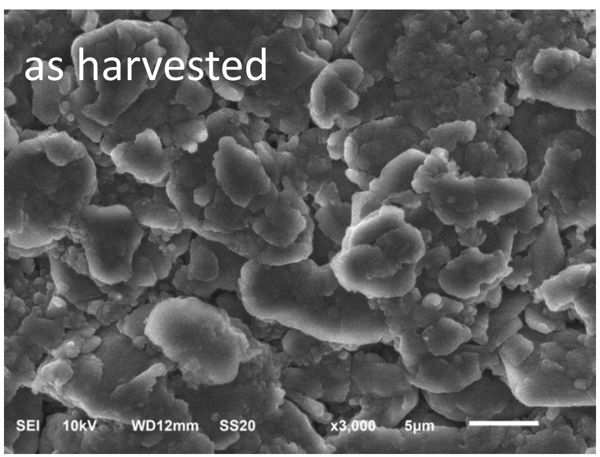
Case study: Aging of Negative in HE5050 Cell SEM/EDS

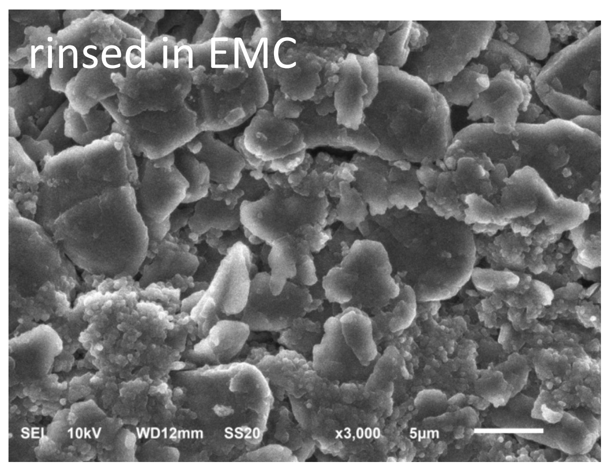
SEM vacuum sample holder for transfer of air-sensitive samples from glove box to SEM column



Representative EDS spectrum of the harvested and rinsed anodes.

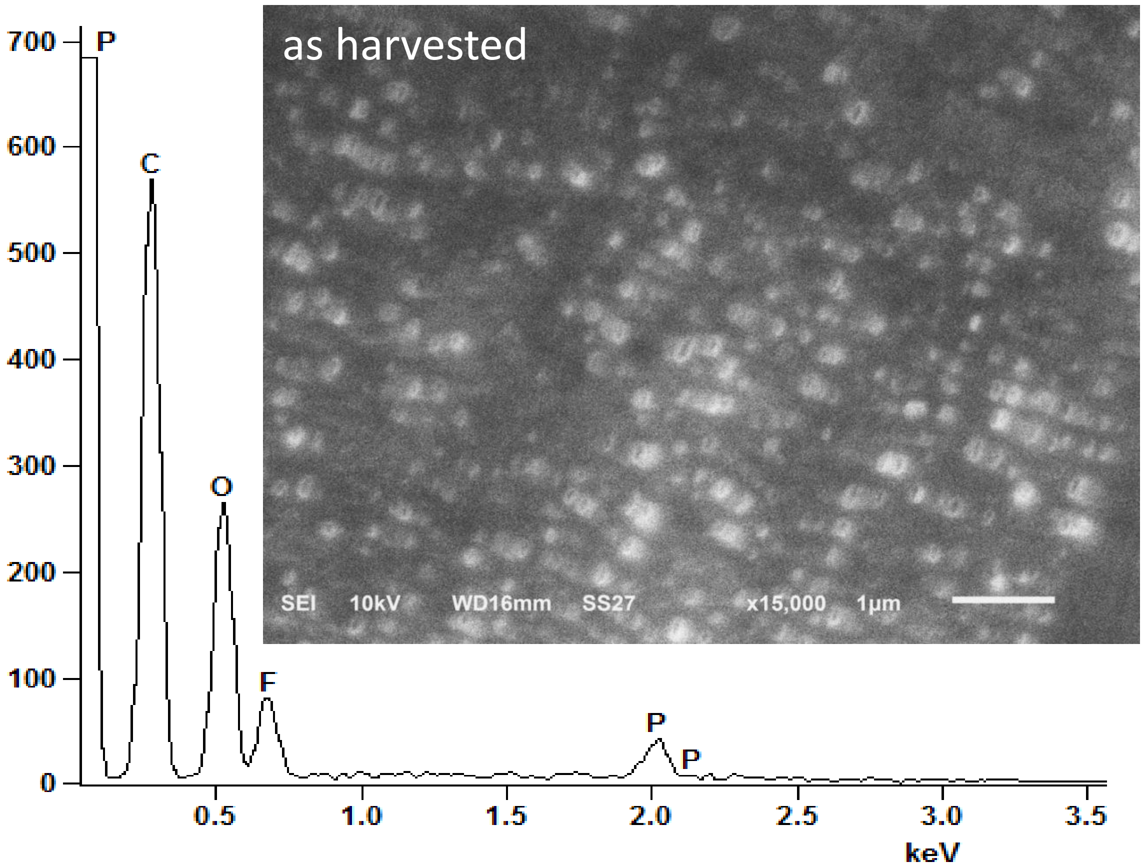
HE5050 Anode Surface



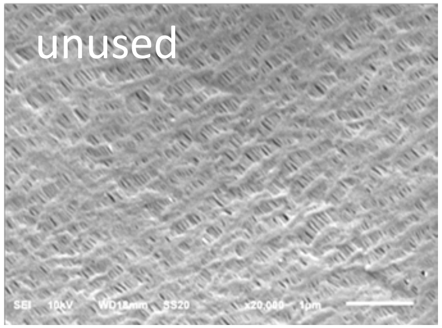


EDS results indicate the presence of insoluble reaction products that formed with the $LiPF_6$ electrolyte salt during cycling.

Case study: Aging of Separator in HE5050 Cell SEM/EDS

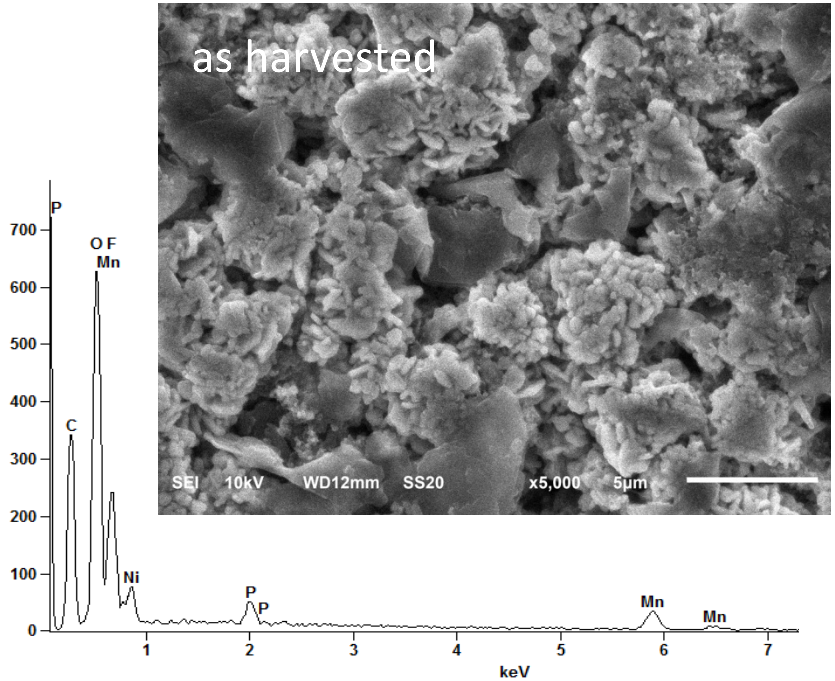


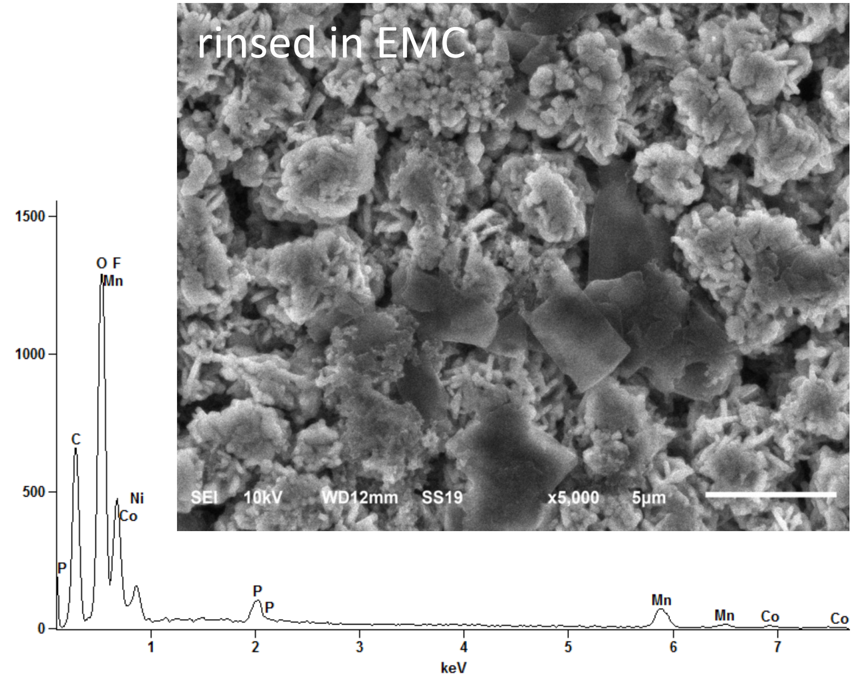
Celgard® Microporous Separator Membrane (25 µm tri-layer: PP-PE-PP)



EDS results indicate the presence of reaction products that formed with the $LiPF_6$ electrolyte salt during cycling.

Case study: Aging of HE5050 Cathode Electrode SEM/EDS

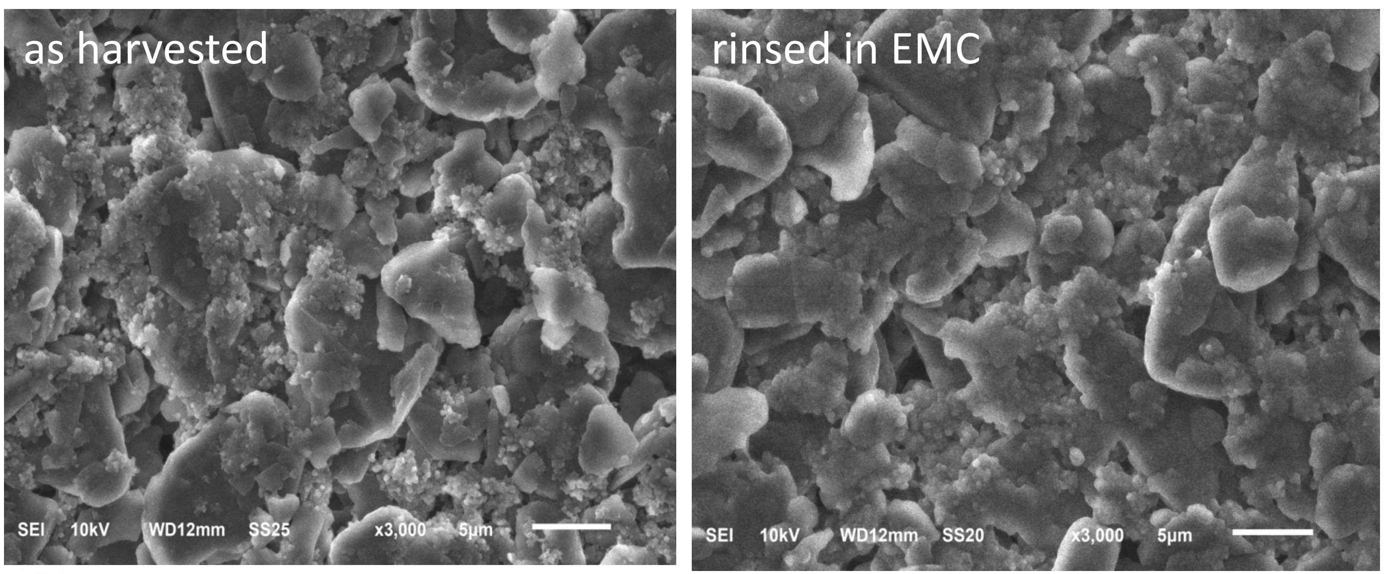




There are no resolvable microstructural differences between the harvested and rinsed cathodes. EDS spectra show that both surfaces have the same composition with the exception of trace Co detected in the rinsed cathode. F and P present in the rinsed cathode confirms the presence of insoluble reaction products on the surface of the cathode

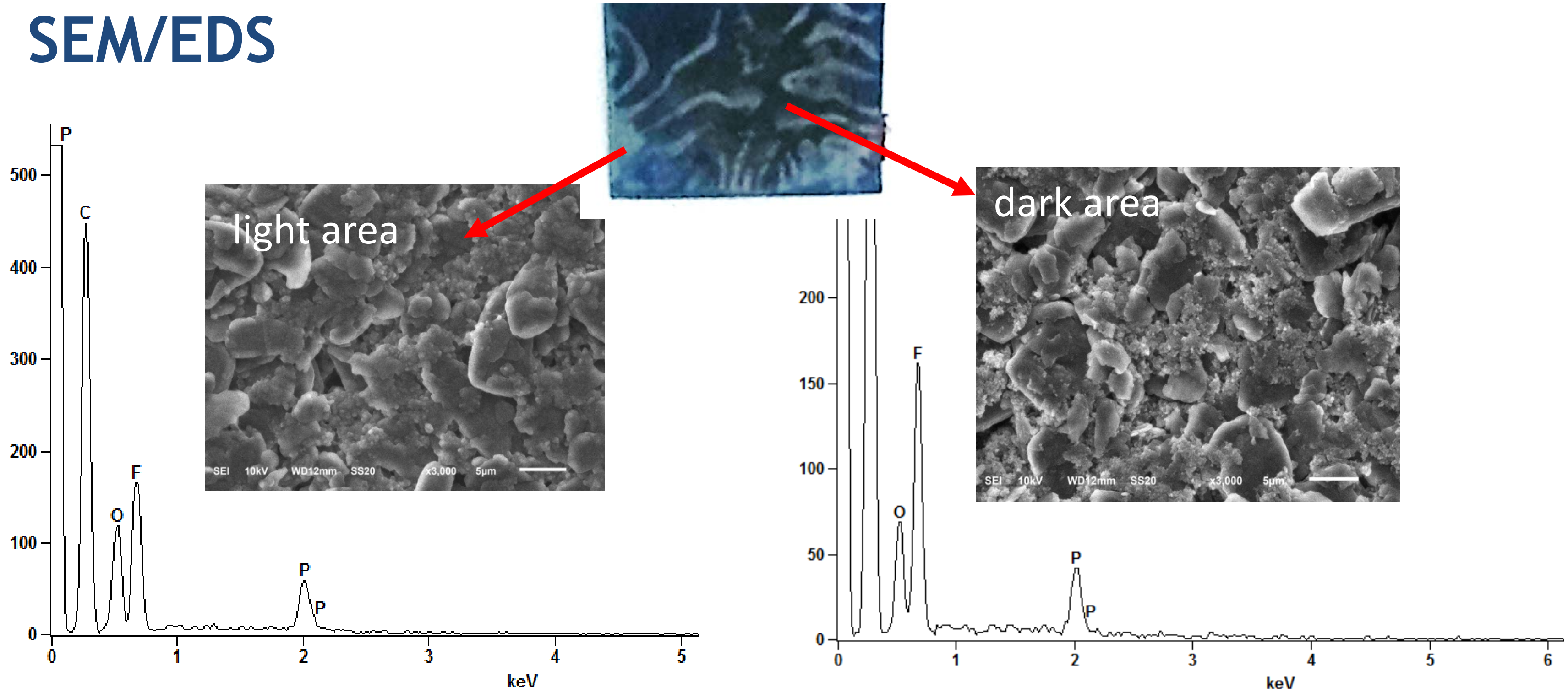
Case study: Aging of Anode in 5-V Spinel Cell SEM/EDS

The spinel anode and separator have a “zebra” pattern distinguished by light and dark areas.



There are no resolvable microstructural differences between the harvested and rinsed anode surfaces.

Case study: Aging of Anode in 5-V Spinel Cell SEM/EDS

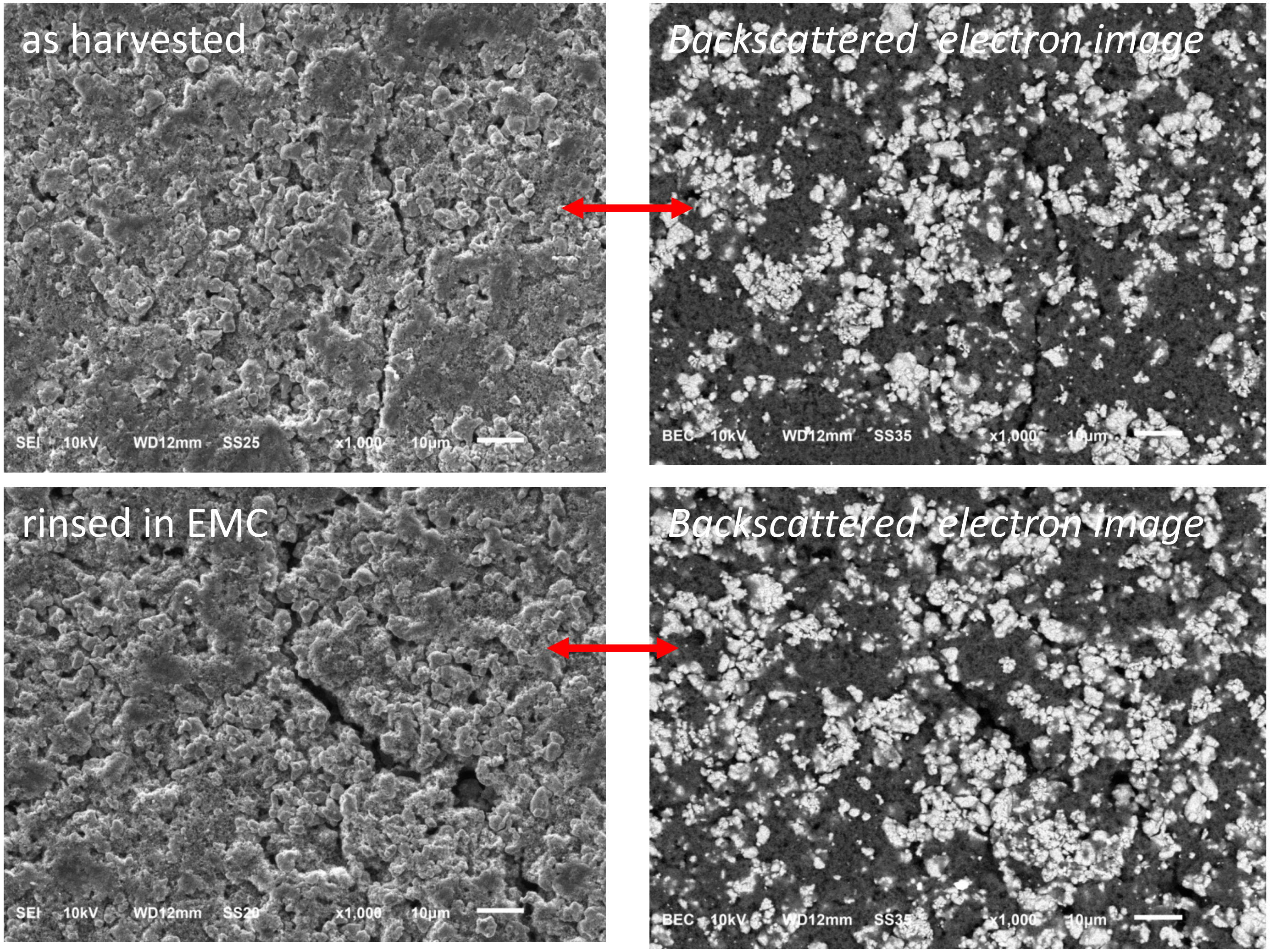


Element Line	Net Counts	Weight %	Weight % Error	Atom %
C K	3231	38.72	+/- 0.70	50.32
O K	704	17.02	+/- 1.57	16.60
F K	1398	33.93	+/- 1.41	27.88
P K	556	10.33	+/- 0.65	5.21
Total		100.00		100.00

Element Line	Net Counts	Weight %	Weight % Error	Atom %
C K	4149	50.05	+/- 0.77	61.72
O K	410	11.68	+/- 1.68	10.81
F K	1144	30.43	+/- 1.38	23.72
P K	382	7.85	+/- 0.66	3.75
Total		100.00		100.00

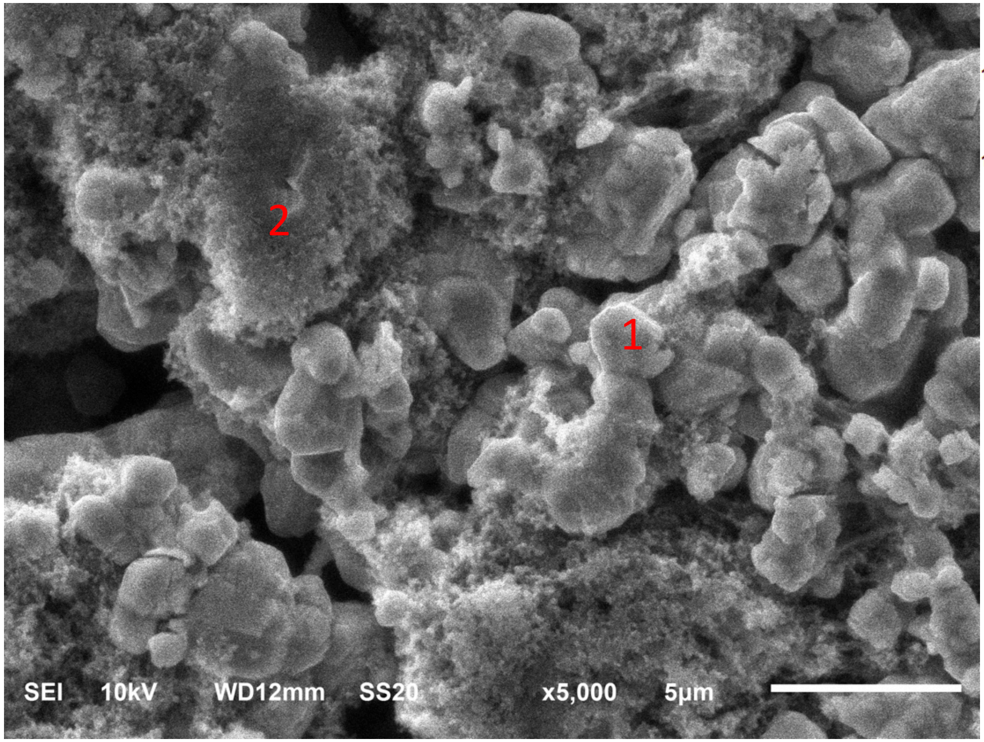
EDS shows the same composition but with more F and P associated with the light areas. This could represent regions with higher concentrations of reaction products formed with the $LiPF_6$ electrolyte salt during cycling.

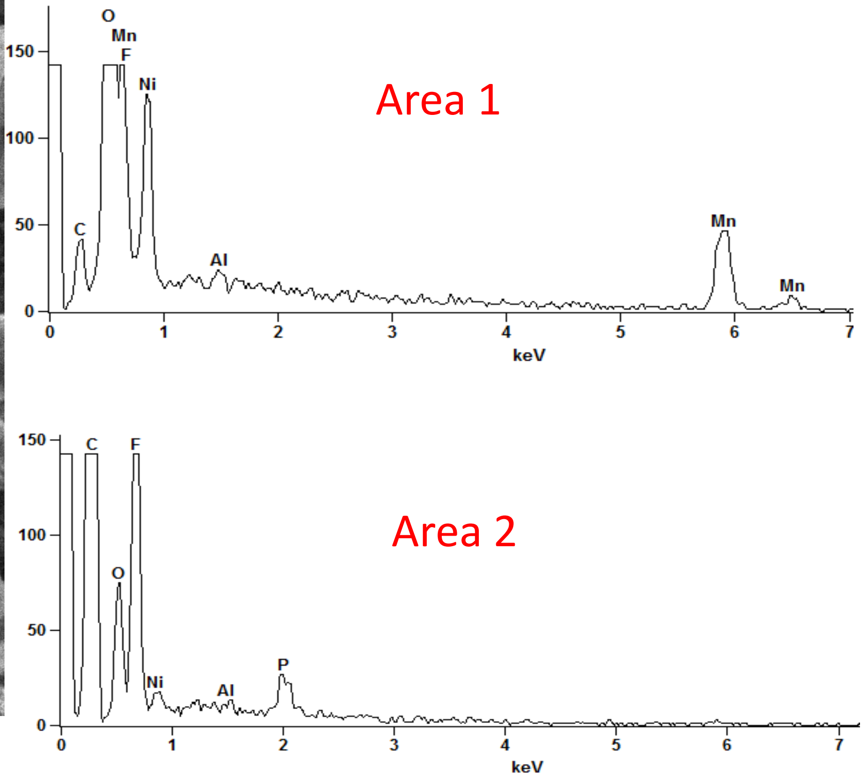
Case study: Aging of 5-V Spinel Cathode Electrode
SEM/EDS



Layer has extensive cracking. Rinsed and harvested surfaces appear similar. Backscattered images show atomic number contrast - carbonaceous regions black, oxide particles white.

Case study: Aging of 5-V Spinel Cathode Electrode SEM/EDS

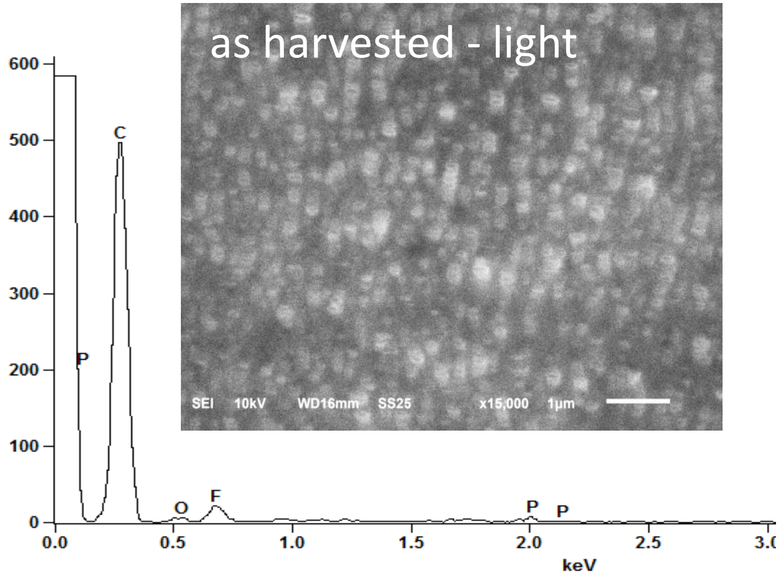


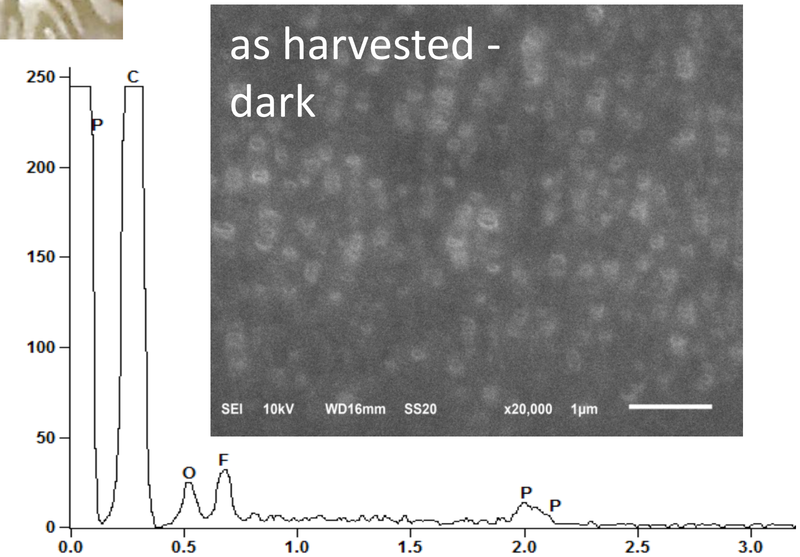


Area 1 of the harvested cathode consists of a spinel particle; area 2 consists primarily of super P carbon with a relatively high concentration of F. F is also present in area 1 but no P is detected.

Note: *EDS of the rinsed cathode surface was the same as above.*

Case study: Aging of Spinel 5-V Electrode - Separator
SEM/EDS





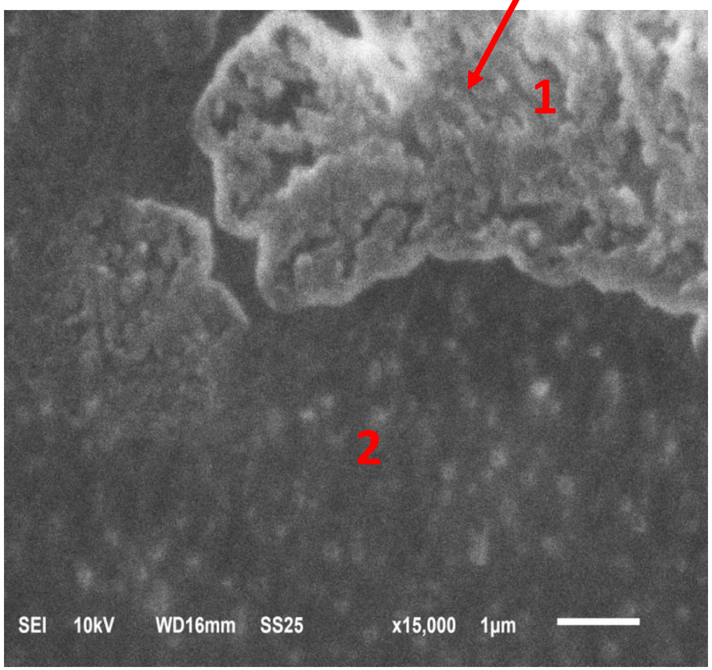
Element Line	Net Counts	Weight %	Weight % Error	Atom %
C K	3153	83.45	+/- 1.30	89.19
O K	23	2.24	+/- 1.17	1.79
F K	150	11.82	+/- 1.02	7.99
P K	42	2.49	+/- 0.53	1.03
Total		100.00		100.00

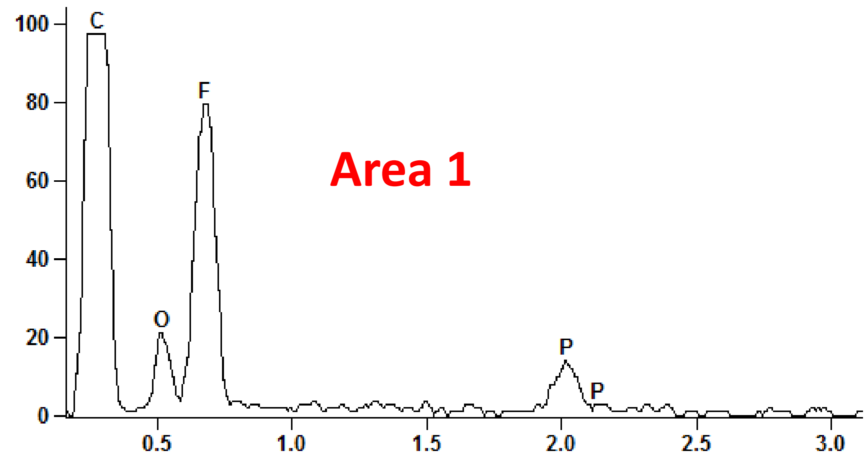
Element Line	Net Counts	Weight %	Weight % Error	Atom %
C K	4463	79.20	+/- 1.05	86.36
O K	116	6.82	+/- 1.06	5.58
F K	163	8.06	+/- 1.19	5.56
P K	164	5.93	+/- 0.80	2.51
Total		100.00		100.00

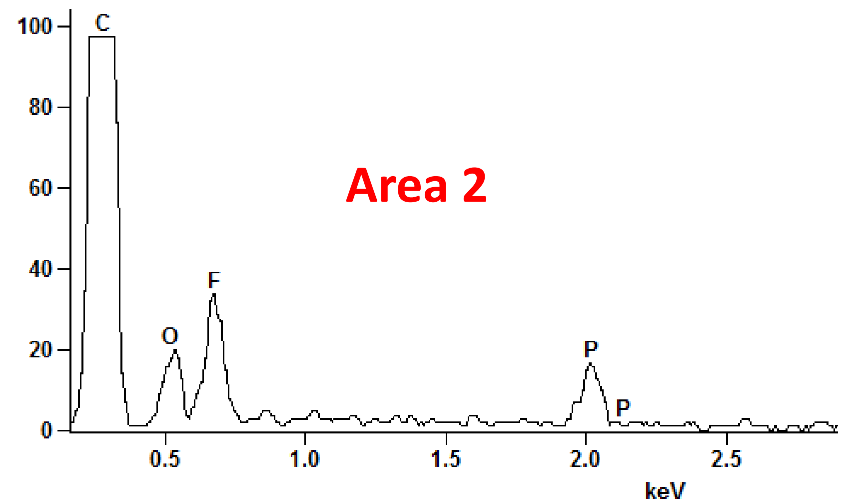
EDS shows the same composition but with more F associated with the light areas. This could represent regions with higher concentrations of reaction products formed with the $LiPF_6$ electrolyte salt during cycling and could correspond to the light areas on the anode.

Stripes could be from the uneven distribution of electrolyte during fabrication or uneven current distribution during testing.

Case study: Aging of 5-V Spinel Electrode - Separator
SEM/EDS

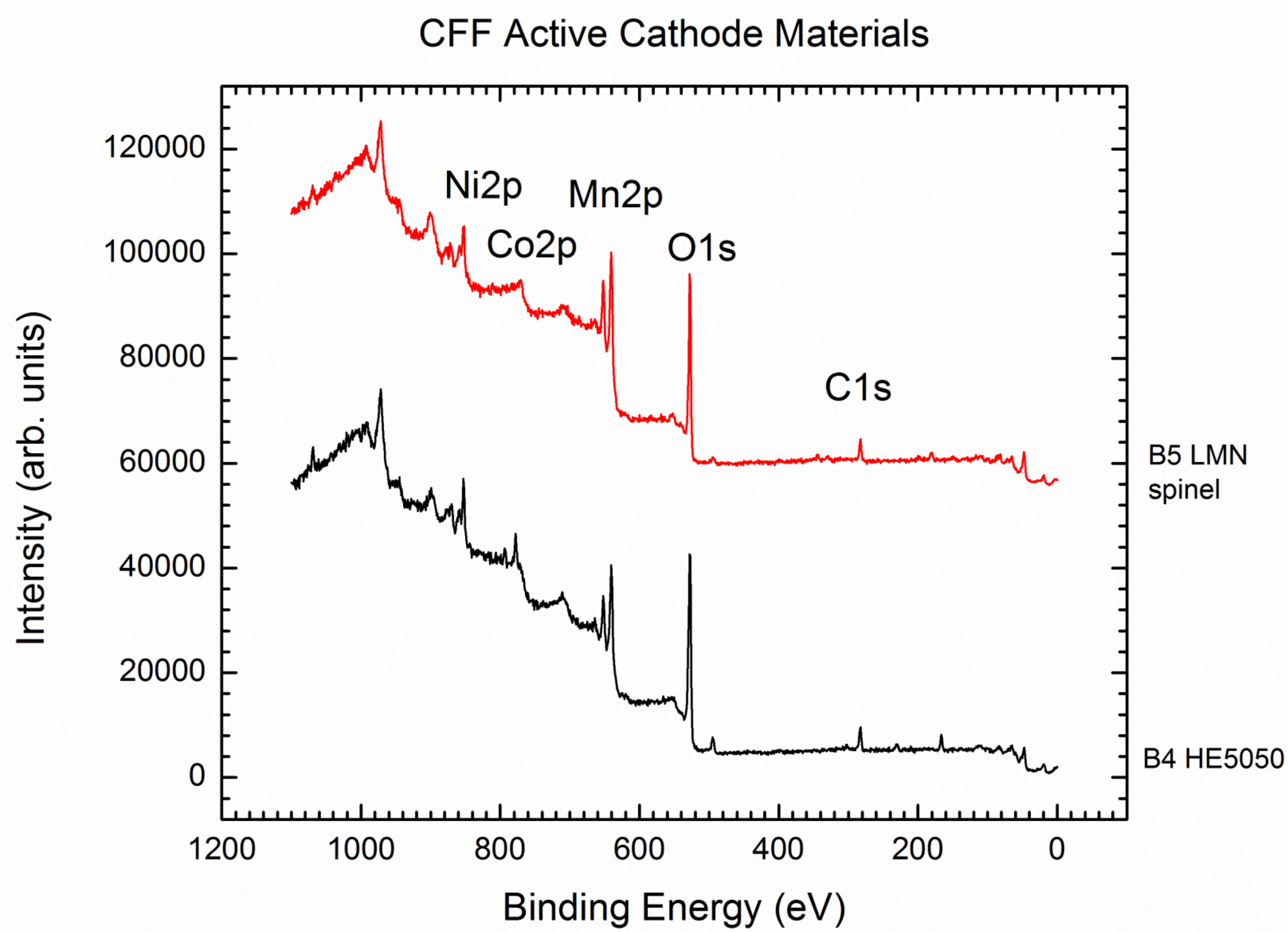




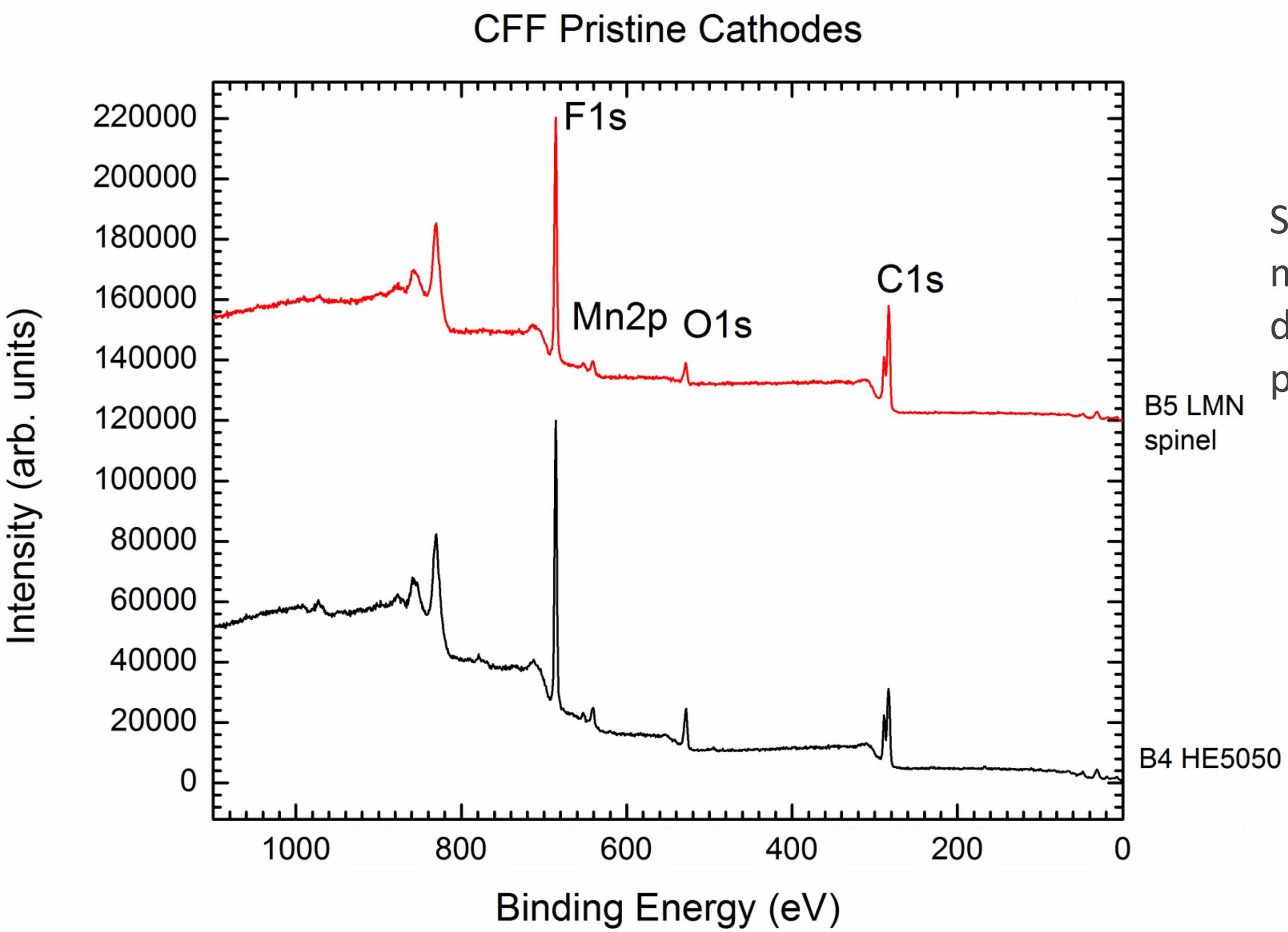


Both areas have the same composition but the lighter regions are significantly higher in F.

Case study: Aging of HE5050 and 5-V Spinel Electrodes -- Characterization of Active Powder



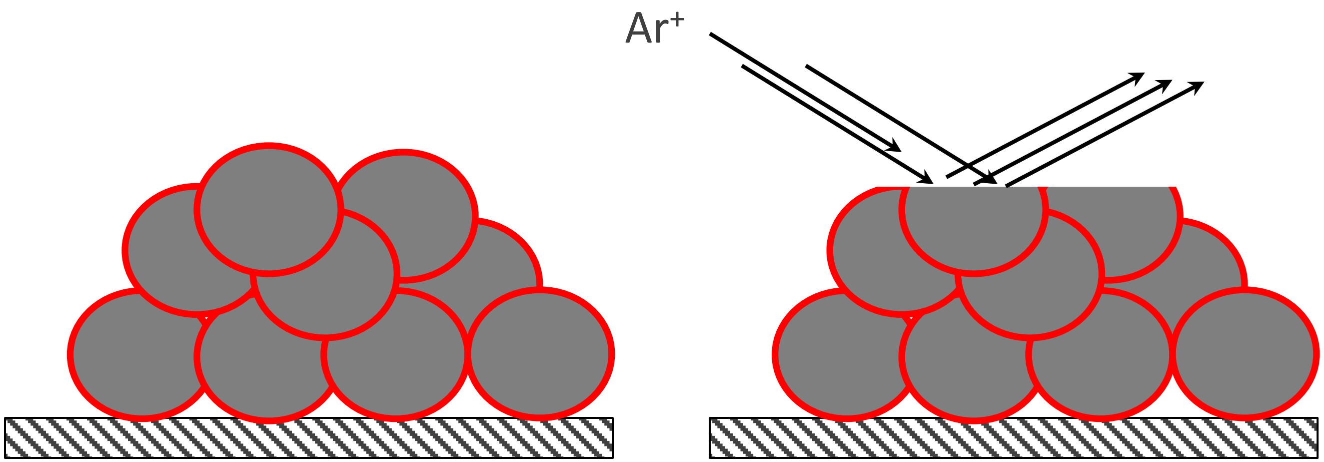
Case study: Aging of HE5050 and 5-V Spinel Electrodes -- Pristine Electrodes



Signals from transition metals are diminished due to coating of particles with binder

Case study: Aging of HE5050 and 5-V Spinel electrodes -- XPS morphology

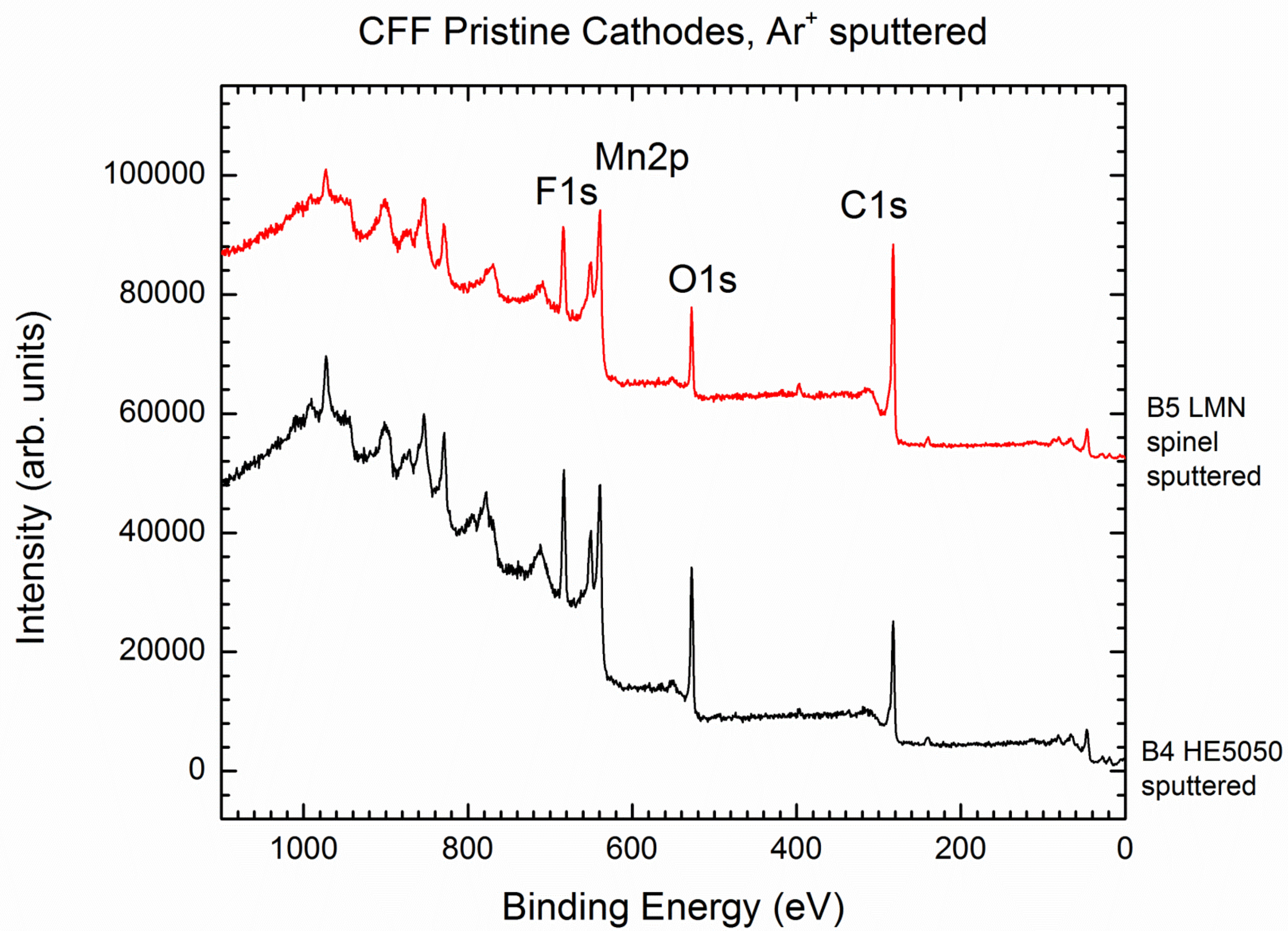
- XPS is extremely surface-sensitive
- Where needed, sputtering was used to remove surface material to observe changes in the materials below.
- Spectra also reflect surface topography; may also include SEI between exposed particles



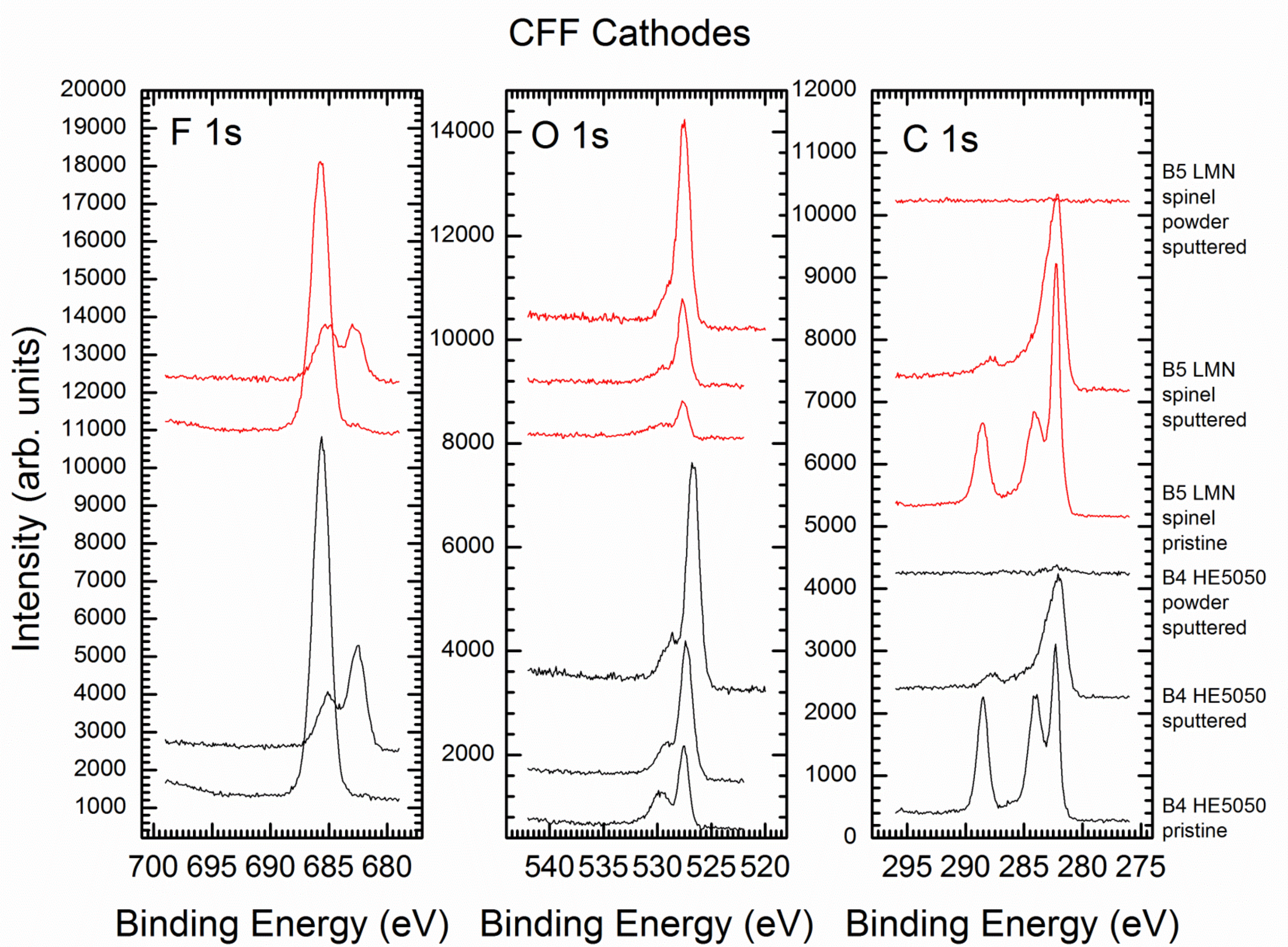
Before sputtering – see native surface materials. The red outline represents a surface layers, such as an SEI

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

Case study: Aging of HE5050 and 5-V Spinel Electrodes -- Pristine Electrodes After Sputtering

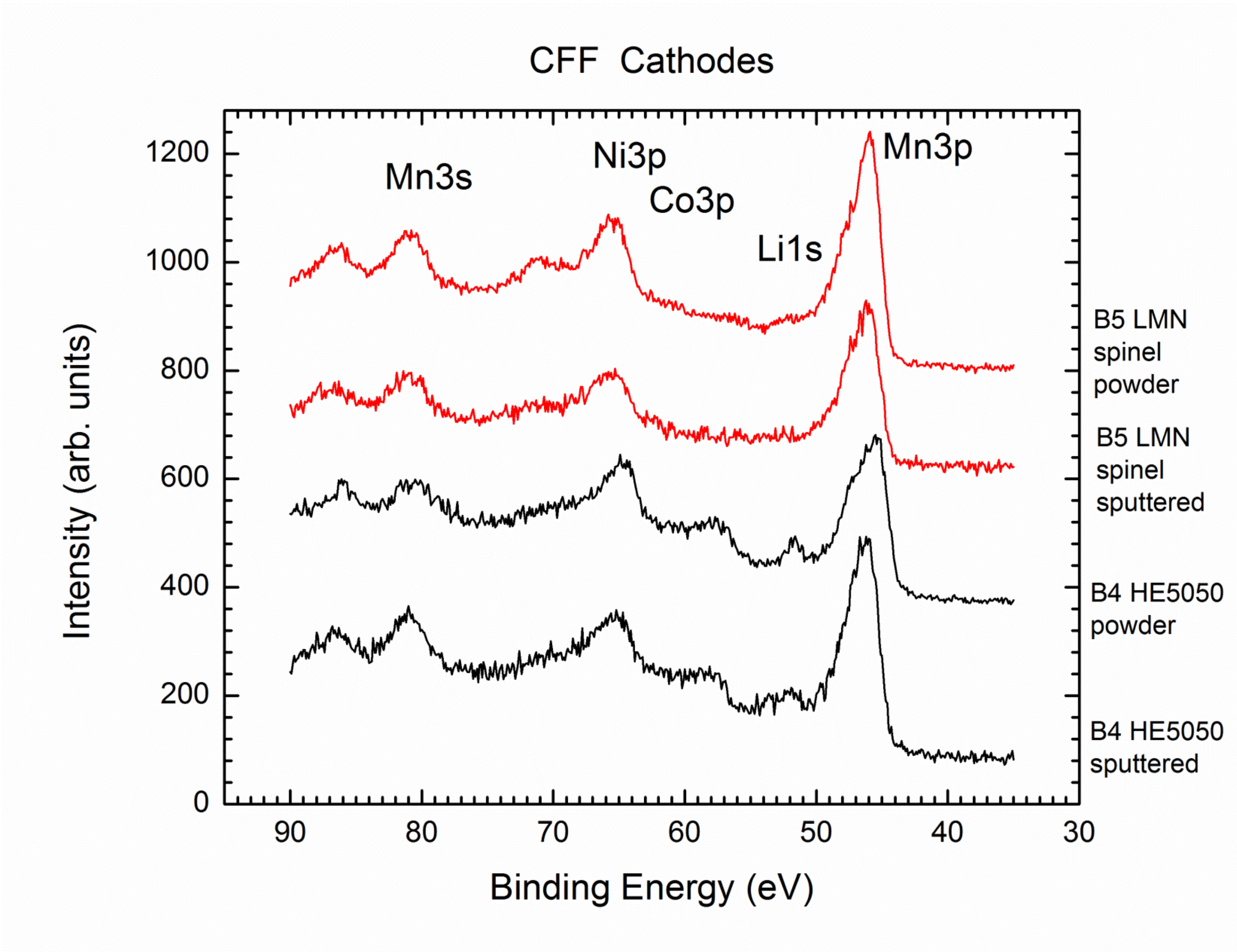


Case study: Aging of HE5050 and 5-V Spinel Electrodes -- Pristine Electrodes

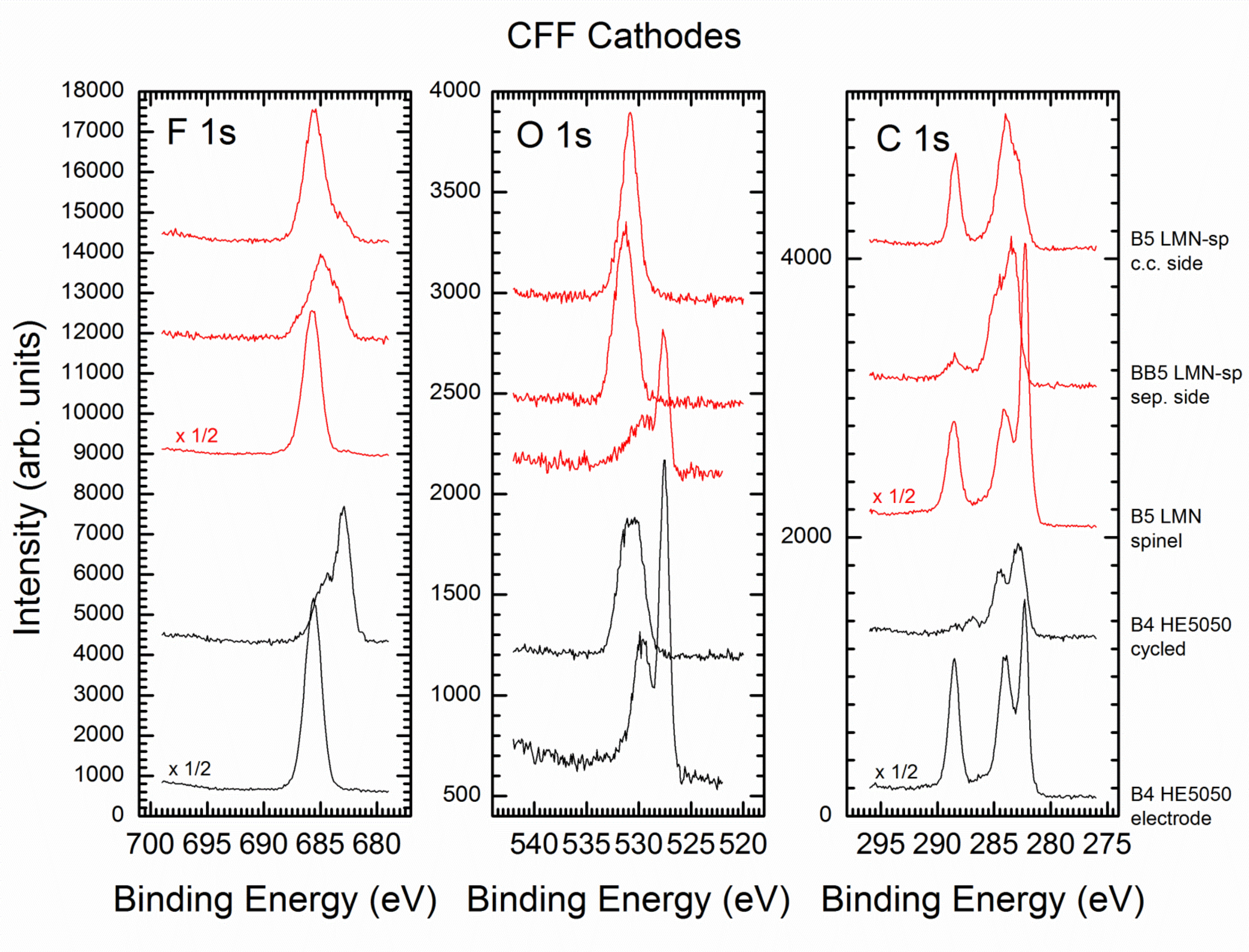


Changes in relative intensities signify changes in chemical states and amounts of each element

Case study: Aging of HE5050 and 5-V Spinel electrodes -- Pristine electrodes



Case study: Aging of HE5050 and 5-V Spinel Electrodes -- Cycled Electrodes



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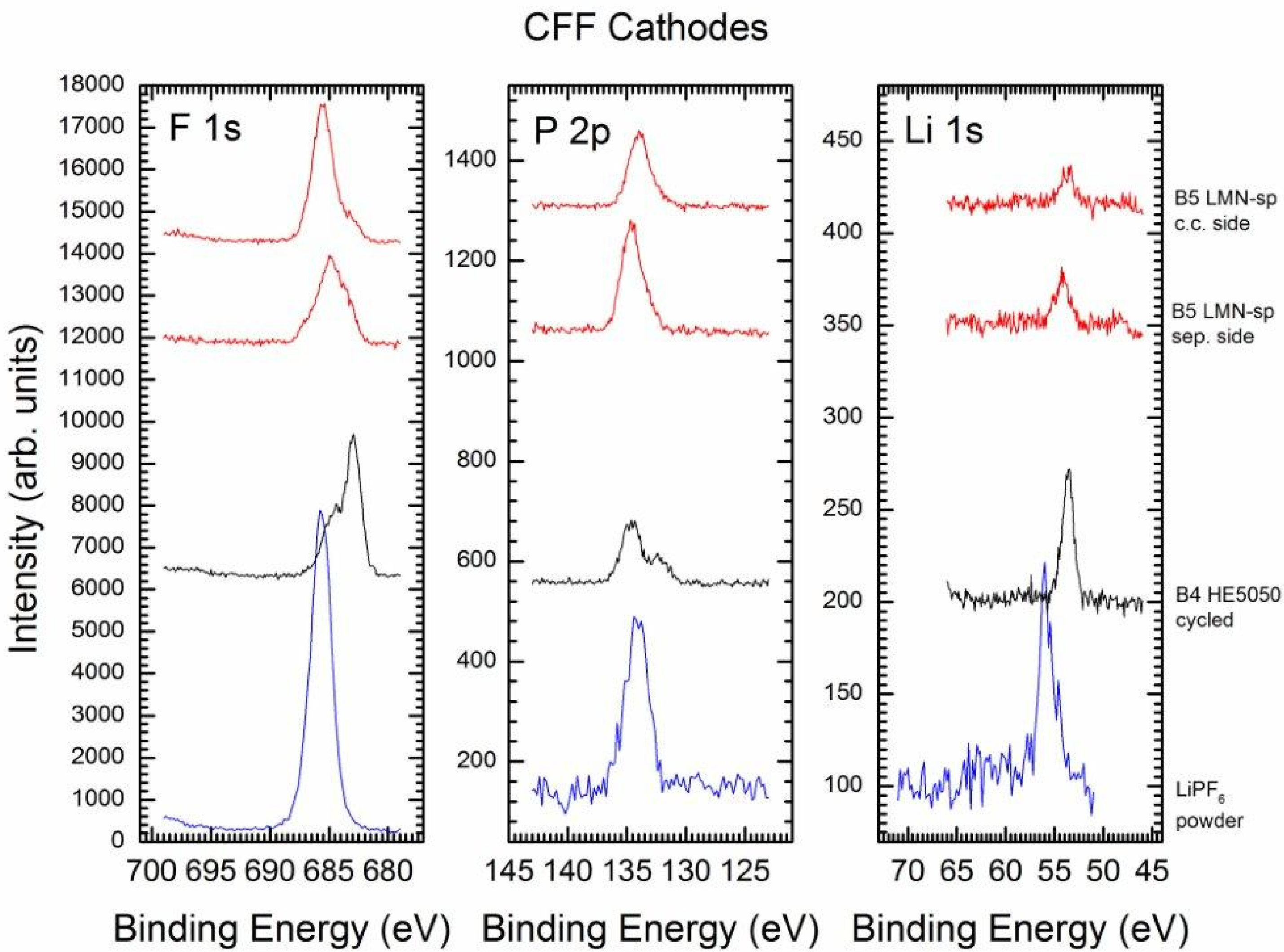

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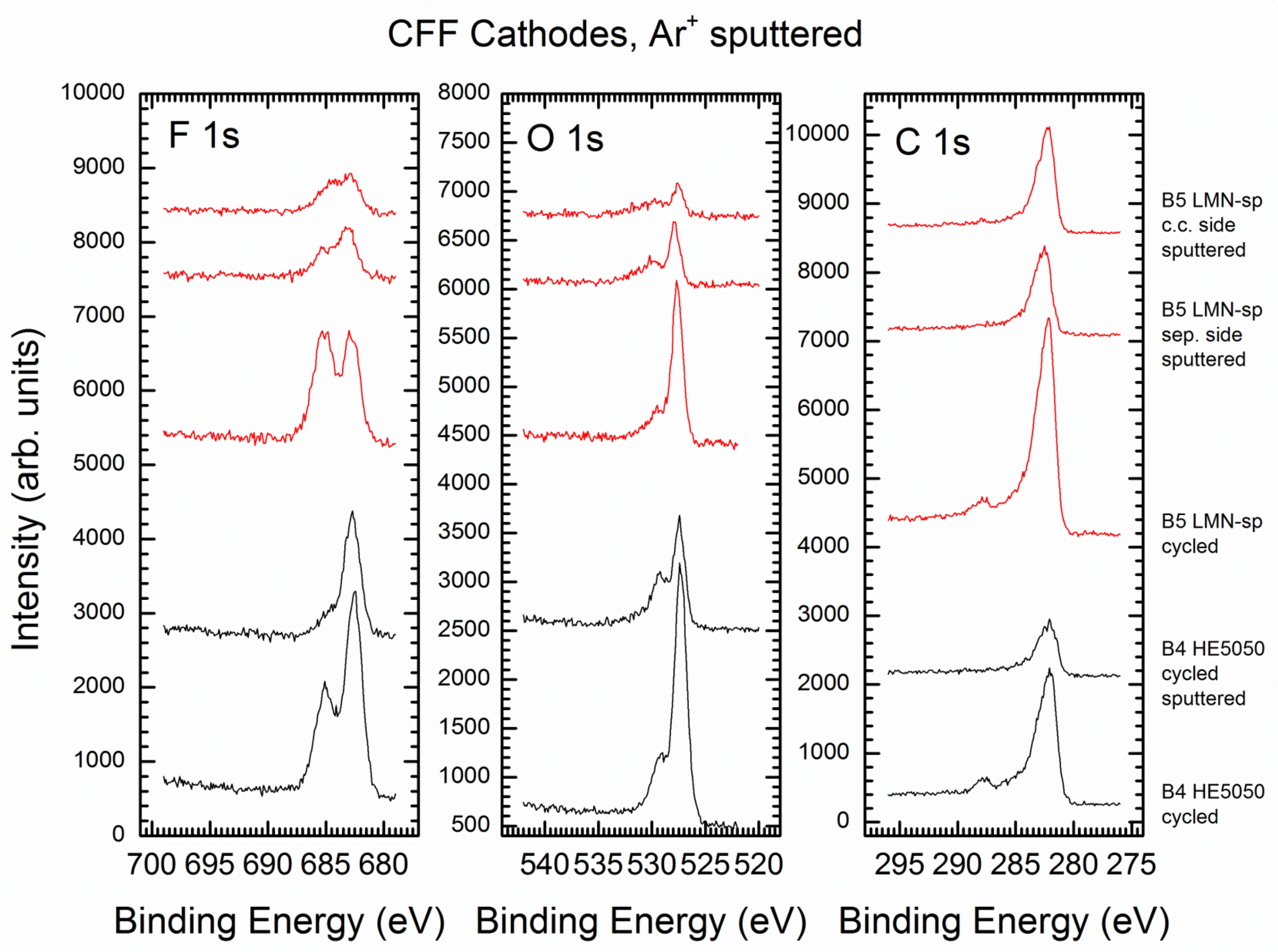

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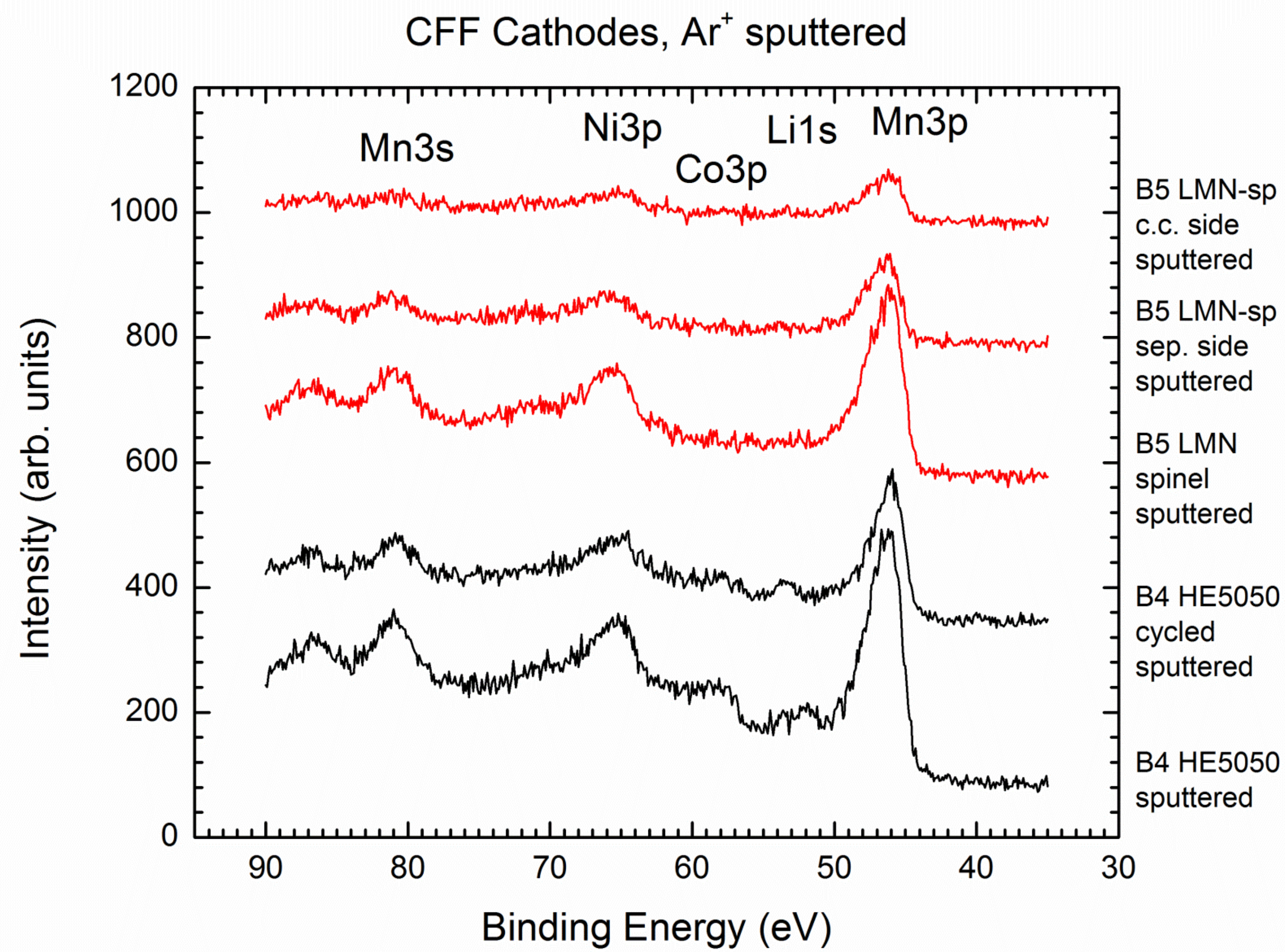

Summary

- A post-test facility has been established at Argonne to support DOE and USABC projects
- The Post-test Facility is integrated with the Battery Testing and Cell Fabrication Facilities
- Sample integrity is preserved by avoiding exposure to air
- Complementary characterization by microscopy, chromatography and spectroscopy
- Visual examination of disassembled cell components allows selection of areas of interest for sample harvesting
- Comparison of pristine and aged materials allows to correlate physicochemical changes at materials level to performance at system level

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- Other Argonne

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