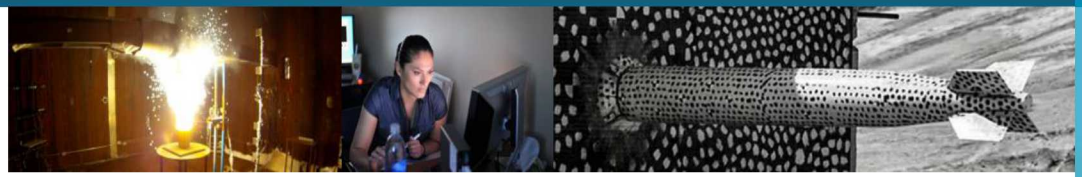
SAND2020-10594C

Sandia National Laboratories

Investigating the Chemical SEI of New and Aged Commercial Li Primary Batteries



Presented by:

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Background

Substantial interest within organization to develop well-characterized, limited-rechargeable Li primary batteries in-house

- Streamline qualification process and surveillance capabilities
- Improve reliability estimates

Underlying goal of project is to develop high energy density Li primary battery with long shelf life that can achieve 1-10 recharge cycles

First step is understanding cell electrode/electrolyte composition across a range of cell chemistries/ages

Methodology

Identify Li primary chemistries with rechargeable capability

Li/MnO_2 | Li/FeS_2 | Li/CF_x

- Extract electrodes (cell disassembly)
- Extract electrolyte (cell puncture/ centrifugation)

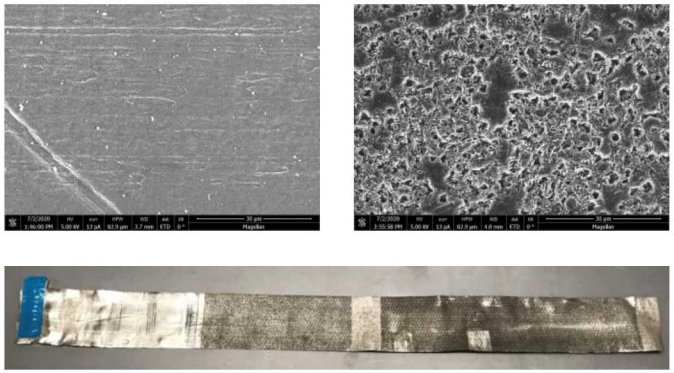
"Frankenstein cells" | Characterization

Characterization

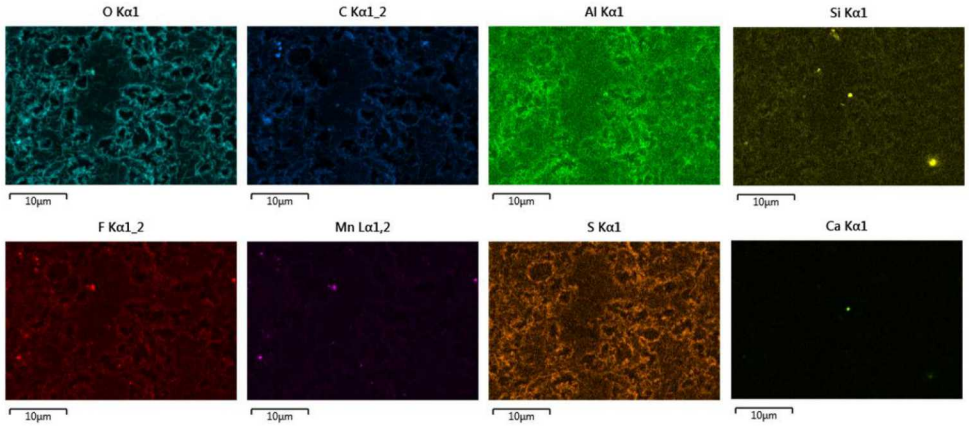
- XRD
- XPS
- SEM/EDS
- FTIR
- CryoFIB

2017 Duracell DL123A (Li/MnO_2) - Anode

SEM



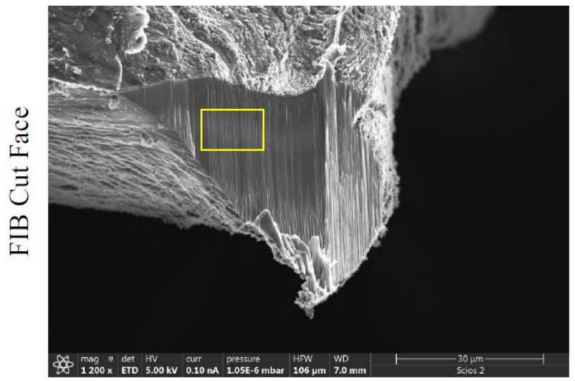
EDS



Observations

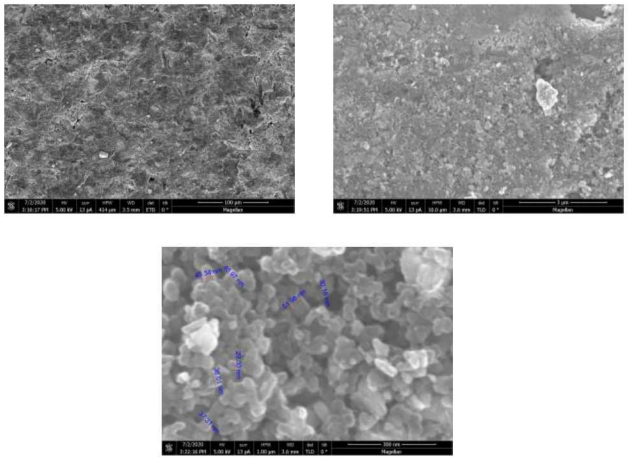
- Substantial Li pitting apparent in bulk anode
- Anode appears to be LiAl alloy (likely small % Al to improve mechanical properties). CryoFIB indicates trace Al, Si in anode bulk
- Particles containing F, S, O at anode surface suggests Li Triflate or Li TFSI salt
- Mn detected in bulk only (presumably an artifact of Mn dissolution)
- Si, Ca potential impurities

CryoFIB

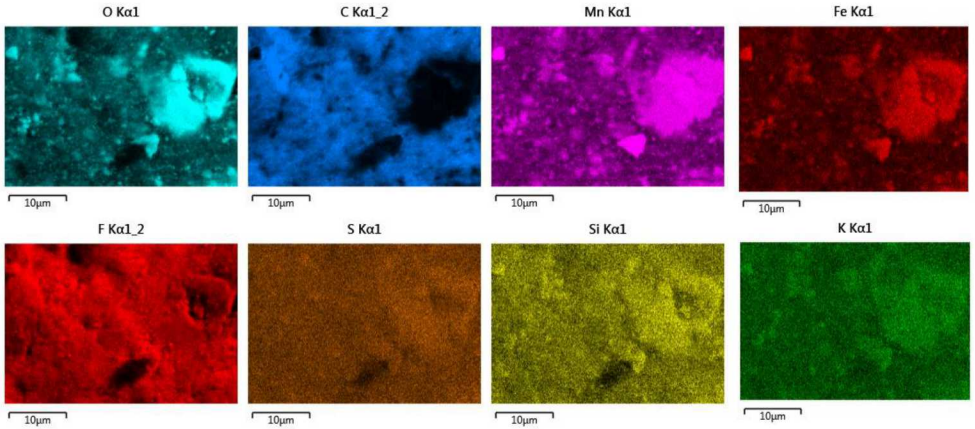


2017 Duracell DL123A (Li/MnO_2) - Cathode

SEM



EDS



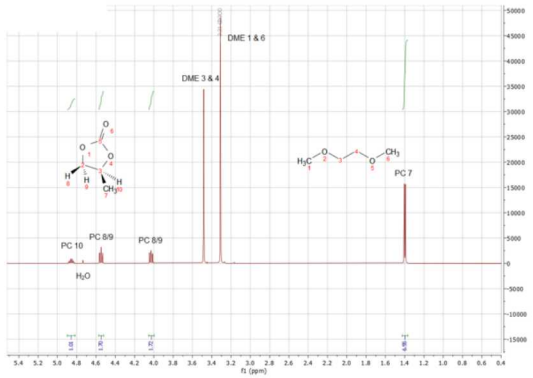
Cathode observations

- Consistent MnO_2 particle size (30 – 50 µm)
- Fe, K unexpected; Fe potential impurity from other batches
- Mesh current collector contains high concentrations of Cr and exhibits magnetic properties, indicating 400 series stainless steel (Note: XRD suggests 410L stainless steel)

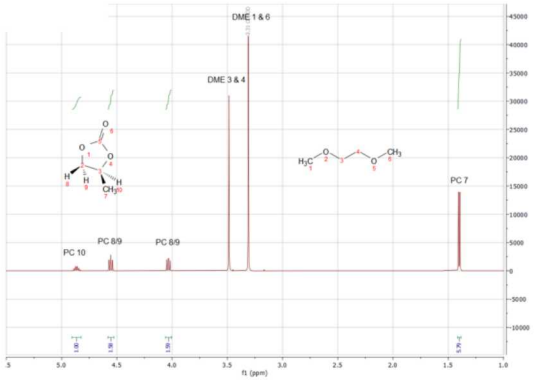
2017 Duracell DL123A (Li/MnO_2) - Electrolyte

NMR

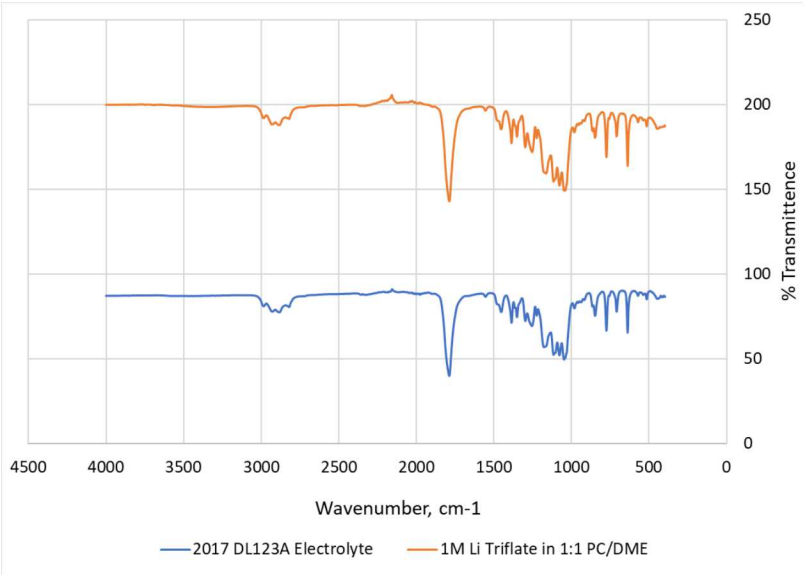
2017 DL123A Electrolyte



1M Li Triflate in 1:1 PC/DME



FTIR



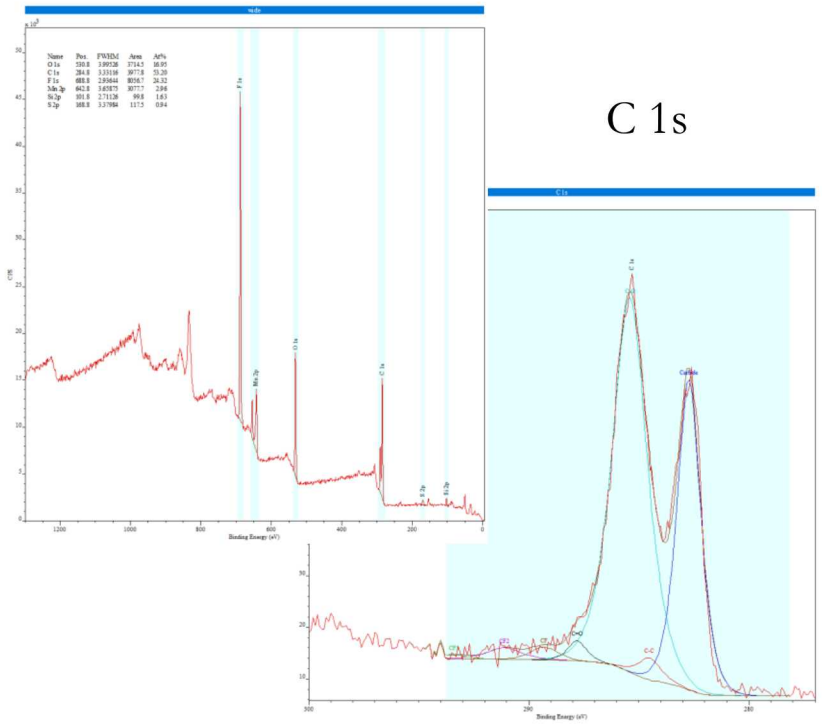
Commercial electrolyte compared to in-house standard using NMR & FTIR

Results indicate a Li Triflate in PC:DME electrolyte

2017 commercial cell electrolyte shows evidence of moisture contamination

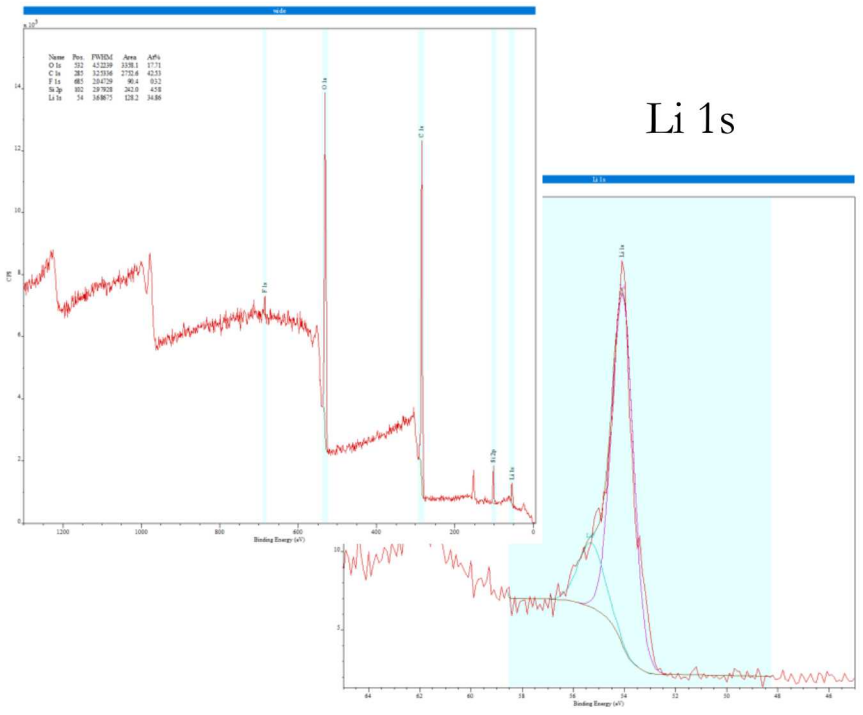
2017 Duracell DL123A (Li/MnO_2) – XPS Analysis

Cathode



C 1s

Anode



Li 1s

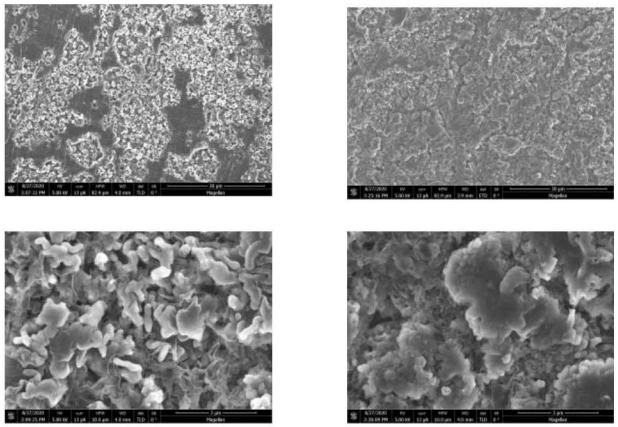
Initial findings

- Survey scan indicates F, Mn, O, C, S, Si (cathode) & F, O, C, Si, Li (anode)
- (Cathode) Consistent mix of C-C, C=C, along with –OH, C=O & ether groups indicate carbon black
- (Anode) F 1s peak becomes more defined with increased sputtering and appears to be LiF (BE = 685 eV, 55.5 eV), indicating potential interaction between Li Triflate & anode (Triflate known to aide in formation of thin, stable SEI)

2017 Energizer L91 (Li/FeS_2) - Anode

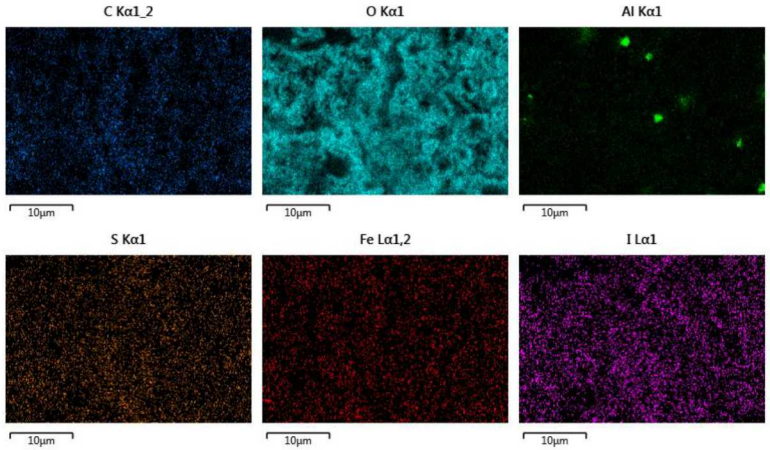
SEM

"Convex" *"Concave"*



EDS

"Concave"



Observations

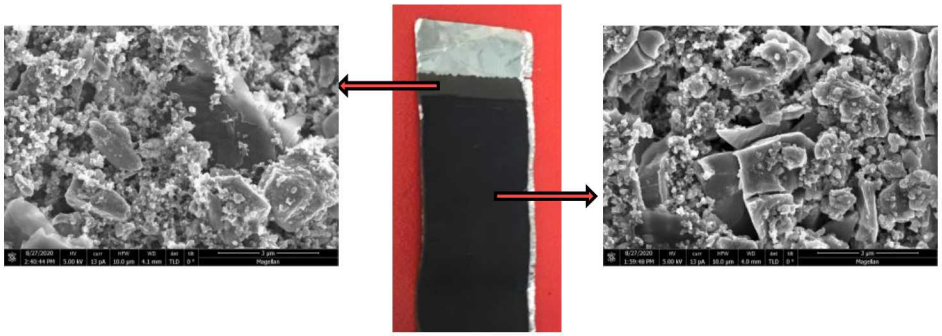
- "Concave" and "convex" samples exhibit substantially different morphology, though EDS tells similar story
  - Convex samples suggest extensive Li pitting (likely artifact of self-discharge)
  - Concave samples have rough and flaky surface, though no Li pitting evident
- Anode does not appear to be alloyed as we saw with DL123A
- Although anode not alloyed, cells do not exhibit poor performance at low discharge rates due to non-uniform anode stripping

2017 Energizer L91 (Li/FeS_2) - Cathode

SEM

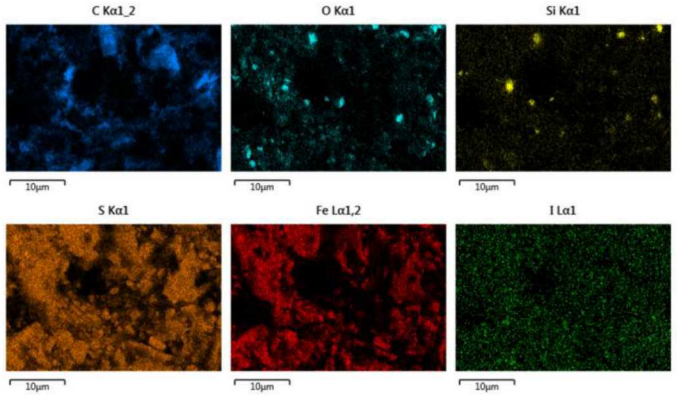
Base layer

Top layer



EDS

Top layer

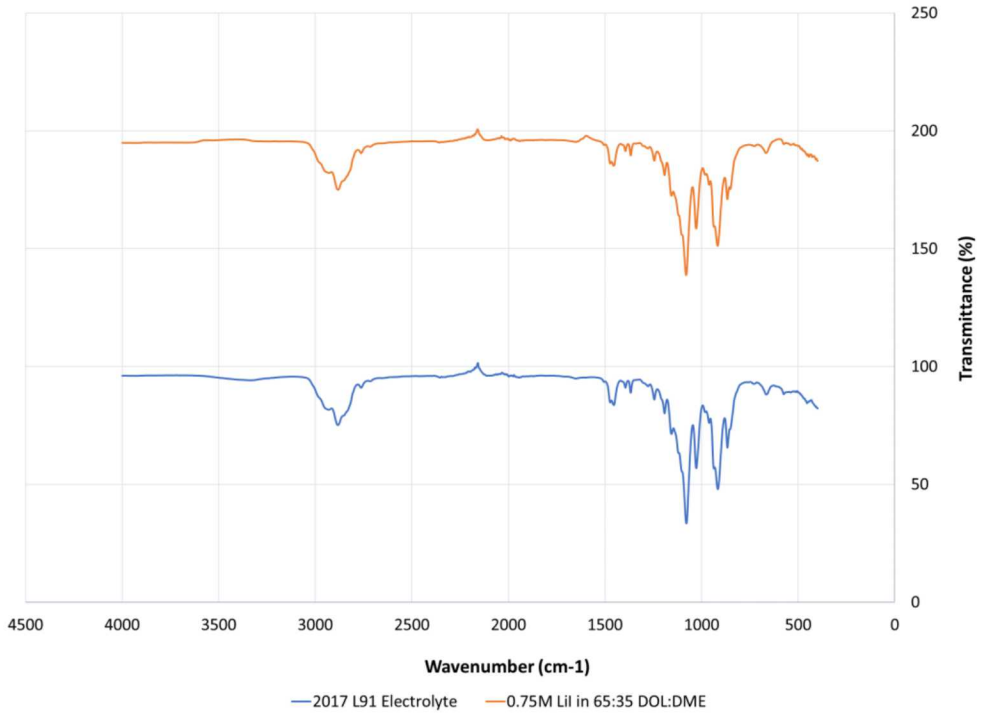


Observations

- Cathode comprises two distinct layers – color varies, but morphologically and chemically similar
  - FeS_2 occupies bulk composition, with amorphous C filling voids
  - Si-O compounds evident across electrode surface
- Uniform Iodine signal across surface indicates potential LiI salt
- Cathode current collector spectrum (not shown) indicates bulk Al composition

2017 Energizer L91 (Li/FeS_2) - Electrolyte

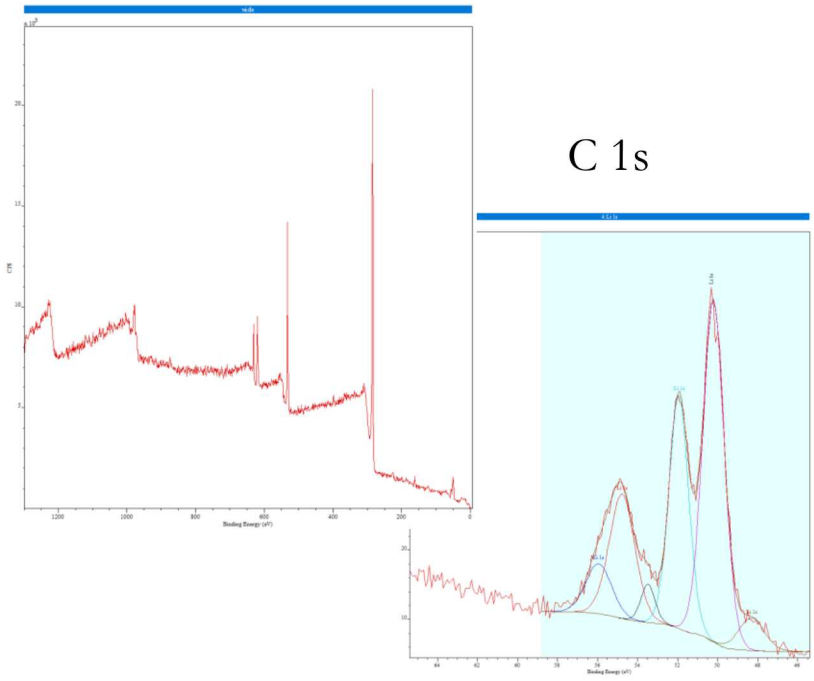
FTIR



- Electrolyte solvent appears to be DOL:DME mixture
- LiI not IR active species; will need to run NMR to determine salt concentration
- EDS indicates LiI salt is highly probably

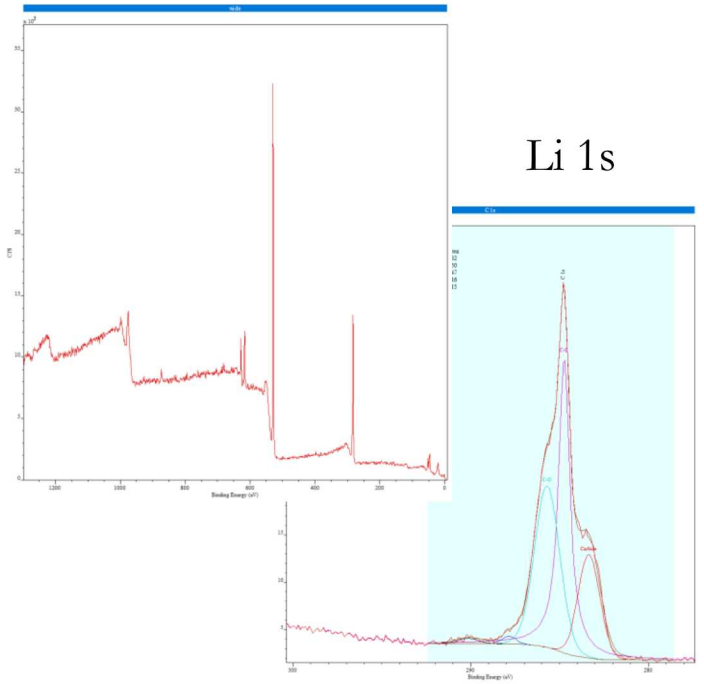
2017 Energizer L91 (Li/FeS_2) – XPS Analysis

Anode



C 1s

Cathode



Li 1s

Initial findings

- (Cathode) Analysis of C- peaks again indicate carbon black (potentially graphite as well)
- If you can identify an ether in the XPS scan, look at how it changes w.r.t sputtering at anode and discuss the ring opening mechanism to create a robust SEI
- (Anode) Samples without sputtering exhibit both I_2 and Alkali Iodide (potentially LiI)
- (Anode) Ether groups in O 1s, C 1s peaks suggest ring-opening mechanism of 1,3-Dioxolane previously outlined in literature – mechanism known to develop robust SEI

Closing thoughts

Anode morphology varies based on concavity, whereas cathode morphology appears consistent – may be an artifact of manufacturing

Initial estimates predict cells contain large excess of anode, presumably intended to extend shelf life as Li corrodes

Were able to partially characterize the SEI layer using XPS, though further analysis required

Conducted full suite of characterization of the anode

Source of Si, Na, K & Fe in cells still under consideration

Rechargeability considerations

- BR1/2AA CF_x electrolyte will likely need to be fortified with ether-based solvent to prevent perpetual Li corrosion during cycling (esters, alkyl carbonate do not form robust SEI)
- DL123A MnO_2 & BR1/2AA CF_x batteries have exhibited poor discharge performance at low discharge rates – may need to limit discharge voltage limit or employ current collector

Acknowledgements

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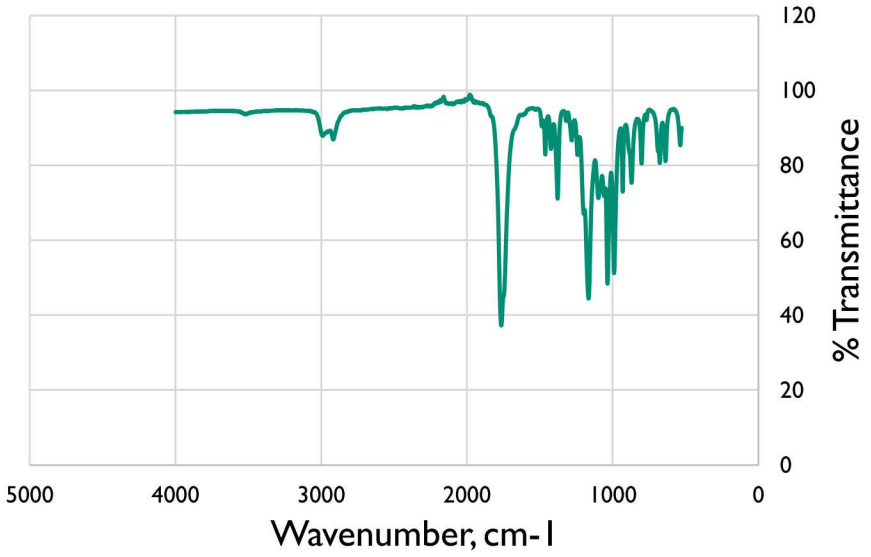
Supplementary Information

FTIR - 2017 Panasonic BR1/2AA

2017 Panasonic BR1/2AA Electrolyte



γ-butyrolactone (GBL)