Thermo Fisher SCIENTIFIC

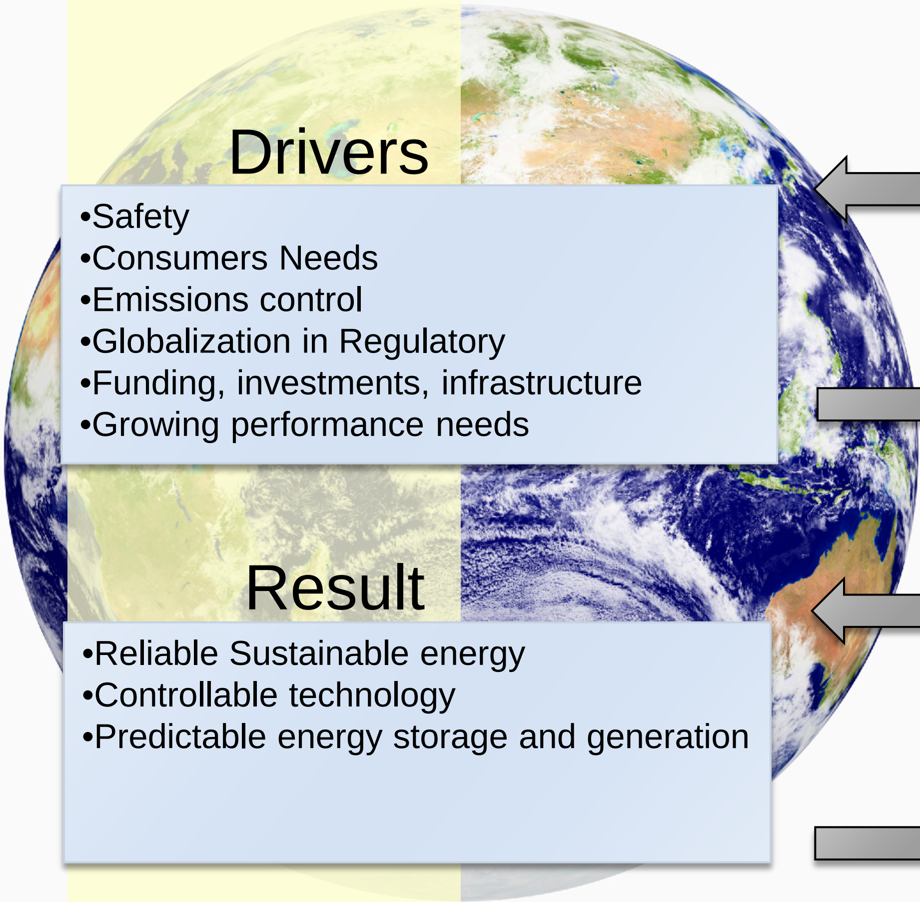
From Surface To Cell: Understanding the Lithium Ion Battery

The world leader in serving science

Content Discharge

- Detail the Li-ion Battery industry drivers & trends
- Our position in industry and our interest in the application
- Battery research overview
- How the LiB works and targeted research problems
- Application capabilities
- Example LiB solutions to tough problems
- Sample Discussions/LiB Inquiries

Global Drivers



Drivers

- Safety
- Consumers Needs
- Emissions control
- Globalization in Regulatory
- Funding, investments, infrastructure
- Growing performance needs

Result

- Reliable Sustainable energy
- Controllable technology
- Predictable energy storage and generation

Global Market Objectives

- Reduce environmental hazard
- Reduce cost to manufacture
- Increase power & energy of LiB
- Breakdown monopoly
- Enhance warranties and consumer confidence

Market Influence

- Pervasive technologies- Auto
- Plateau of available LiB power
- Limit to fuels and alternative energy resources
- Start-ups, JVs, regional shifts

Forecast

- End market CAGR 23.3% 2013-2020
- By 2013 >100 competitive players in LiB
- EV market to be 2X consumer LiB by 2023
- Strong funding of academic, contract labs, and government funded test-houses

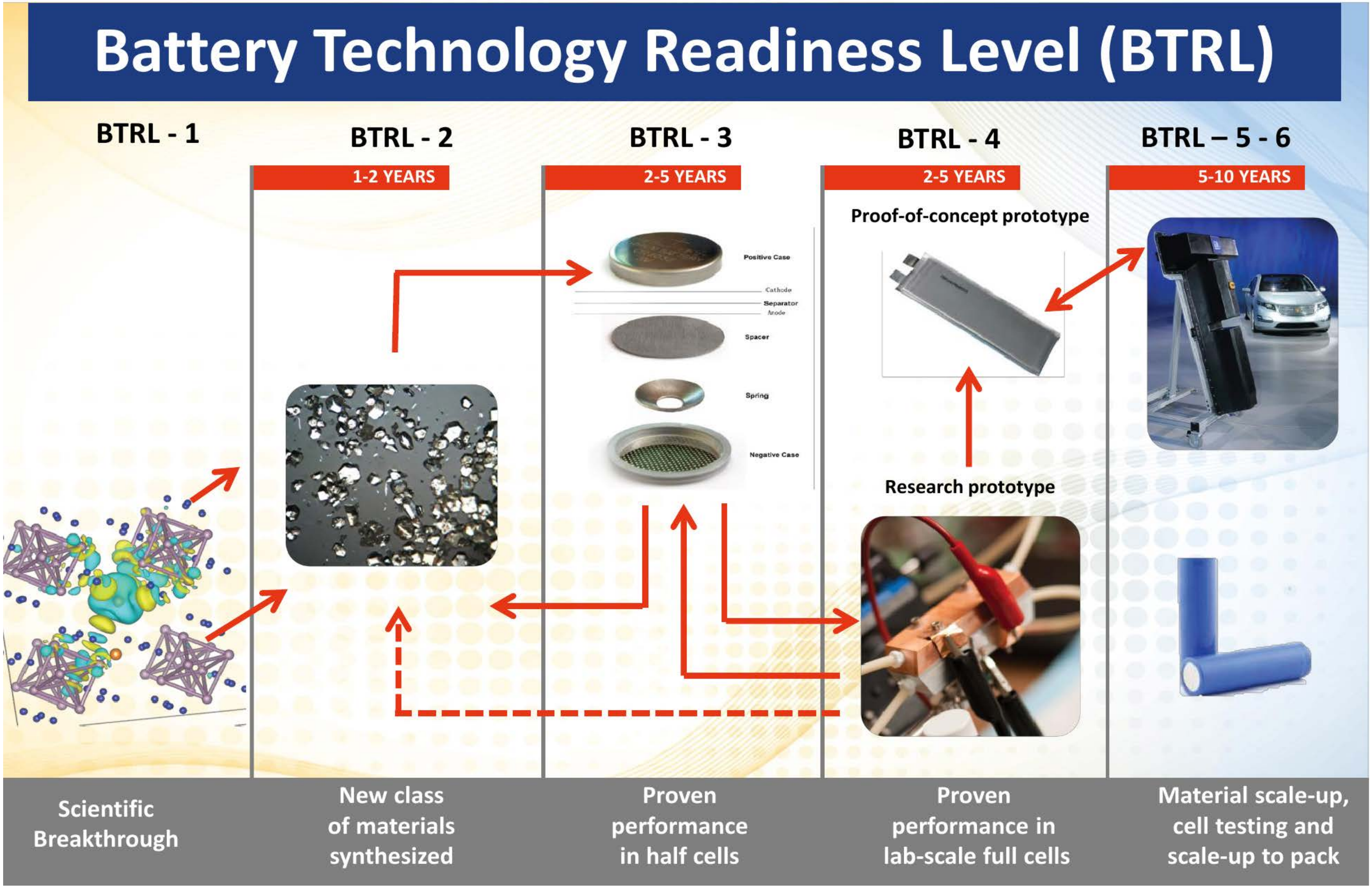
Our Responsibility Behind Understanding LiB

We have the responsibility to add our experience in the areas of research that make our world healthier, cleaner, and safer.

Build new Solutions that take a closer look at the materials, changes, and future of battery analysis.

Help our global partners achieve their long term research goals!

The Ten Year Cycle of R&D to Market

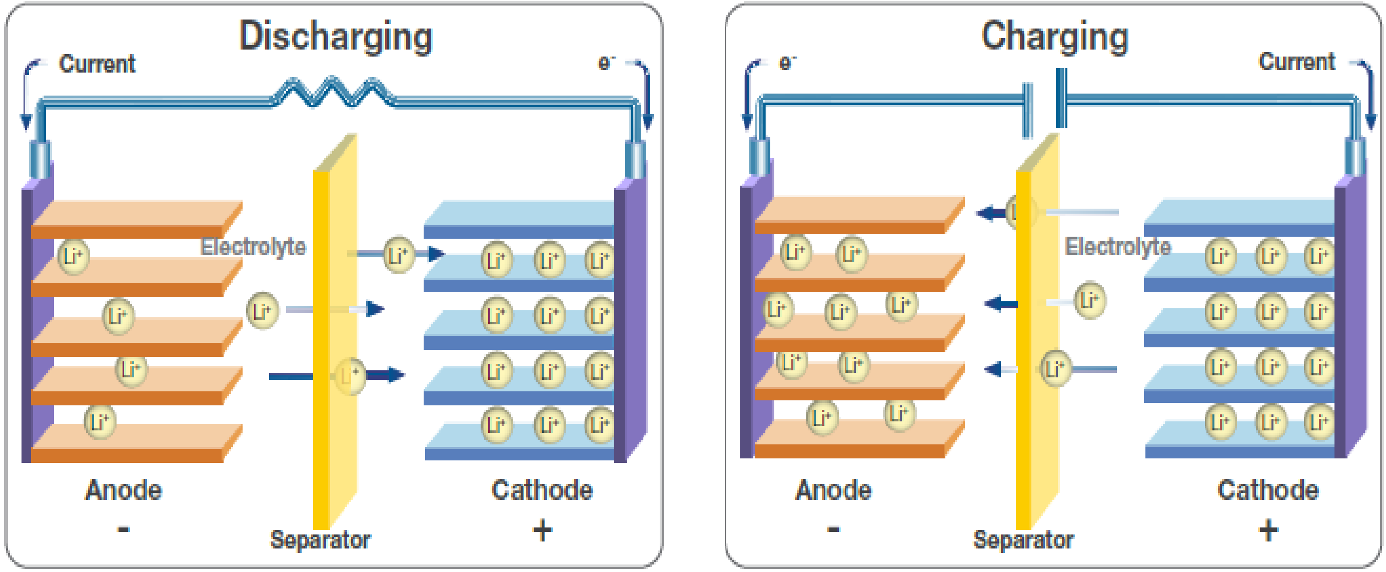


Property of Argonne National Laboratory: https://anl.app.box.com/batterytechnologyreadiness

How the Lithium-ion Battery Works

Chemistry:

- **LCO**
  Lithium Cobalt Oxide
- **LFP**
  Lithium Iron Phosphate
- **LMO**
  Lithium Manganese Oxide
- **NMC**
  Nickel Manganese Cobalt Oxide
- **NCA**
  Ni Cobalt Al Oxide
- **LTO**
  Lithium Titanate



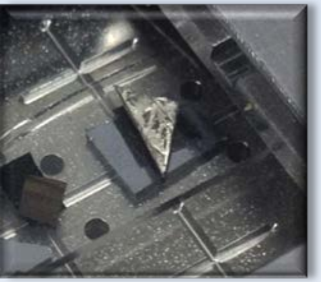
Rechargeable

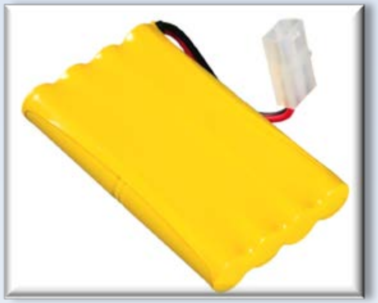
Deintercalation

Intercalation

LiB Value Chain

Raw Materials → **Cell Components** → **Systems** → **End Market**





Raw Materials
- Lithium Compounds
- Electrolyte organics
- Graphite
- Manganese
- Nickel
- Cobalt
- Copper
- Aluminum

Cell Components
- Anode
- Cathode
- Electrolyte
- Separator
- Binders
- Chemicals
- Carbon Materials

Systems
- Cells
- Packs
- Electrode coating
- Cell Assembly
- Testing Houses

End Market
- Proprietary technology for output and operation
- Battery Pack Design for host

Accountable for almost half of the costs in LIB!

Research Tradeoffs

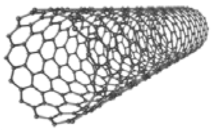
Balance between tradeoffs is critical to successful research!
How do we maximize the balance?

SAFETY

- Fires
- Environmental Impact
- Temperature Risks
- Consumer & Laboratory Safety
- New Materials & Adverse Risks

CAPACITY / ENERGY

- Predictability
- Cycle Effects
- Reproducibility
- New Materials
- Physical & Chemical Impact
- Charge Transfer



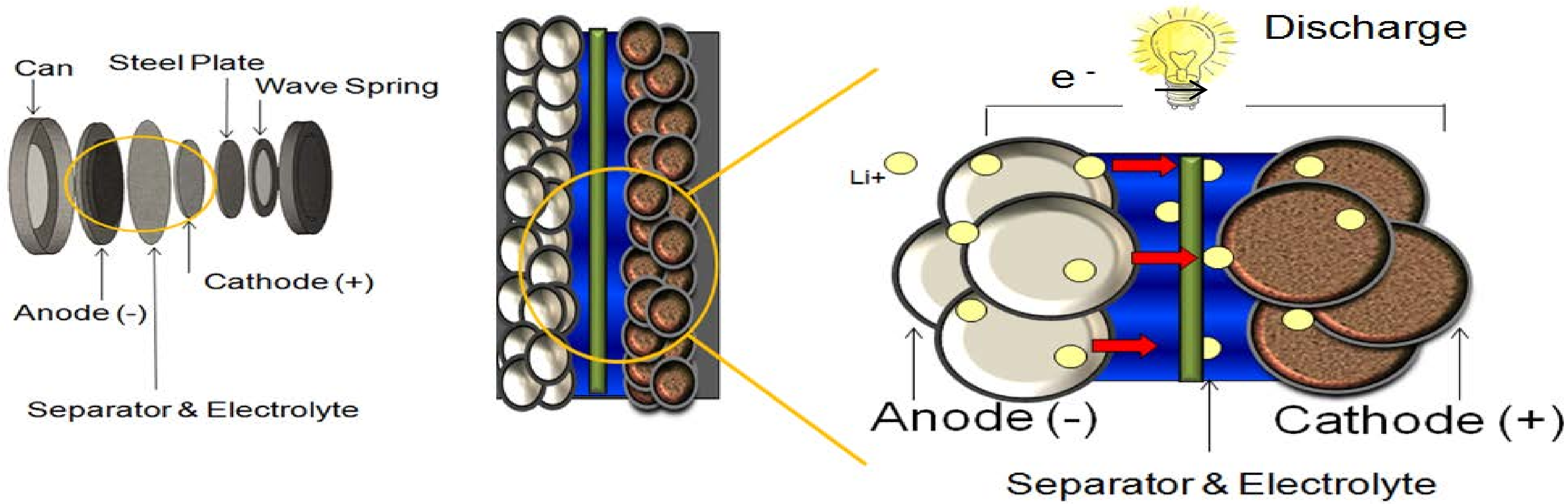
LIFETIME

- Warranty Enhancements
- Reliability of Fuel Source
- Short Prevention
- Chemical Changes
- Physical Problems

POWER/ SCALE

- Consumer Electronics and Automobile
- Scalable Research
- Commercial Transfer

Key Problem Areas- The Battery Breakdown

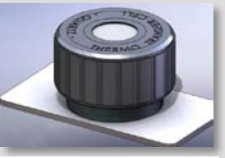


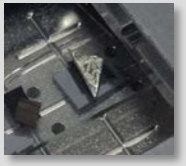
Cell	Electrolyte	Separator	Binder	Anode	Cathode
•*In situ* activity •Optimum cell chemistry •Prevention of leaks •Internal Impedance •Stability of varying components and cell	•Additives •Ion dispersion •Gas generation •Flammability •Low flashpoint •Breakdown products	•Porosity effects •Copolymer characterization •Resistance •Mechanical strength •Impurities •Thickness •Temperature Limits	•Homogeneity •Surface area control •Composition •Heat resistance •Material variance •Impurities •Viscosity •Adhesion	•Lithium deposition •Dissolution •Expansion •SEI Layer •Silicon Behavior •Ion Dispersion •Particle Morphology	•Oxide formations •Volume changes •Film growth •Functional group ID •Dendrites •Impurities •Capacity effects

How Might One Analyze the Battery?

Define Battery Question and Problems

ex situ





Battery disassembly to analyze Individual Components Upon change/failure.

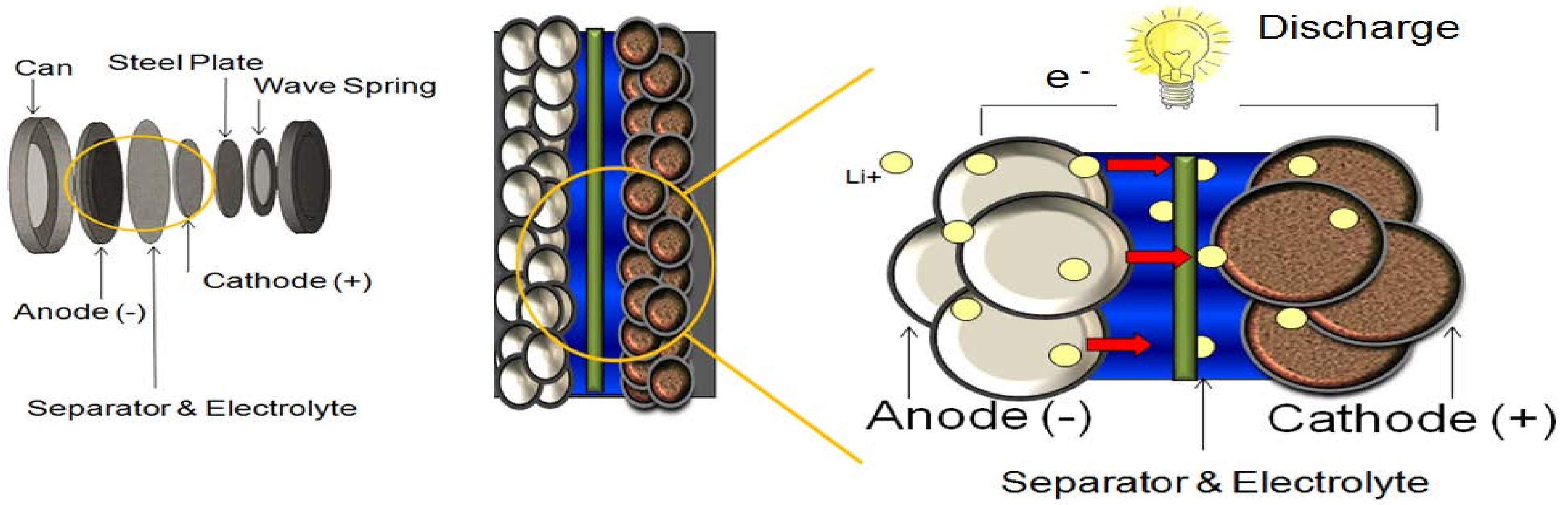
- Inert Sample Transfer
- Reactive Analysis
- Destructive analysis (Battery De-assembled)

in situ

Analysis under load, in a working environment to observe real-time cell activity.

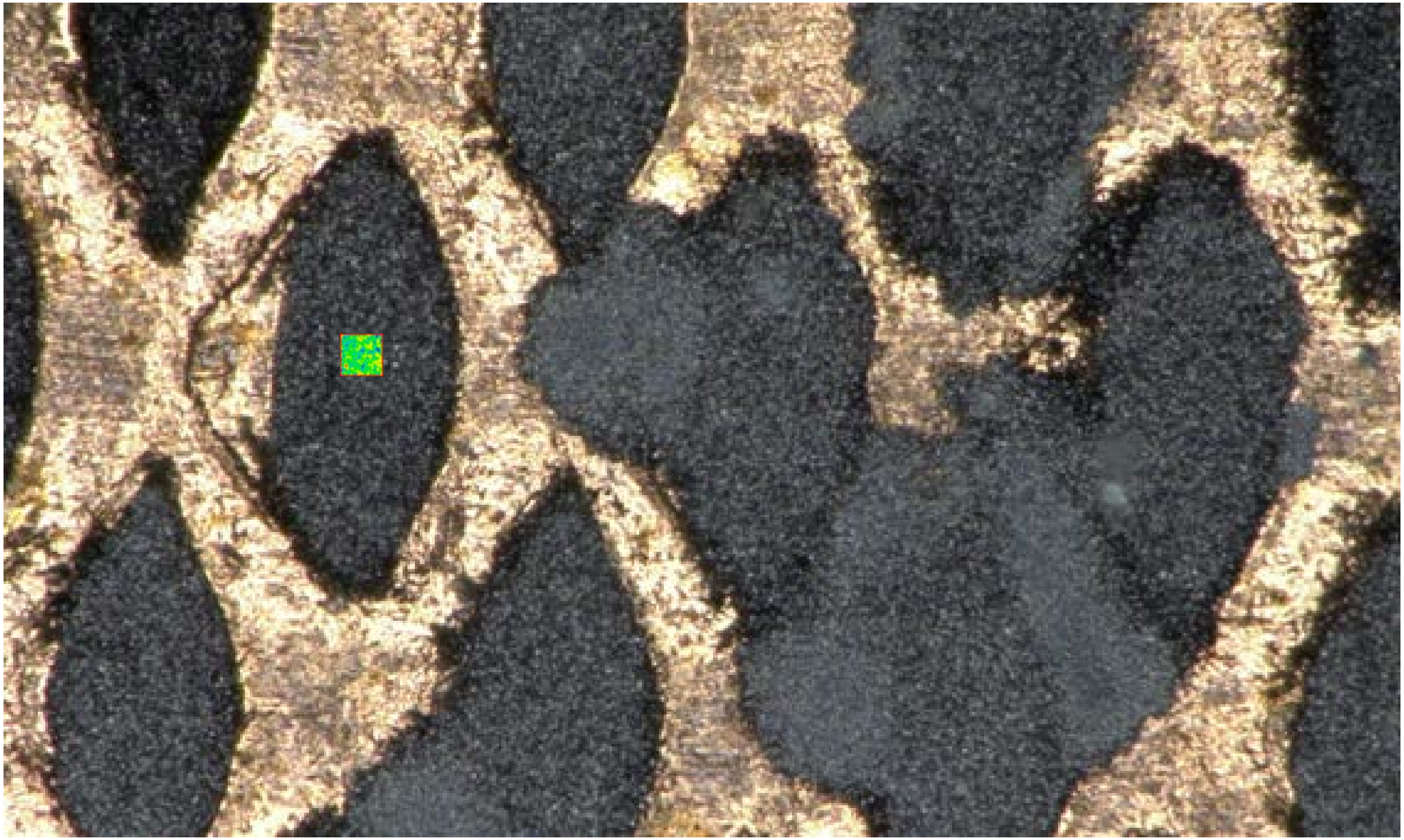
- Can view during operation/charge cycles
- Put into a ‘real’ situation
- Assemble a battery
- Proactive Analysis

Key Problem Areas- *in situ* Cell Investigations



Cell	Electrolyte	Separator	Binder	Anode	Cathode
•***In situ* activity** •Optimum cell chemistry •Prevention of leaks •Internal Impedance •Stability of components and cell	•Additives •Ion dispersion •Gas generation •Flammability •Low flashpoint •Breakdown products	•Porosity effects •Copolymer characterization •Resistance •Mechanical strength •Impurities •Thickness •Temperature Limits	•Homogeneity •Surface area control •Composition •Heat resistance •Material variance •Impurities •Viscosity •Adhesion	•Lithium deposition •Dissolution •Expansion •SEI Layer •Silicon Behavior •Ion Dispersion •Particle Morphology	•Oxide formations •Volume changes •Film growth •Functional group ID •Dendrites •Impurities •Capacity effects

in situ Raman: Lithiation of Graphite



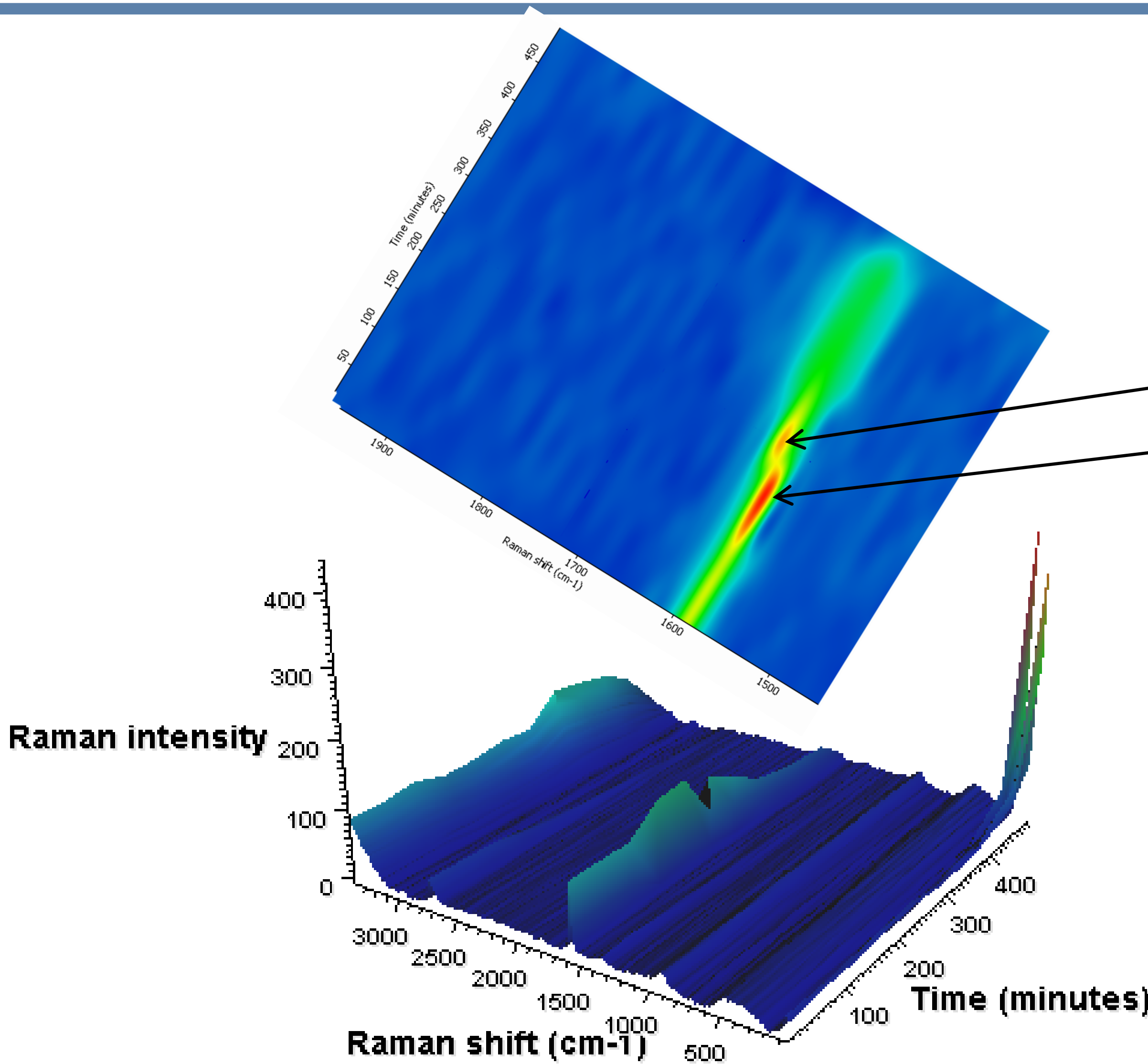
- Graphite coated on wire mesh current collector
- Representative area examined by Raman

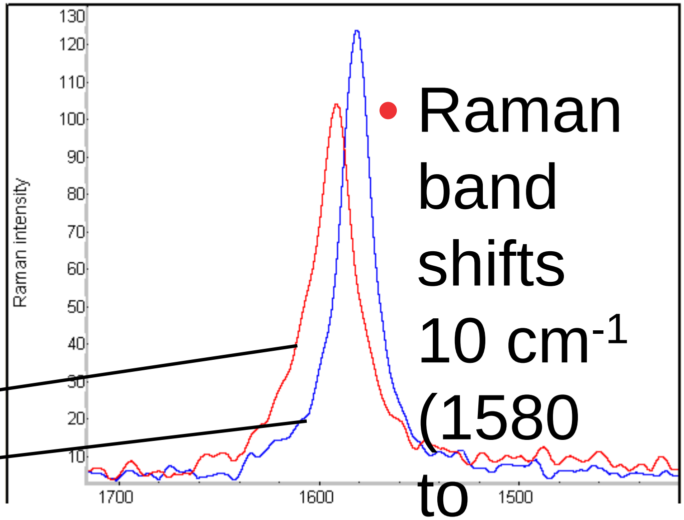
Image and electrochemical data provided by EL-CELL, use of ECC-Opto-Std optical electrochemical cell, 2015

EL-CELL® electrochemical test equipment

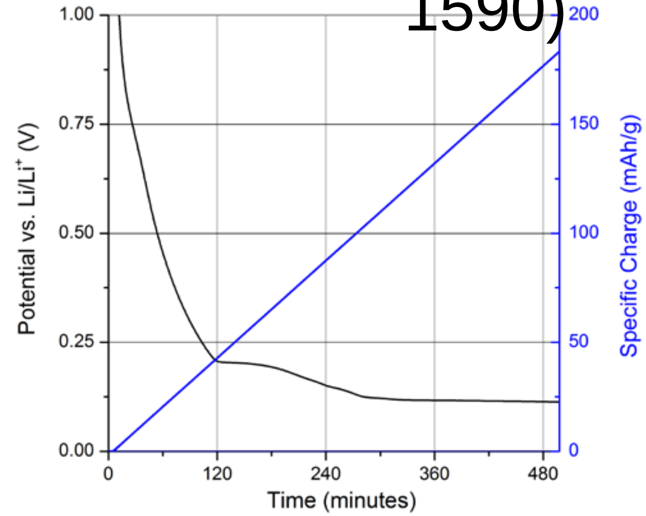
ThermoFisher SCIENTIFIC

in situ Raman: Change in Spectrum Over Time

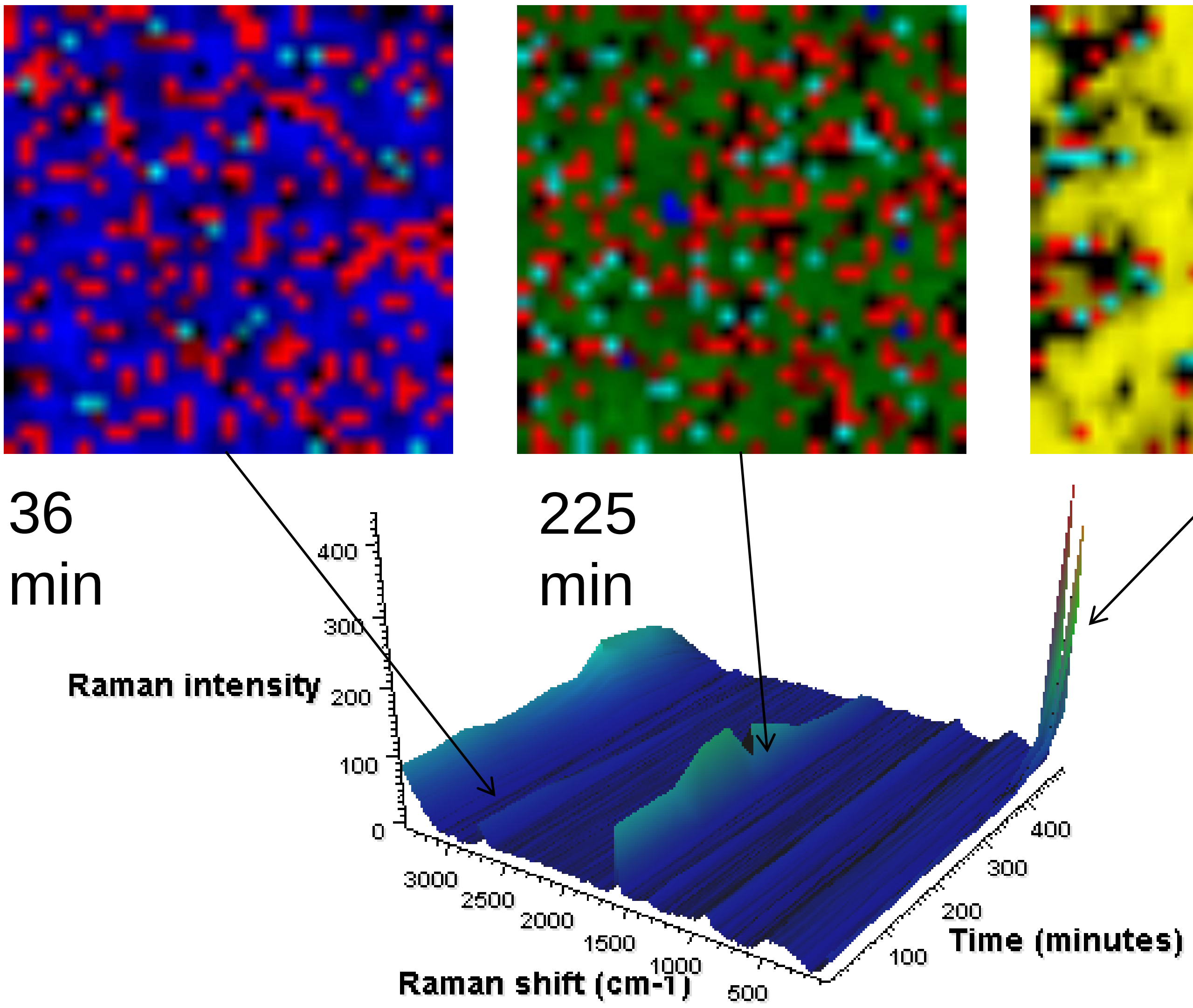




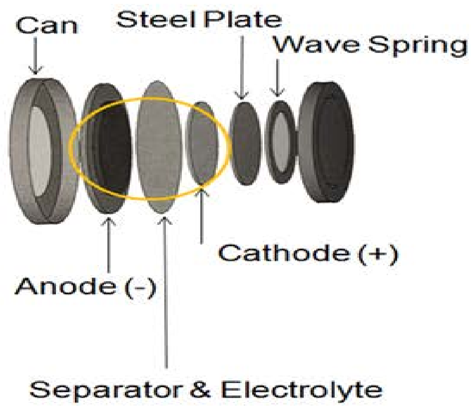
- Raman band shifts 10 cm^{-1} (1580 to 1590)

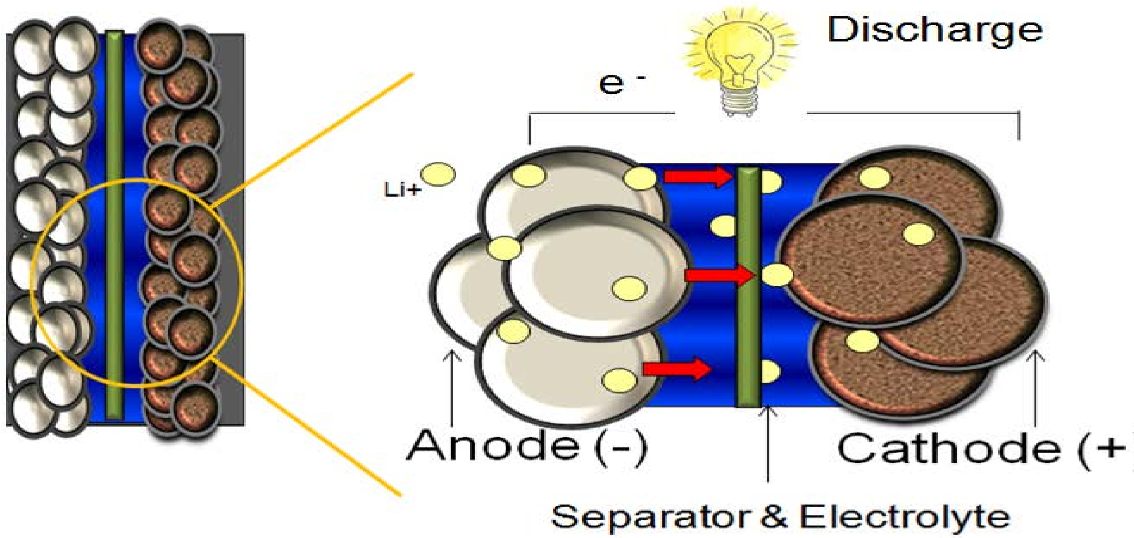


in situ Raman: Change in Raman Image Over Time



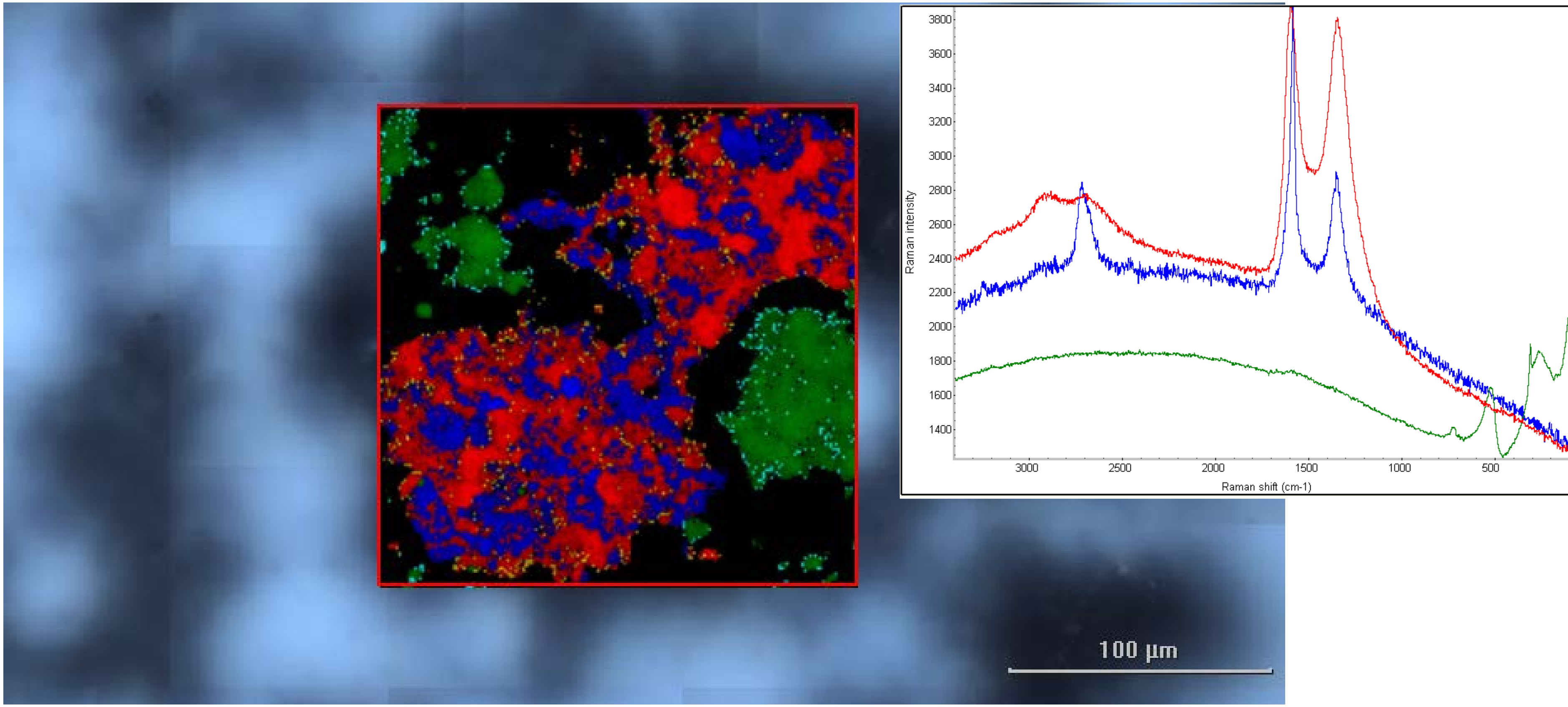
Key Problem Areas- Ex Situ Electrode Investigations





Cell	Electrolyte	Separator	Binder	Anode	Cathode
•*In situ* activity •Optimum cell chemistry •Prevention of leaks •Internal Impedance •Stability of varying components and cell	•Additives •Ion dispersion •Gas generation •Flammability •Low flashpoint •Breakdown products	•Porosity effects •Copolymer characterization •Resistance •Mechanical strength •Impurities •Thickness •Temperature Limits	•Homogeneity •Surface area control •Composition •Heat resistance •Material variance •Impurities •Viscosity •Adhesion	•Lithium deposition •Dissolution •Expansion **•SEI Layer** •Silicon Behavior •Ion Dispersion •Particle Morphology	•Oxide formations •Volume changes •Film growth •Functional group ID •Dendrites •Impurities •Capacity effects

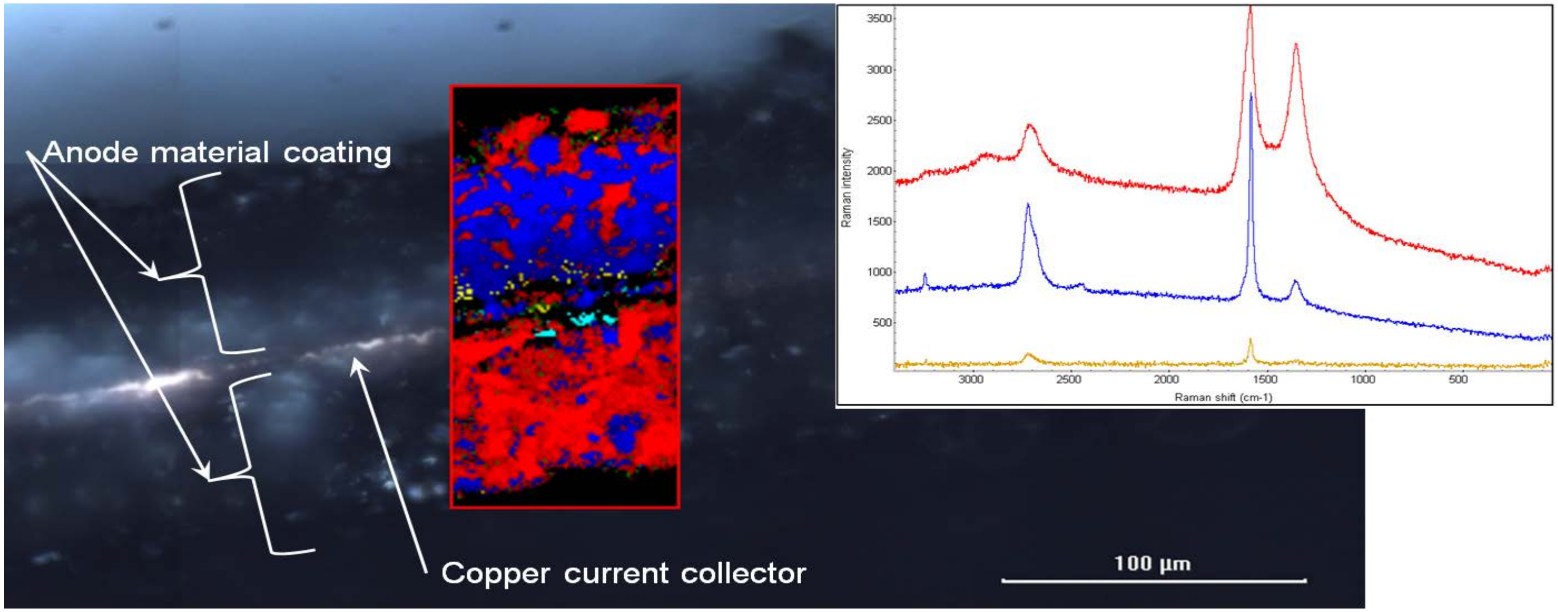
Post Diagnostic Li-ion Battery Anode, 2yr Cycle



- Electrode material (dark areas) lies between overlayer of separator particles (light areas)
  - Red (29% area) & blue (20% area) are variations in SEI layer
  - Green is separator particle

Ex situ Analysis of a Cross-Sectioned Anode Material

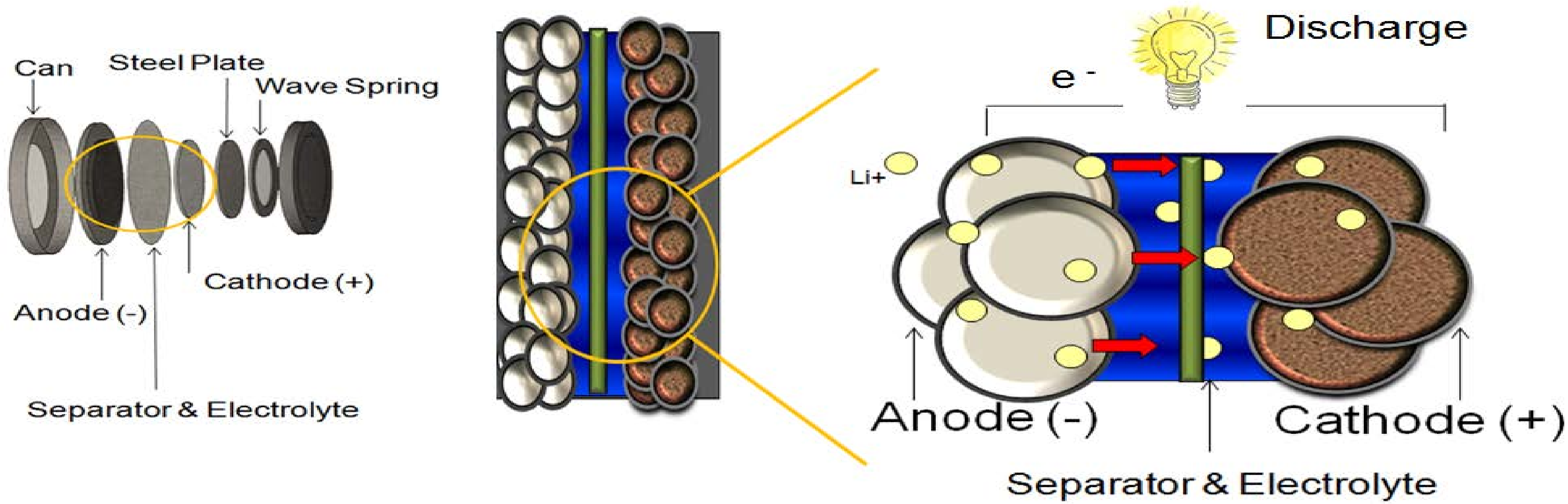
Cross-sectioned anode material in the ex situ transfer cell



The red color indicates the presence of carbon black while the blue color represents graphite. The distribution of these materials on the two sides of the electrode is significantly different. The copper current collector is in the center.

50X long working distance objective, 532 nm laser (2.0 mW), area imaged 76 µm x 160 µm, image pixel size 1 µm, 0.2 s exposure time, 4 scans

Key Problem Areas- Surface analysis of Cathodes



Cell	Electrolyte	Separator	Binder	Anode	Cathode
•***In situ* activity** •Optimum cell chemistry •Prevention of leaks •Internal Impedance •Stability of components and cell	•Additives •Ion dispersion •Gas generation •Flammability •Low flashpoint •Breakdown products	•Porosity effects •Copolymer characterization •Resistance •Mechanical strength •Impurities •Thickness •Temperature Limits	•Homogeneity •Surface area control •Composition •Heat resistance •Material variance •Impurities •Viscosity •Adhesion	•Lithium deposition •Dissolution •Expansion •SEI Layer •Silicon Behavior •Ion Dispersion •Particle Morphology	•Oxide formations •Volume changes •Film growth •Functional group ID •Dendrites •Impurities **•Capacity effects** **•Lithium Transfer**

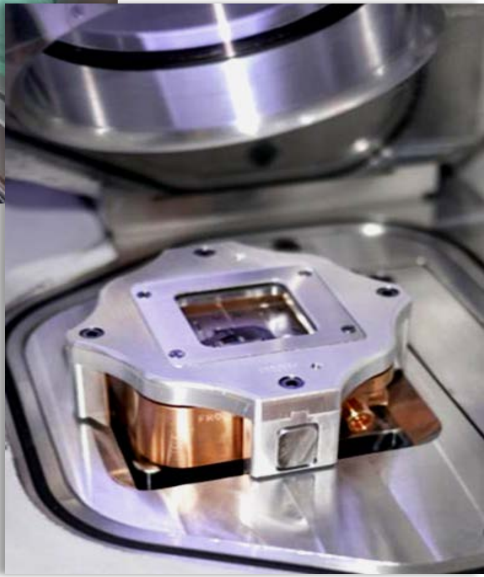
K-Alpha^{+} Sample Transfer Capability and weak signal detection

Analysis Examples:

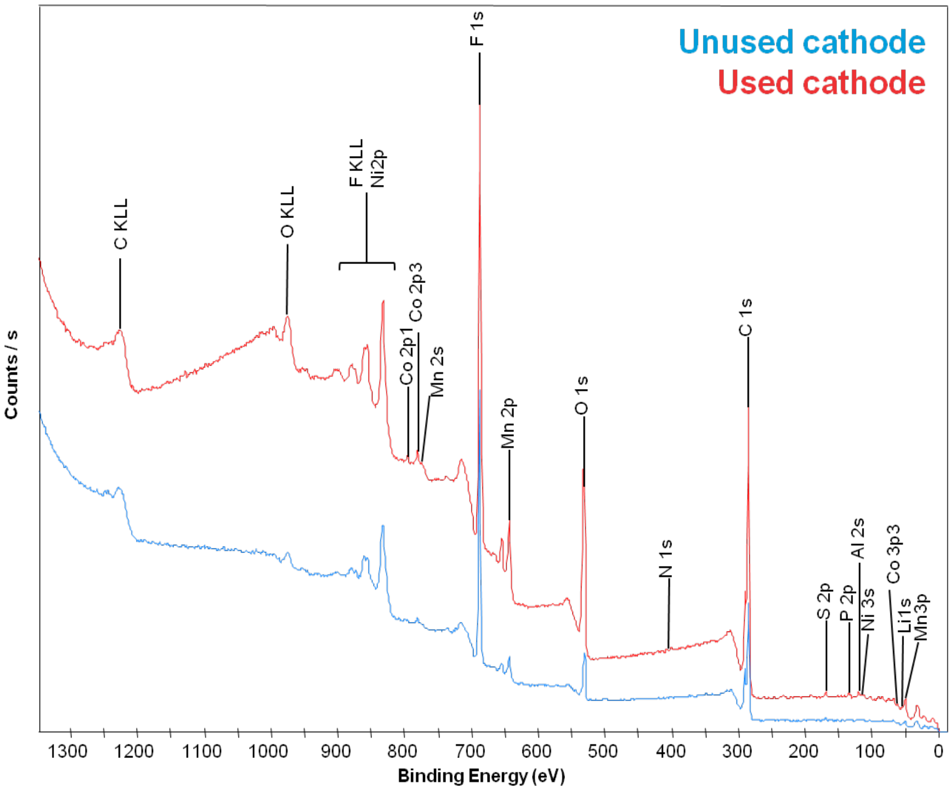
- <u>Electrodes</u>
  - Surface characterization of pristine material
    - Confirm oxidation state, composition, Li gradients
  - Ex-situ characterisation after cycling
    - Composition & variation with depth of SEI
    - Variation in surface composition of electrode material
- <u>Separators</u>
  - Surface characterization of pristine material
    - Confirm surface chemistry
  - Ex-situ characterisation after cycling
    - Look for polymer degradation
    - Deposition of material from electrodes & electrolyte

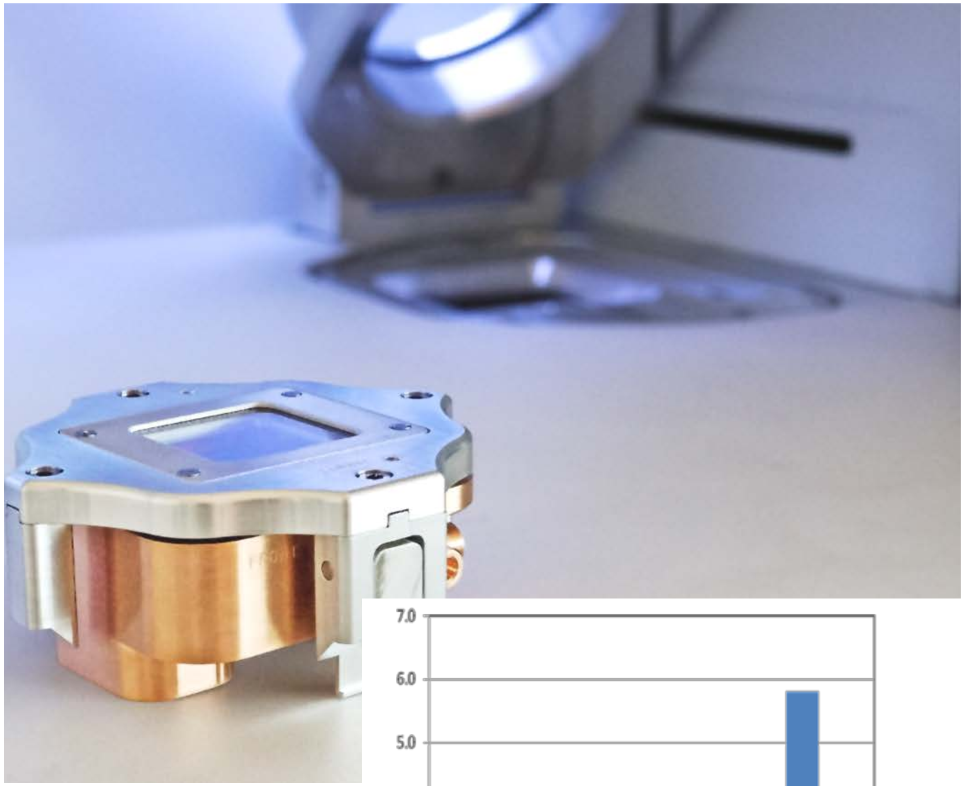
Inert atmosphere transfer

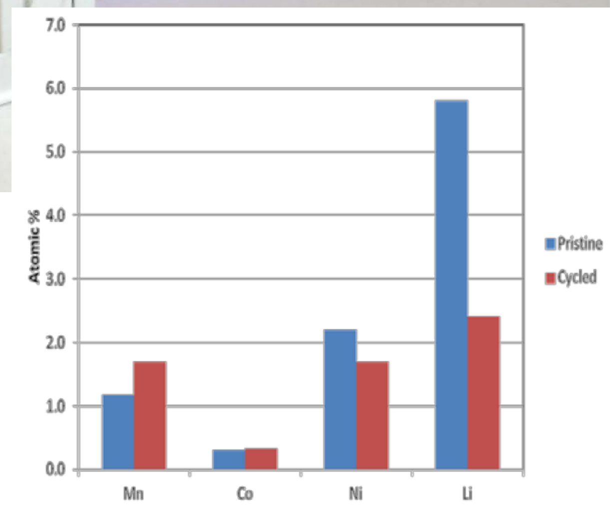
- Load samples in glove box
- Transfer under vacuum to K-Alpha^{+}



XPS Comparison of Pristine and Cycled Cathode

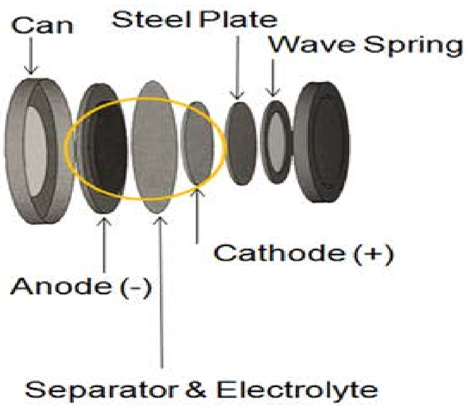


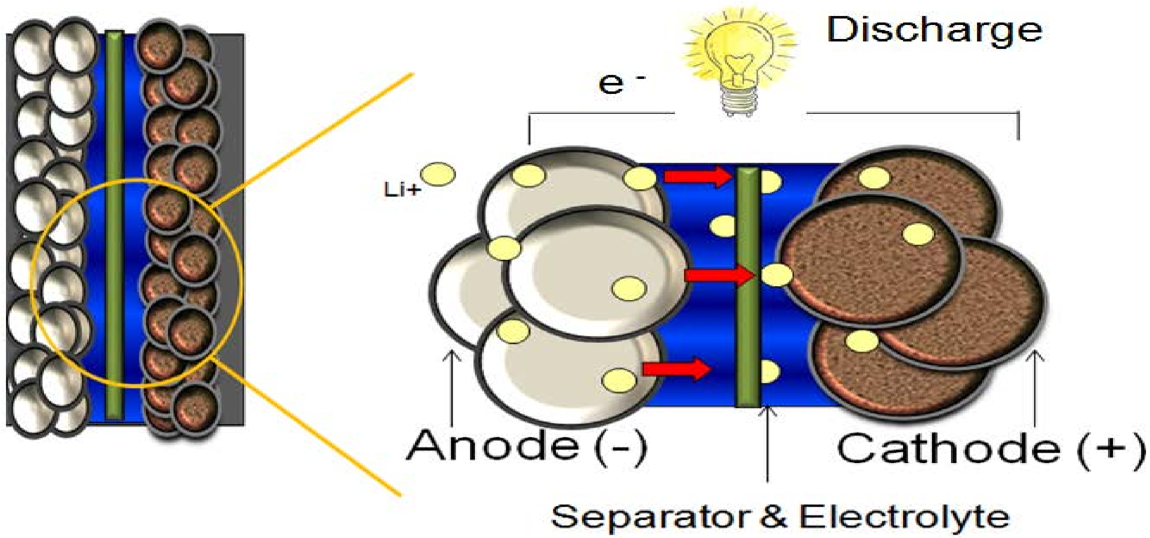




Verification of Atomic %
Lithium loss from cathode post-cycling

Key Problem Areas- Electrolytes

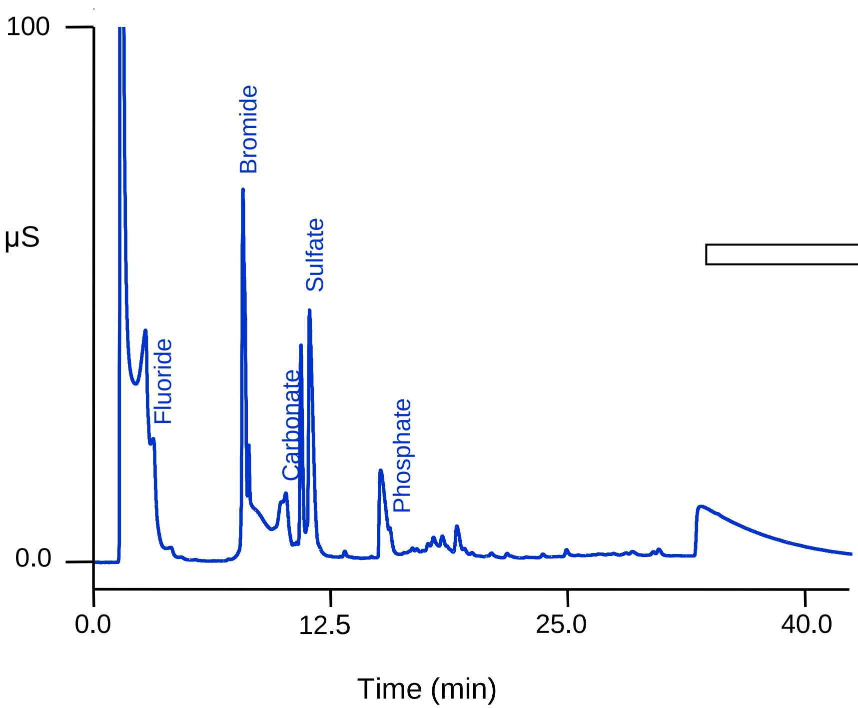




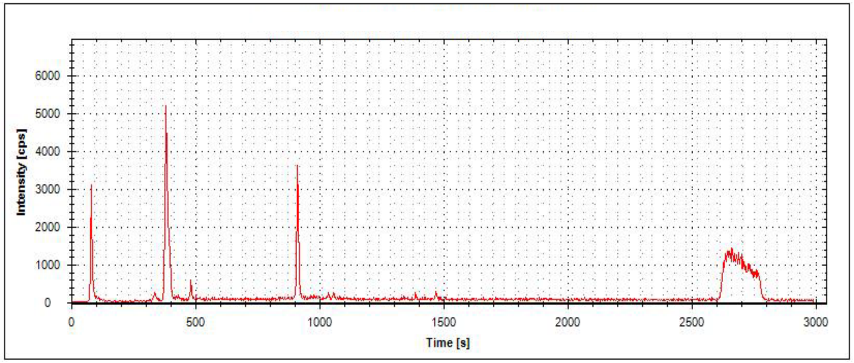
Cell	Electrolyte	Separator	Binder	Anode	Cathode
•*In situ* activity •Optimum cell chemistry •Prevention of leaks •Internal Impedance •Stability of varying components and cell	•Additives •Ion dispersion •Gas generation •Flammability •Low flashpoint •Breakdown products **•Degradation Products**	•Porosity effects •Copolymer characterization •Resistance •Mechanical strength •Impurities •Thickness •Temperature Limits	•Homogeneity •Surface area control •Composition •Heat resistance •Material variance •Impurities •Viscosity •Adhesion	•Lithium deposition •Dissolution •Expansion •SEI Layer •Silicon Behavior •Ion Dispersion •Particle Morphology	•Oxide formations •Volume changes •Film growth •Functional group ID •Dendrites •Impurities •Capacity effects

Example 1: Li-Ion Battery Analysis: IC-ICP-MS

IC-CD
Suppressed Conductivity Detection



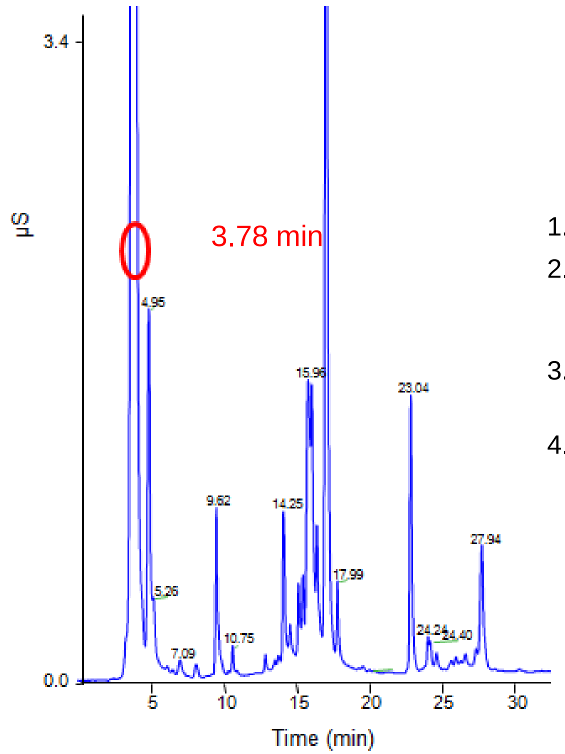
IC-ICP-MS
iCAP Q ICP-MS



- Analyze ^{31}P Containing Products in the Presence of Other Elements

Example 2: Li-ion Battery Analysis: IC-HRMS

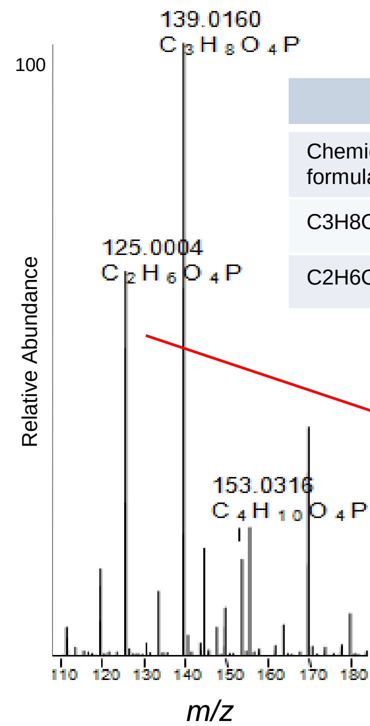
IC-CD
Suppressed Conductivity Detection



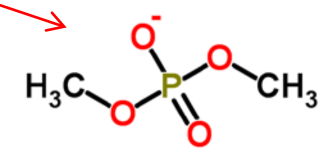
Step-wise Approach

1. IC Separation using a KOH eluent
2. Full scan MS/MS acquisition
3. Component ID based on HRAM Data
4. Propose Structure

IC-HRMS
Q Exactive Orbitrap MS



Phosphate esters		
Chemical formula	Exact mass	Delta ppm
C3H8O4P	139.0166	0.2
C2H6O4P	125.0009	-0.1



- Component *Identification* in Untargeted and Unknown Workflows

Source for Dimethyl phosphate image: CSID:2982799, http://www.chemspider.com/Chemical-Structure.2982799.html (accessed 00:59, Feb 5, 2015)

Thermo Fisher SCIENTIFIC

Thermo Scientific Building Block of Application Solutions

Fourier Transform Infrared Spectroscopy (FTIR)

- Composition changes
- Crystallization
- SEI growth
- Dendrite formations
- Functional Group ID
- Additive confirmation/ID
- Gas Emissions
- Copolymer Characterization

DXRxi Raman Imaging Microscope

- SEI formation
- Electrolyte degradation
- Electrode volume and structure changes
- Morphology of components
- Homogeneity of electrode
- Composition changes
- Ionic Dispersion

K-Alpha$^+$: X-ray Photoelectron Spectrometer (XPS)

- SEI growth
- Graphite changes
- Porous Changes
- Electrode structure changes
- Dendrite formation

UltraDry Windowless EDS Detector

- Oxide formations
- Electrode volume changes
- Electrode composition
- Electrolyte solutions

ICP-OES, ICP-MS, IC, HPLC, GCMS

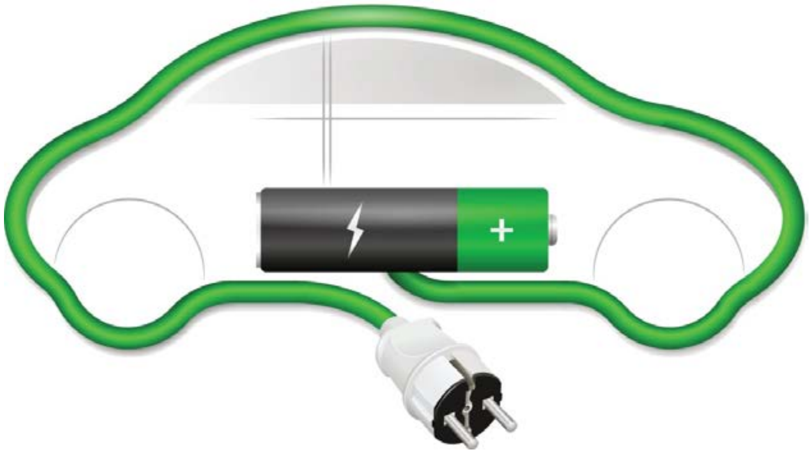
- Impurities
- Electrolyte solutions
- Emissions Degradation byproducts
- Metallic dissolution

ThermoFisher SCIENTIFIC

The Automotive and Advanced Materials Industry

Targeted Pieces

- Carbon Materials
- Glass technology
- Display Materials
- Lighting Advancements
- PowerTrain
- New Energy
- Renewable Energy
- Secondary Batteries (Li-ion)
- Carbon Filled Materials
- Brake Advancements
- Lubricants
- Rubbers
- Adhesives
- Recyclables
- Plastics
- Paints & Coatings
- Laminates



Goals in Research

- Materials: Weight
- Reduction
- Materials: Strength Enhancement
- Catalysis
- Scratch Resistance
- Safety
- Failure Analysis
- Fire Prevention (Flame Retardants)
- Emissions Control
- Lifetime of Product
- Corrosion
- Resistance
- Corrosion Resistance
- Reduce, Reuse, Recycle
- Heat Resistance
- Color Retention