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Lecture on experimental techniques of lithium-ion and alkali-ion cells

Roby Gauthier

Li-ion cells are used in a lot of different products

https://en.wikipedia.org/wiki/Plug-in_electric_vehicle

https://zenebikes.com/collections/electric-bikes/products/saral-step-through

https://www.homedepot.com/p/RYOBI-40V-HP-Brushless-20-in-Cordless-Battery-Walk-Behind-Push-Lawn-Mower-with-6-0-Ah-Battery-and-Charger-RY401170/317061059

https://www.macworld.com/article/605114/iphone-features-mac-5g-truedepth-camera-touch-screen.html

https://chargedevs.com/newswire/are-evtol-companies-starting-a-charging-standards-war/

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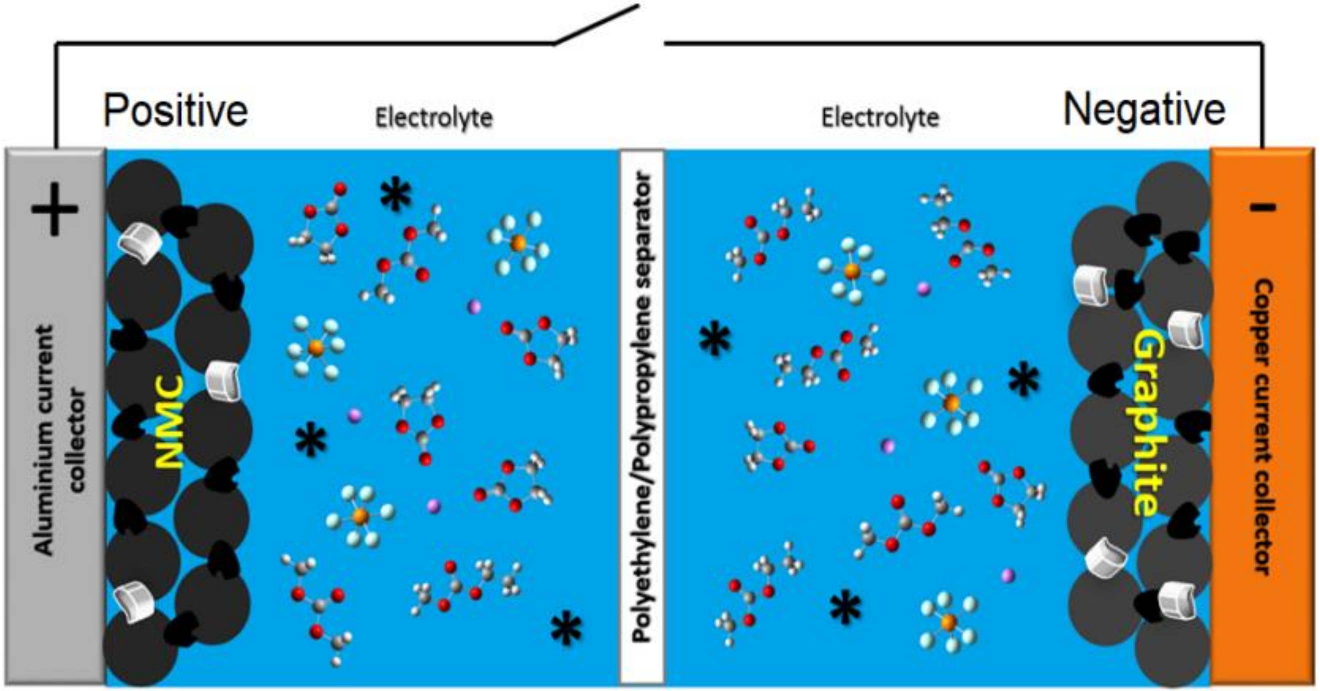
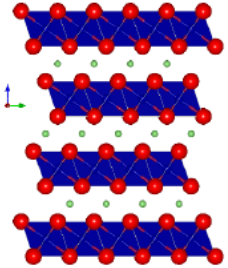
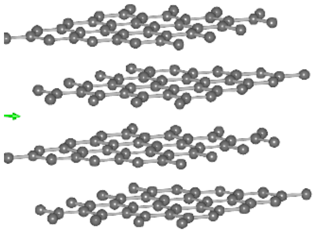
Li-ion cell: what is inside?



Cathode (NMC)



Anode (graphite)



NMC: $LiNi_xMn_yCo_{1-x-y}O_2$

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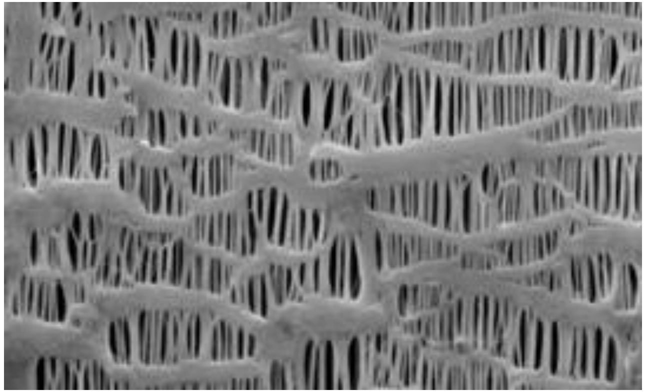
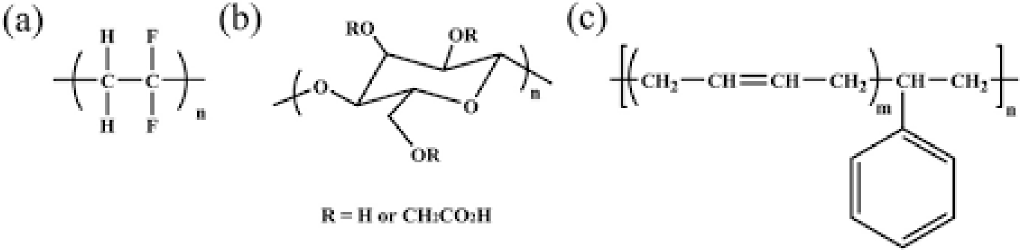
Celgard Separator and binders



Celgard separator



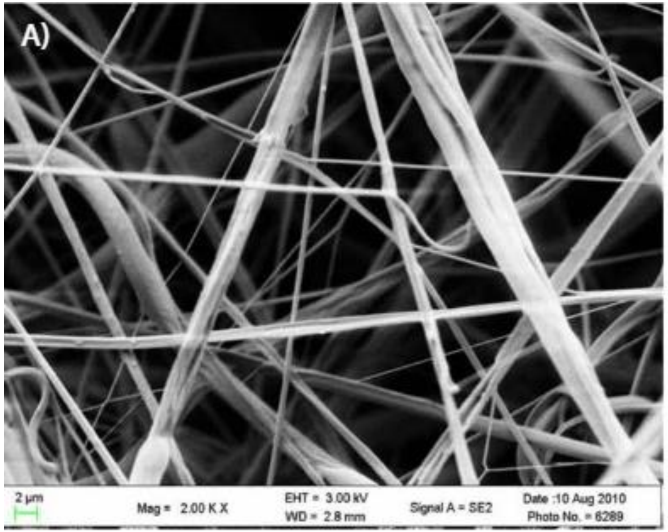
PVDF CMC SBR

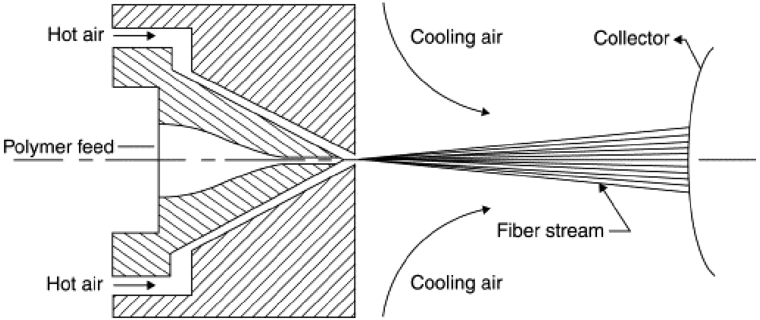
Binders

https://celgard.shop/products/celgard%C2%AE-2500-hand-sample

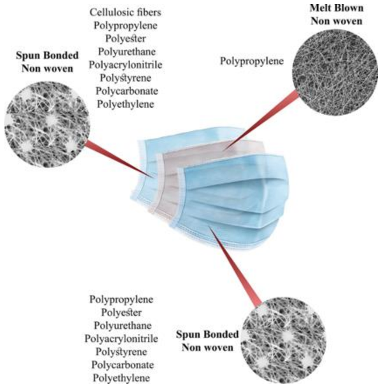
Nanoscale Res Lett **12**, 575 (2017)

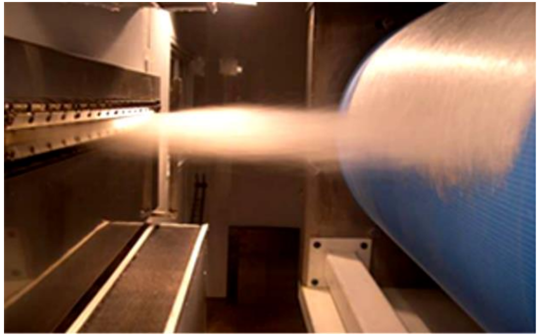
Blown microfiber separator





Used in masks





Hiremath N, Bhat G (2015) Melt blown Polymeric Nanofibers for Medical Applications- An Overview. Nanosci Technol 2(1): 1-9.

Int. J. Environ. Sci. Technol. **20**, 9205–9224 (2023)

https://www.sciencedirect.com/topics/engineering/melt-blown-process

https://en.wikipedia.org/wiki/Melt_blowing

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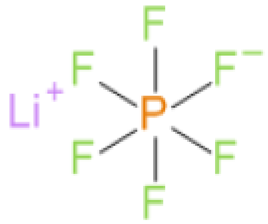
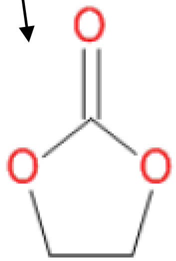
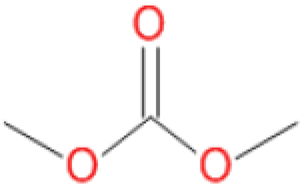
Example of an electrolyte (often used as a control)

1.2M LiPF6 Ethylene carbonate: Dimethyl carbonate (EC:DMC) 3:7







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Multiple cell formats are used in academia and the industry

Coin cell

Pouch cell

Cylindrical cell

https://www.batterydesign.net/battery-cell/formats/

https://www.electriccarpartscompany.com/Bestgo-10Ah-LiFePO4-Lithium-Pouch-Cell-Model-BP-HK-10A

https://www.bzbuas.com/shop/18650-3500mah-li-ion-battery-1005

In academia, how to choose the appropriate format?

Testing new **electrode** materials

(Why? → Easy to assemble, can use lithium metal (in excess) as the anode for cathode studies.)

Testing new **electrolytes** on commercially available electrodes.

(Why? → Highly reproducible results, can't use an excess of lithium as the anode)

Testing **commercial** products

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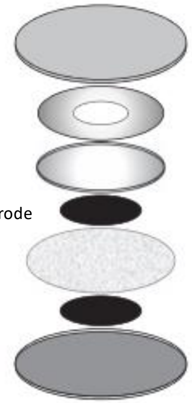
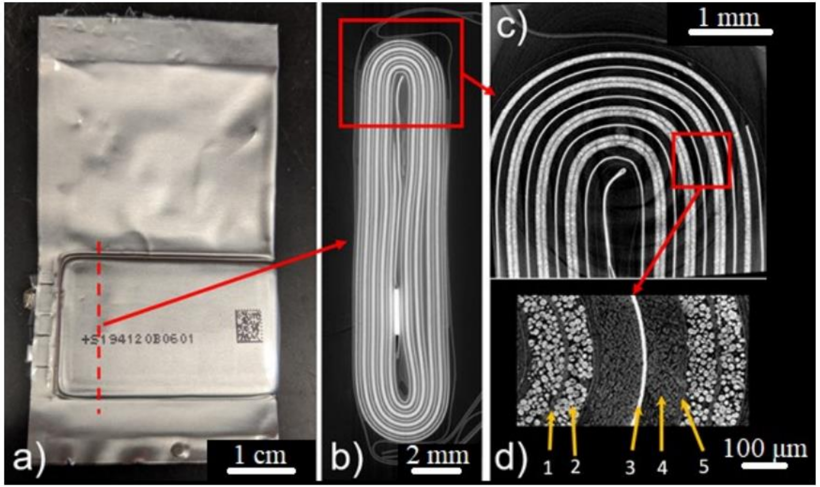
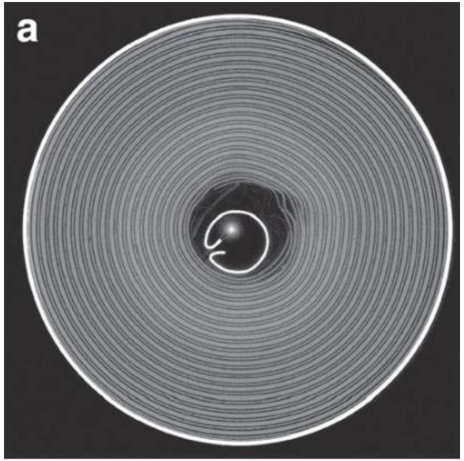
What is inside each cell format?

CT-scans

Jelly roll







Coin cells

Pouch cells

1. Aluminium current collector
2. Cathode active particles
3. Copper current collector (white line)
4. Anode active particles
5. The separator.

Cylindrical cells

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Journal of The Electrochemical Society, 166 (2) A329-A333 (2019)

Finegan, D., Scheel, M., Robinson, J. *et al.* *In-operando* high-speed tomography of lithium-ion batteries during thermal runaway. *Nat Commun* **6**, 6924 (2015)

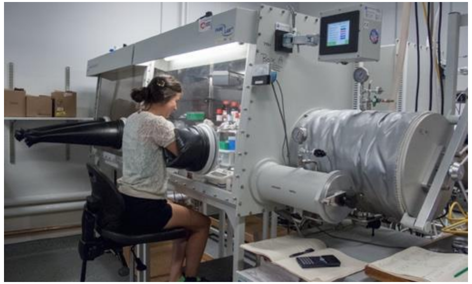
Preparing a pouch cells (electrolyte studies)

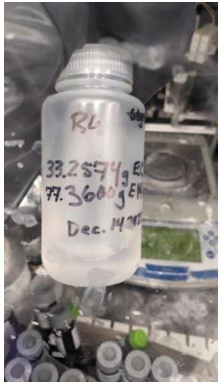
Important: Avoid water contamination!

Order pouch cells without electrolyte from the manufacturer

Cut the seal and measure the dry mass

Make electrolyte in a glovebox





Add electrolyte to the cell in a glovebox
(4 mg/mAh is usual in academia)

Vacuum seal the cell

https://mtixtl.com/products/msk-115-iii

Measure mass and volume after filling

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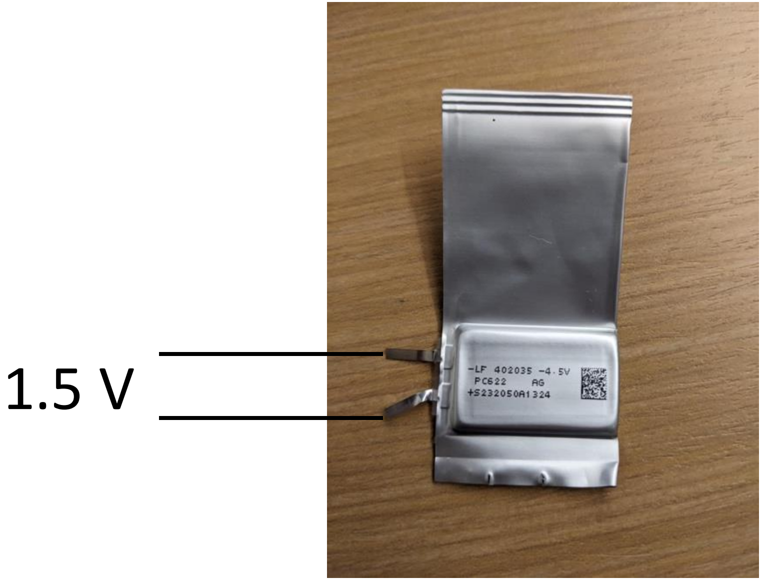
Wetting at 1.5 V (Conditioning)

- To prevent corrosion of the copper current collector during wetting of the electrodes and separator, the cell is kept at 1.5 V during the 24h wetting period.



Cell “boat” (holder) for pouch cells

- Rubbers and spacers are used to keep a constant pressure on the cell. Prevent deformation of the jelly roll due to gas formation.

Next, cell characterization

Why do cell characterization? → To understand the mechanism of degradation to improve the cell performance.

What are we characterizing?

- Capacity
- Cell lifetime and general degradation
- Electrolyte parasitic reactions (reduction, oxidation, redox shuttle)
- Lithium transport and ohmic resistance
- Electrode cracking and disconnection
- Gas volume
- Electrode swelling
- Etc.

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Common Electrochemical characterization for alkali-ion cells in R&D

- Formation dQ/dV
- Electrochemical impedance spectroscopy (EIS)
  - Full cell EIS
  - Symmetric cell EIS
- Long-term cycling
  - Q(n): Capacity versus cycle number
  - Q(t): Capacity versus time
  - ΔV: $V^{avg}_{charge} - V^{avg}_{discharge}$
- Ultrahigh precision coulometry (UHPC)
  - Coulombic efficiency (CE)
  - Charge endpoint capacity slippage
  - dV/dQ analysis

- Open circuit voltage storage

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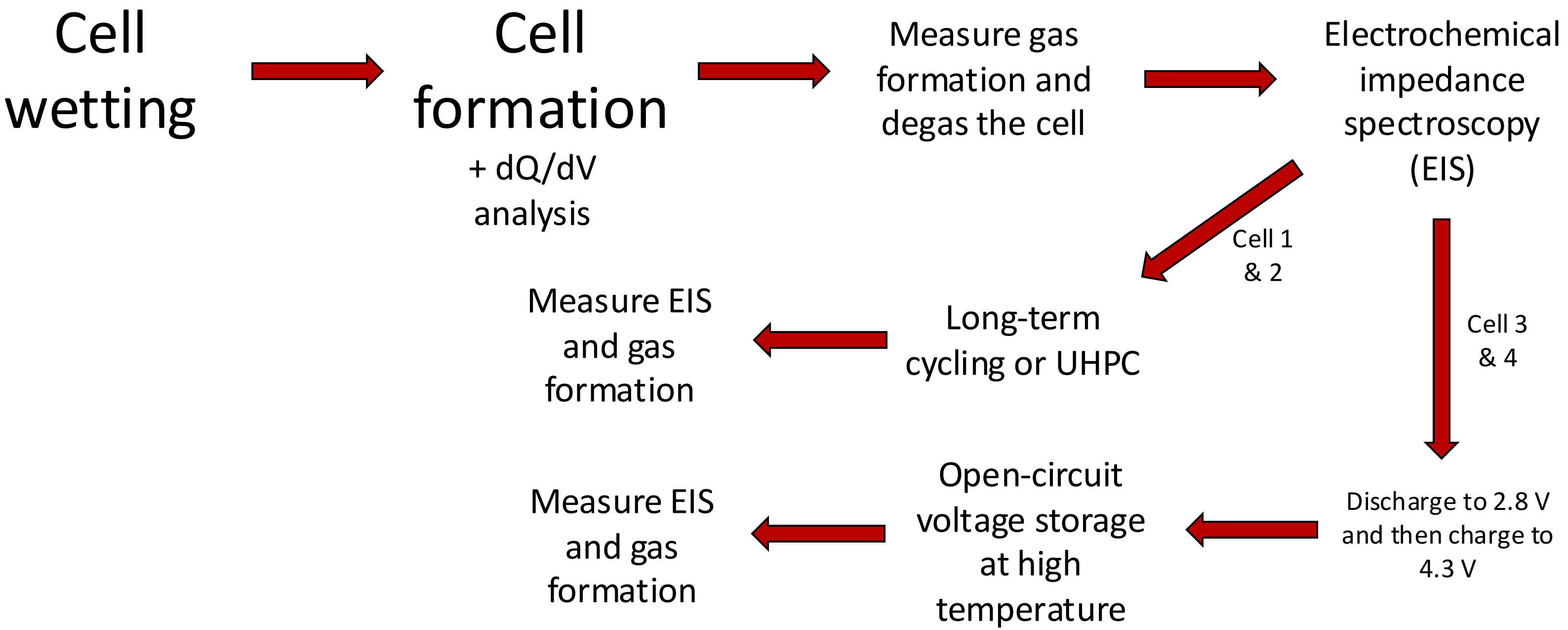
Overview of routine cell conditioning and characterization



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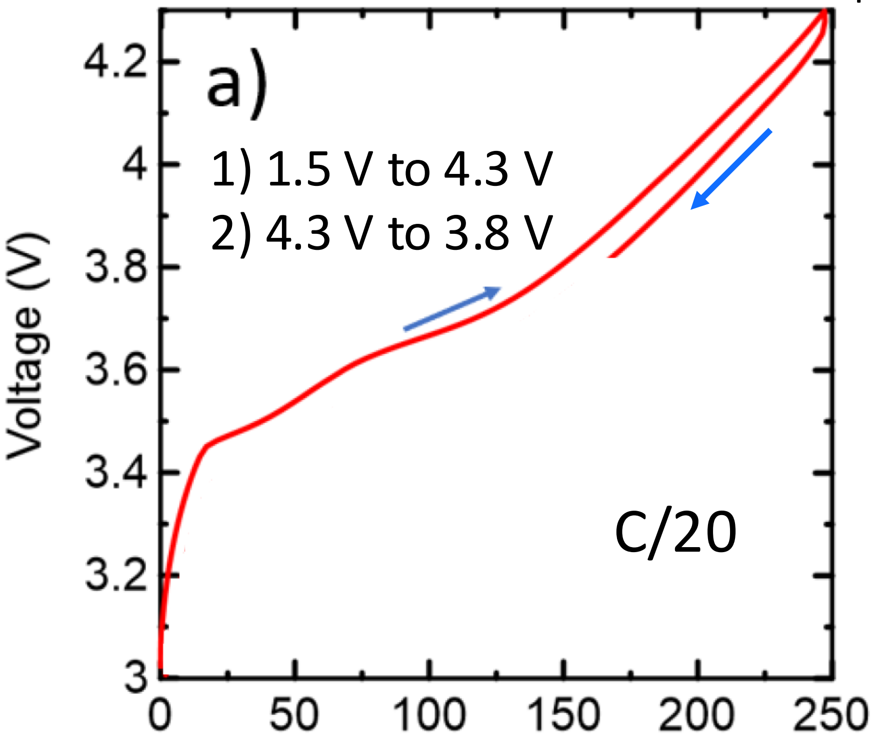
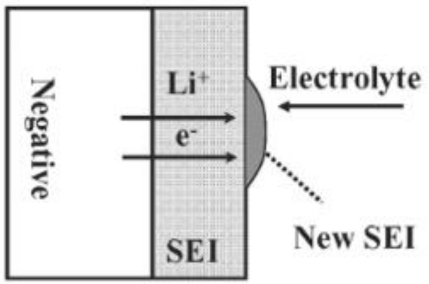
Formation: First charging of the cell



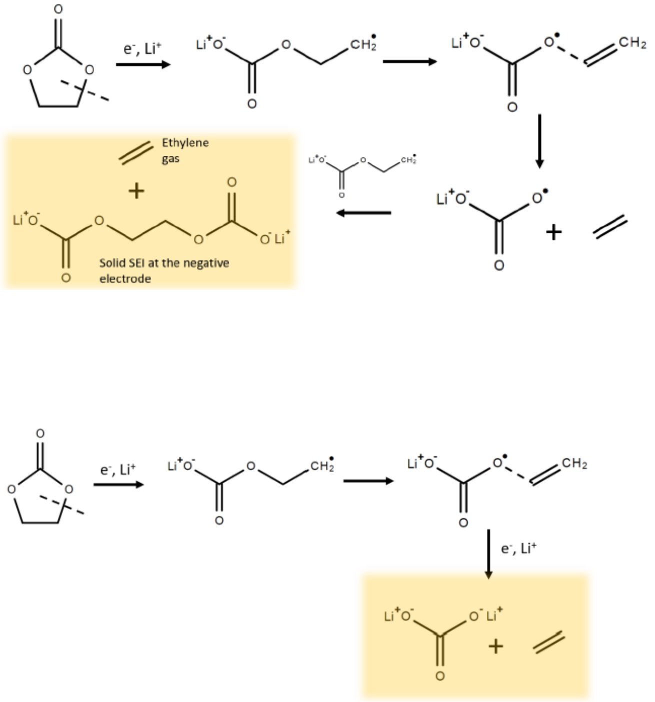
Formation charger: Maccor

Pouch cells in a temperature box (40°C)

During formation, the solid electrolyte interface forms at the anode

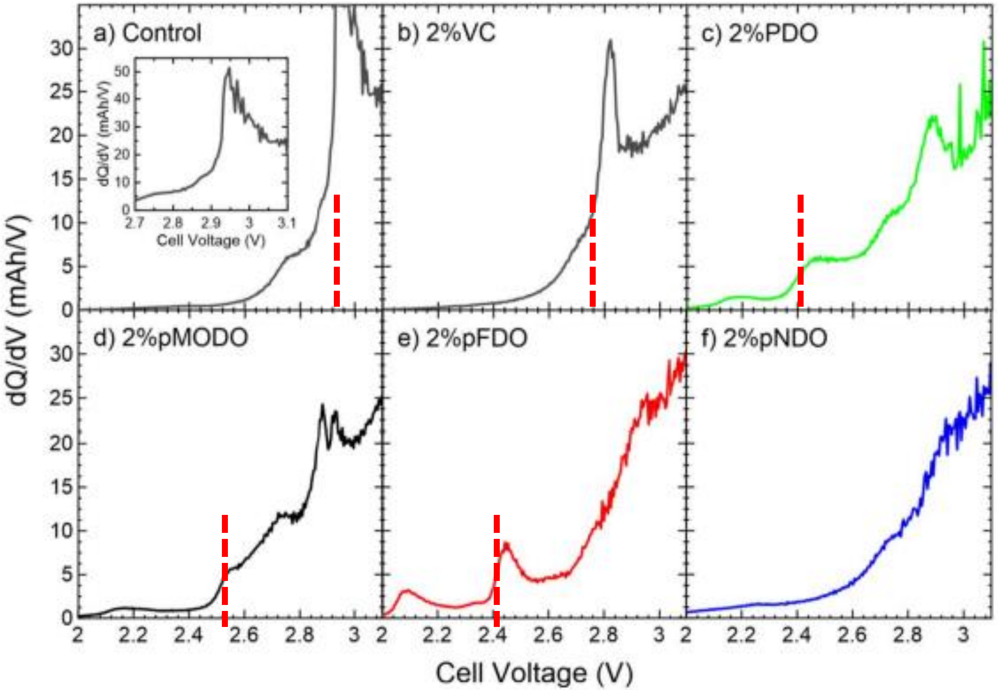


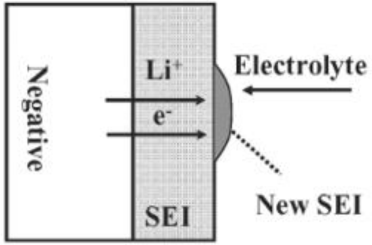
Electrolyte reduction



dQ/dV analysis: analysis of SEI formation

Can figure out the full-cell reduction potential of electrolyte components at the anode. Add 2% of additives to control electrolyte.





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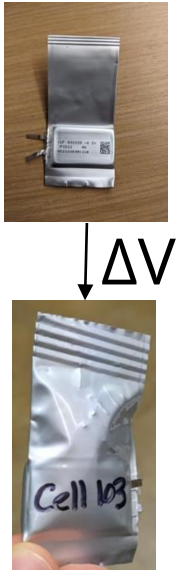
Why measure the volume and how?

- We measure the volume before and after formation to see how much gas is formed. Too much gas is bad for cell performance.
- The Archimedes' principle is used.



$$\sum F = F_{weight} + F_{buoyant} + F_{tension}$$

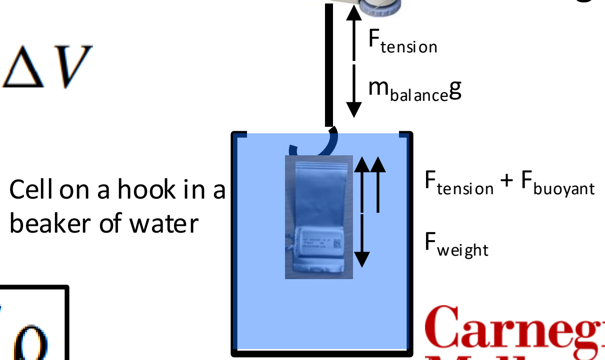
$$\Delta F_{tension} = -\Delta F_{buoyant} = -\rho g \Delta V$$

$$F_{tension} = m_{balance} g$$

$$\boxed{\Delta V = -\Delta m_{balance}/\rho}$$

(Shimadzu model AUW220D)

$\Delta F_{weight}=0$



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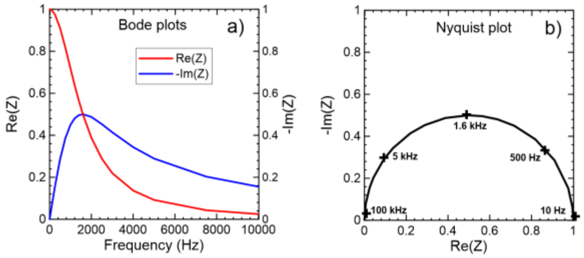
Journal of The Electrochemical Society, 161 (10) A1548-A1554 (2014)

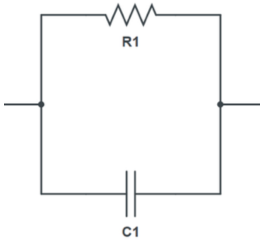
ρ = 1 g/mL for water

Electrochemical impedance spectroscopy (EIS)

Theory

(electrode interface)

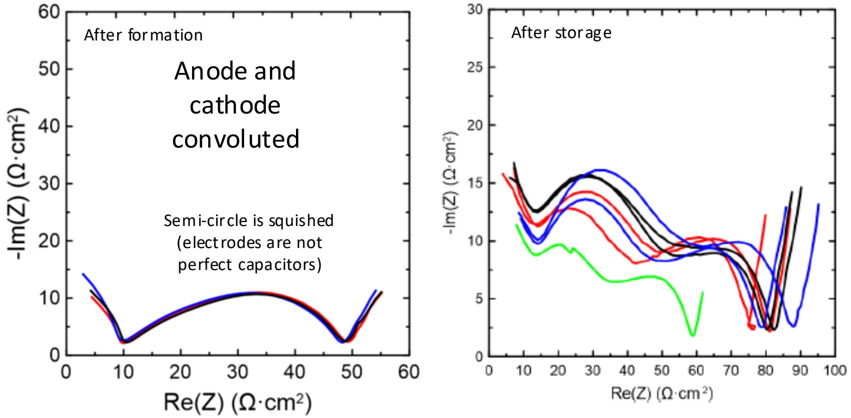




$$Z = R/(1 + i\omega RC)$$

The diameter of the semicircle represents the charge transfer resistance at the electrodes

Experiment



Bio-Logic VMP3 with temperature chamber (10° C)

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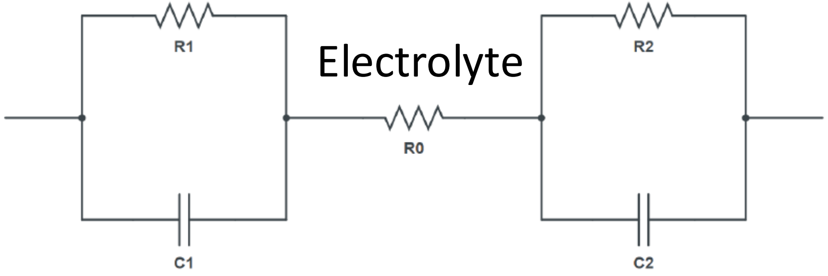
EIS Model fitting

Simple model

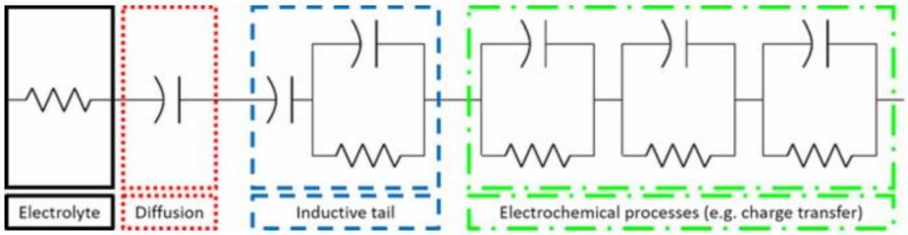
Anode interface

Cathode interface



Two semi-circles

Complex model



Component Name	Circuit Representation	Formula
Resistor	R	$Z_{\text{ohm}}(\omega) = R$
CPE	(Q/φ)	φ = 1 -> capacitor $Z_{\text{CPE}}(\omega) = \frac{1}{Q(i\omega)^{\varphi}}$

Constant phase element: Imperfect capacitor (leaky capacitor)

Symmetric cell

EIS of symmetric cells allows for determining which electrode has the highest impedance

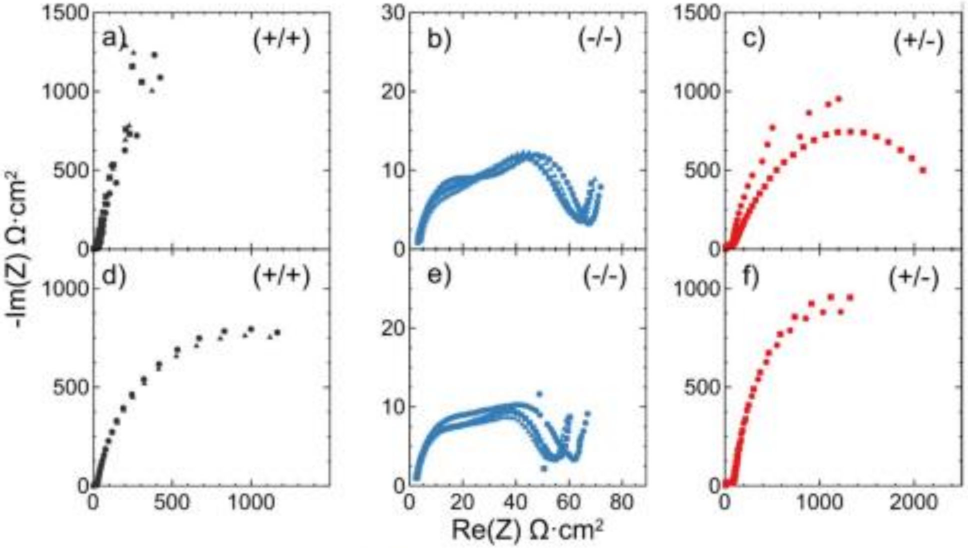


Figure 11. EIS spectra after formation of a) positive-positive (+/+), b) negative-negative (−/−), and c) positive-negative (+/−) coin cells and after storage of d) positive-positive (+/+), e) negative-negative (−/−), and f) positive-negative (+/−) coin cells built from a NMC532/gr pouch cell. Two or three coin cells were constructed and tested for each type of coin cell. The pouch cells from which the coin cells were made, as well as the coin cells themselves, used 2% DMI as the electrolyte. The impedance of the symmetric cells has been divided by two.

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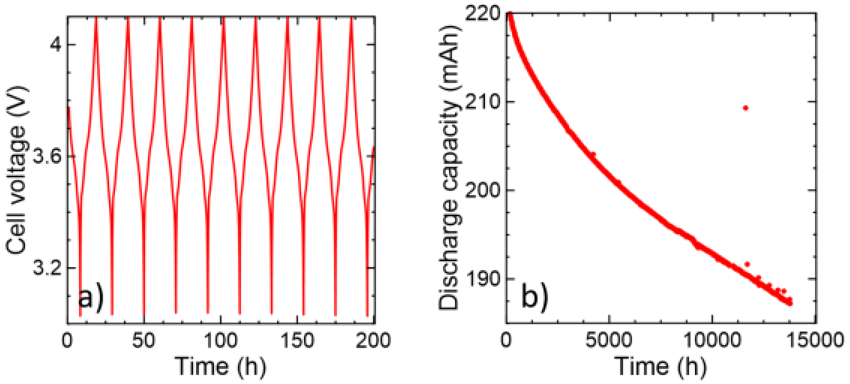
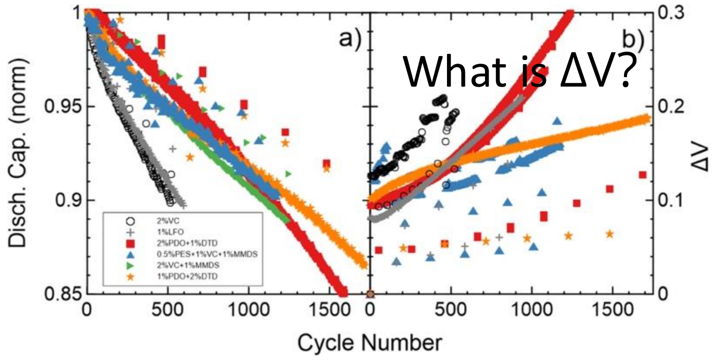
Journal of The Electrochemical Society, 166 (15) A3707-A3715 (2019)

Long-term cycling

Done at constant current. The duration of one cycle is proportional to the cell capacity.





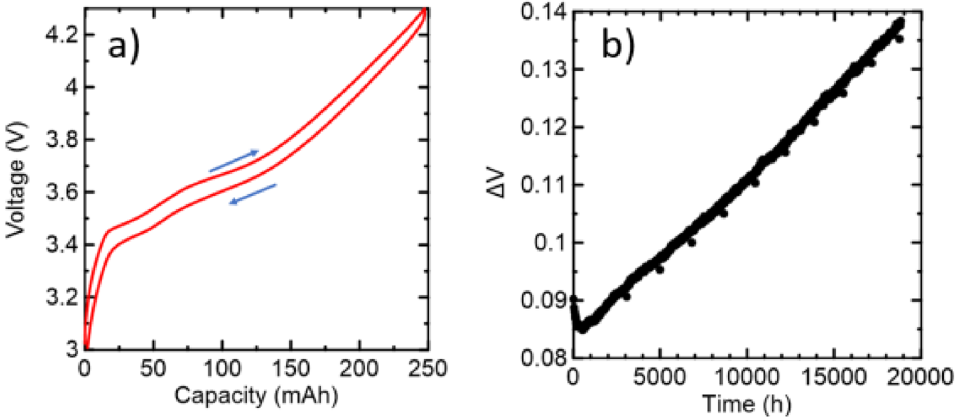
Neware cycler BTS4000 5V SERIES

Neware cycler. Each wire is attached to one cell.

Roby Gauthier *et al* 2020 *J. Electrochem. Soc.* **167** 080540

ΔV

Resistance grows
during cycling



ΔV = average charge voltage – average discharge voltage

ΔV proportional to RI (Ohm’s law)

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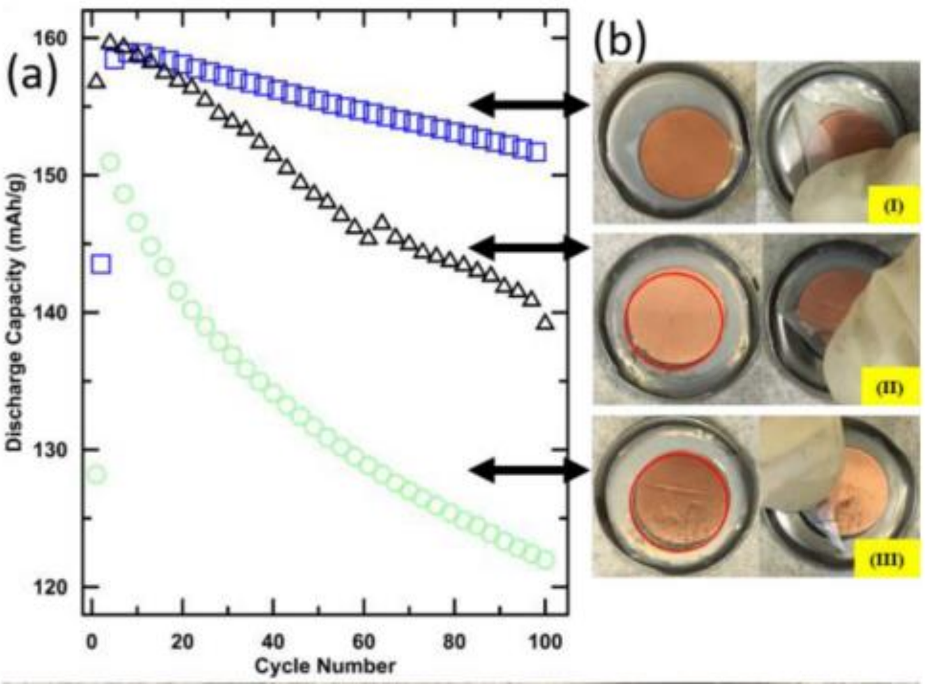
Why should coin cells not be used to test new electrolytes?



Three identical cells, very different results.

Hard to say if a new electrolyte is worse than a control.

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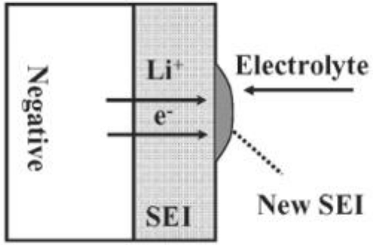
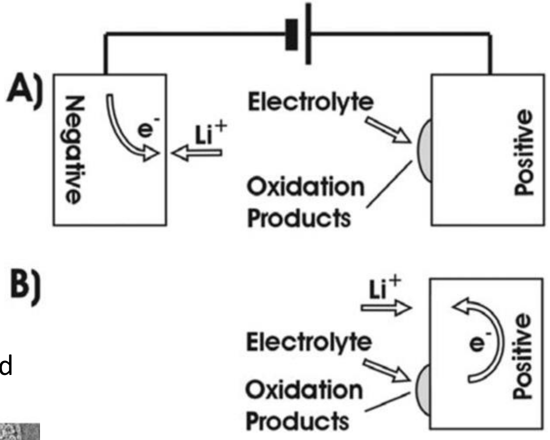
Journal of The Electrochemical Society, 166 (2) A329-A333 (2019)

Type of cell degradation and how to decouple them?

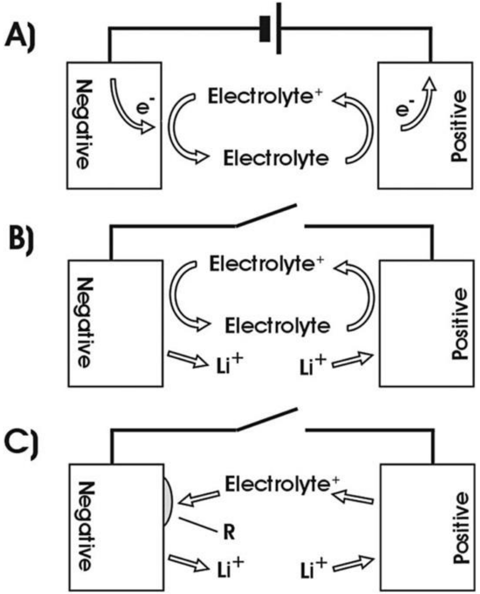
Electrolyte reduction (q_{Li})



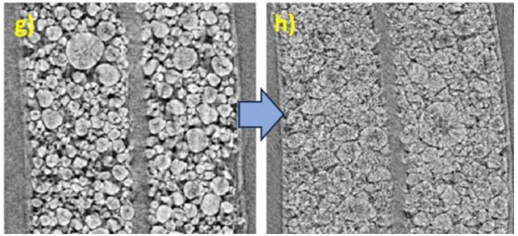
Electrolyte oxidation (q^a_{ox})



Redox shuttle (q^b_{ox})



Positive electrode particle cracking and isolation (q_p)



A. J. Smith *et al* 2011 *J. Electrochem. Soc.* **158** A1136 Toby Bond *et al* 2024 *J. Electrochem. Soc.* **171** 110514

Capacity inventory

Redox shuttle effect not included

Table I. Capacity inventory of a hypothetical Li ion cell for its first 1 ½ cycles.

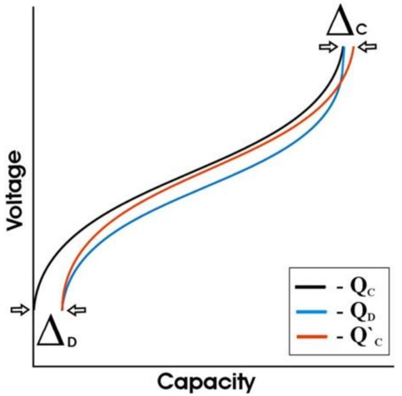
	Intial state	First charge(Q_c)	First discharge(Q_d)	Second charge(Q'_c)
Electrolyte	E	$E - q^a_{ox}$	$E - 2q^a_{ox}$	$E - 3q^a_{ox}$
Pos. electrode	Q_o	q_p	$Qo - 2q_{Li} - 2q^a_{ox}$	$3q_p$
Active Li inneg. electrode	0	$Qo - q_{Li} + q^a_{ox} - q_p$	0	$Q_o - 3q_{Li} + 3q^a_{ox} - 3q_p$
SEI	S	$S + q_{Li}$	$S + 2q_{Li}$	$S + 3q_{Li}$
SUM	$E + Q_o + S$	$E + Q_o + S$	$E + Q_o + S$	$E + Q_o + S$
Cycle capacity		$Q_o + q^a_{ox} - q_p$	$Q_o - 2q_{Li} + 2q^a_{ox} - q_p$	$Q_o - 2q_{Li} + 3q^a_{ox} - 3q_p$

Coulombic efficiency and charge endpoint capacity slippage

$$CE = \frac{Q_d}{Q_c} = \frac{Q_o - 2q_{Li} + 2q^a_{ox} - q_p}{Q_o + q^a_{ox} - q_p}$$

$$\Delta_C = Q'_C - Q_D = 3q_{ox}^a - 3q_p - 2q_{ox}^a + q_p$$

$$\Delta_C = q_{ox}^a - 2q_p$$



$$\text{Fade per cycle} = \Delta_D - \Delta_C = 2q_{Li} - 2q_{ox}^a + 2q_p$$

Discharge endpoint capacity slippage

$$\Delta_D = Q_C - Q_D = q_{ox}^a - q_p + 2q_{Li} - 2q_{ox}^a + q_p$$

$$\Delta_D = 2q_{Li} - q_{ox}^a = [1 - (CE)]Q_o,$$

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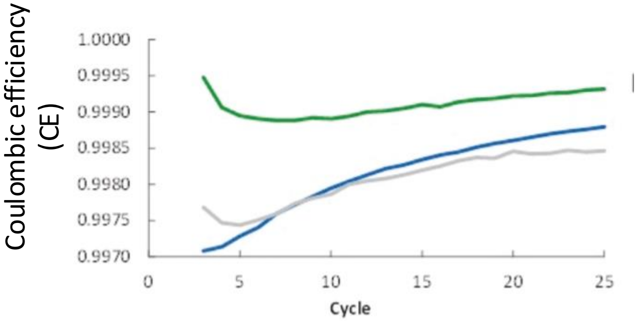
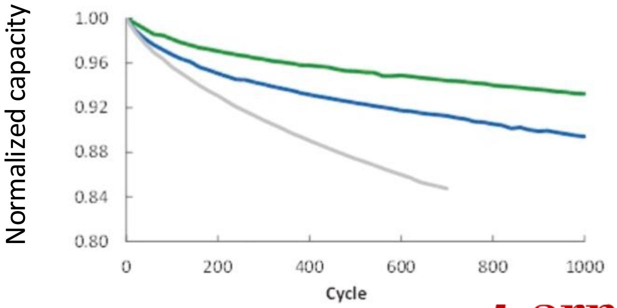
A. J. Smith *et al* 2011 *J. Electrochem. Soc.* **158** A1136

UHPC: Ultra High Precision Chargers





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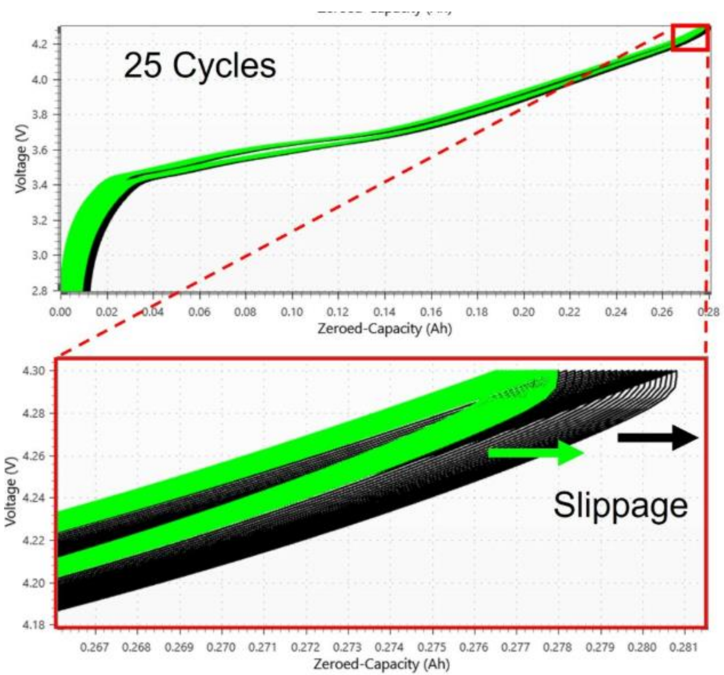
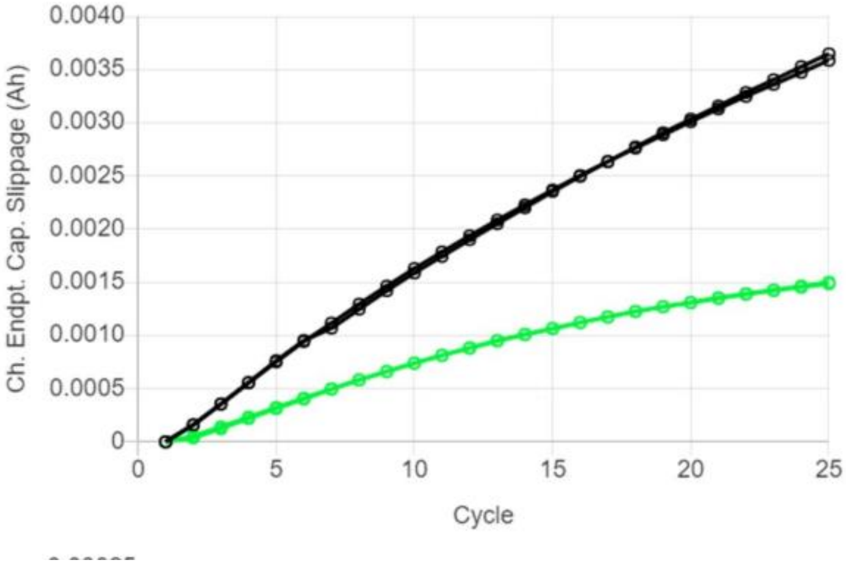
A. J. Smith *et al* 2011 *J. Electrochem. Soc.* **158** A1136

https://www.sec.gov/Archives/edgar/data/1859795/000114036122000877/ny20001370x3_20fr12b.htm

Charge endpoint capacity slippage





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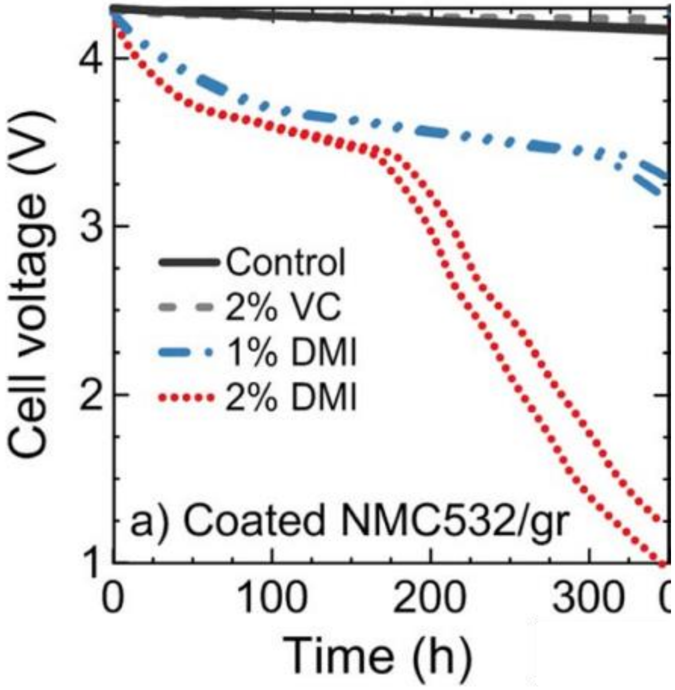
https://www.novonixgroup.com/battery-technology-solutions/uhpc/exploring-charge-end-point-capacity-slippage/

Open circuit voltage storage at high temperature (40°C or 60°C)



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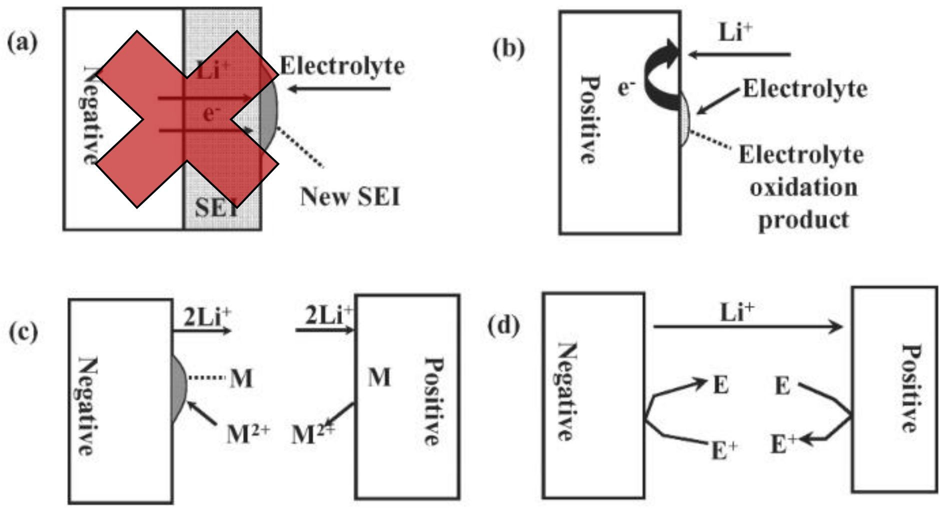
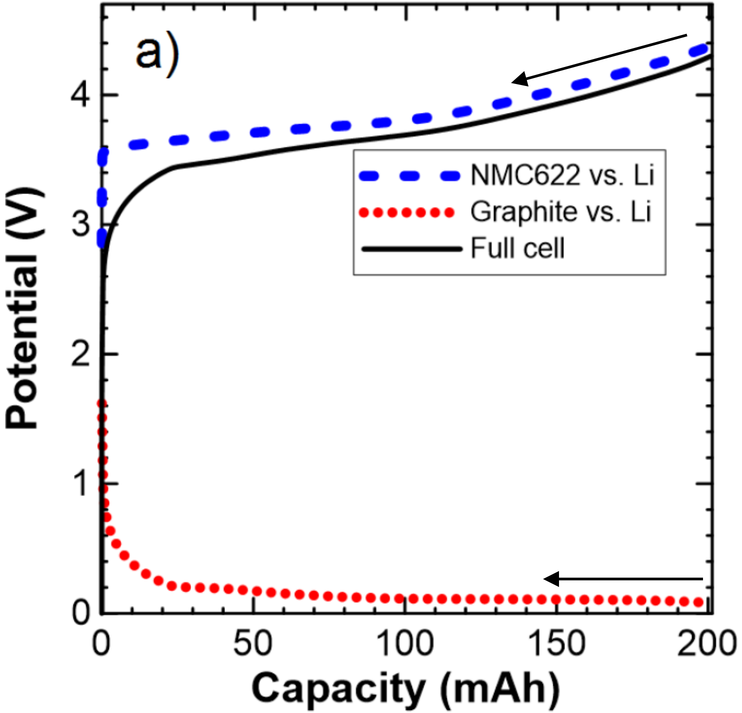
Roby Gauthier et al 2019 J. Electrochem. Soc. 166 A3707

Self-discharge mechanism



$$V_{drop} \cdot dQ / dV = q_{ox}^{a} + q_{ox}^{b}.$$



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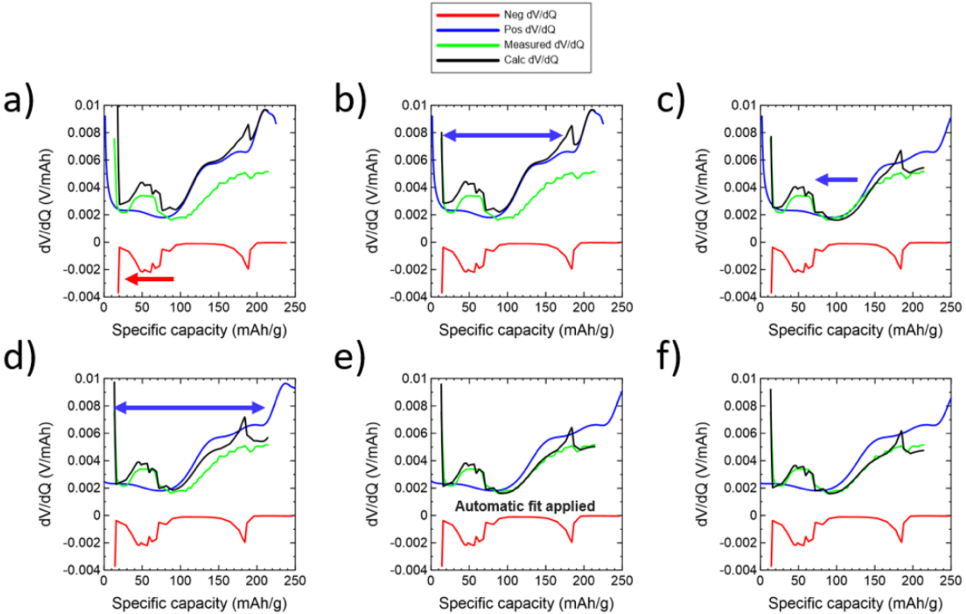
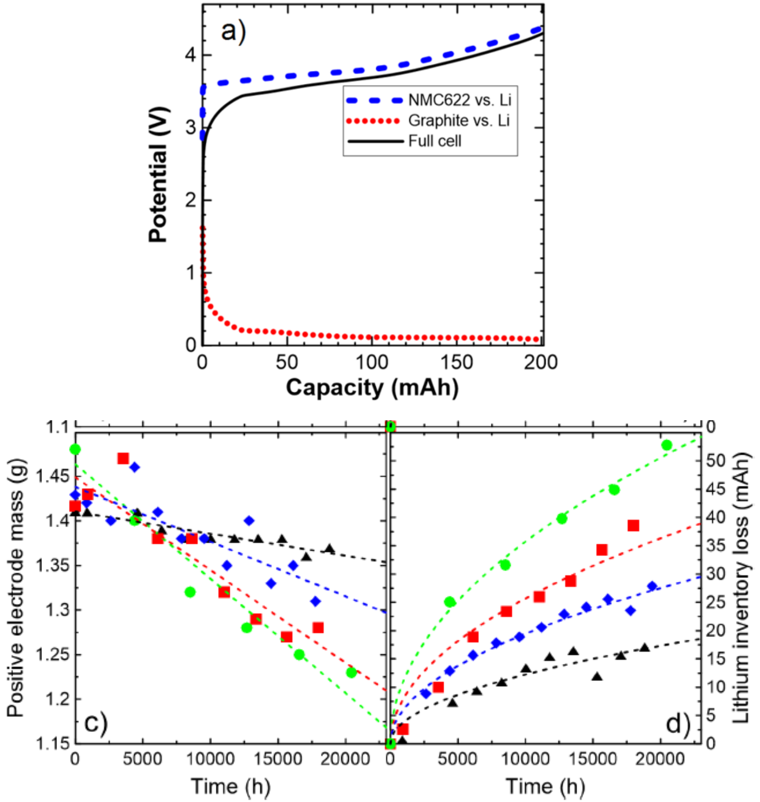
N. N. Sinha *et al* 2011 *J. Electrochem. Soc.* **158** A1194

dV/dQ analysis

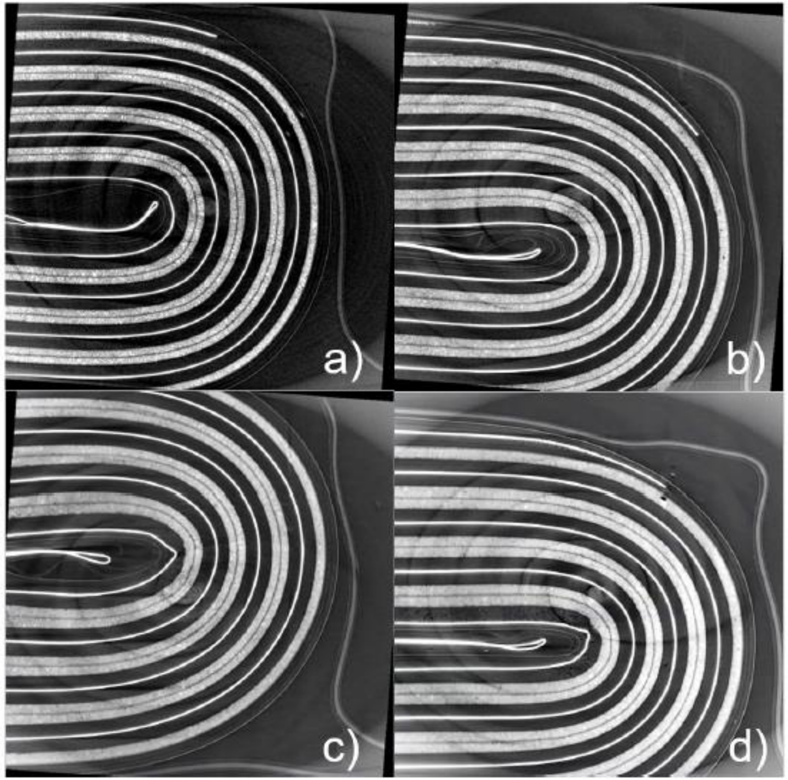
What is slippage and active mass loss?





Additional characterization techniques

CT-scans



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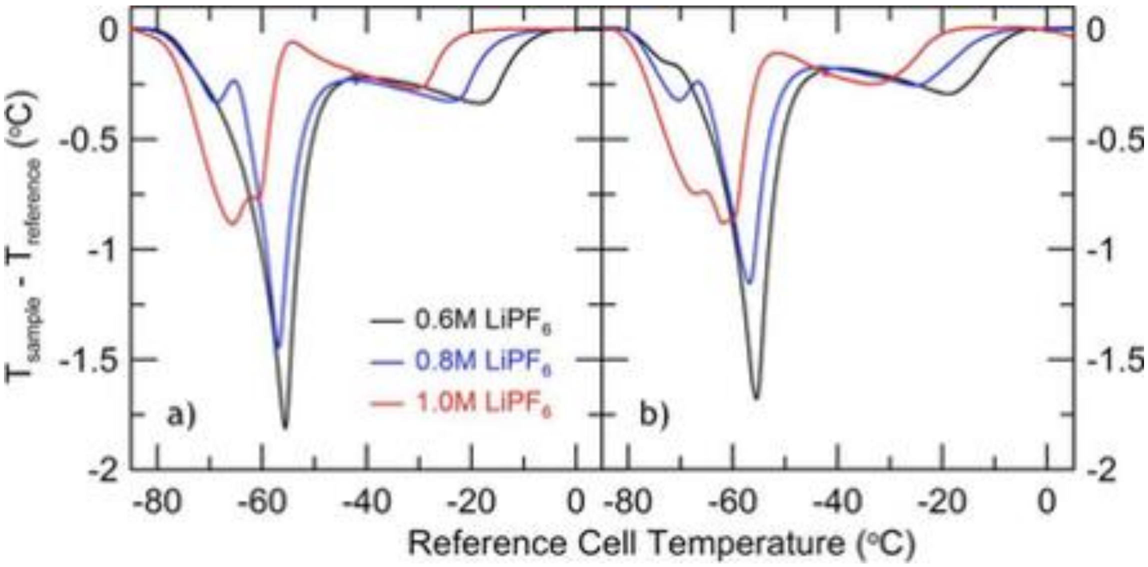
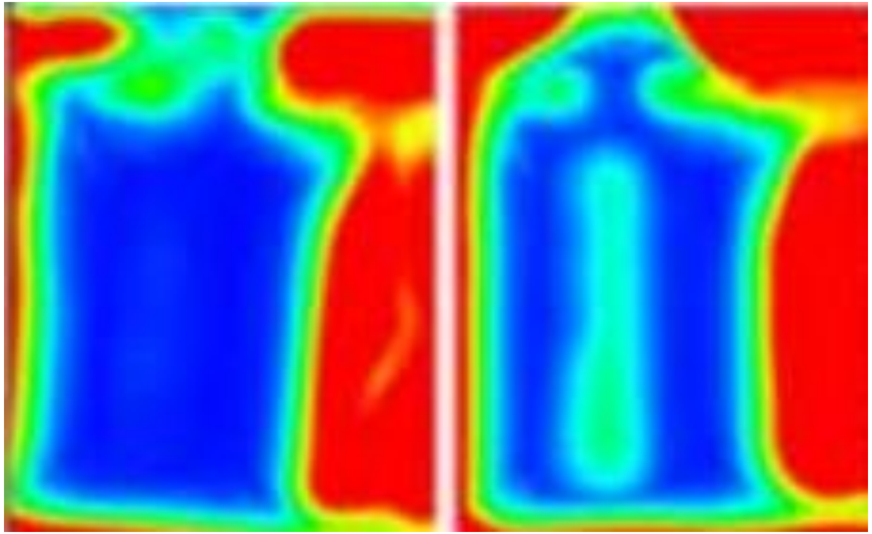
Additional characterization techniques

Differential thermal analysis

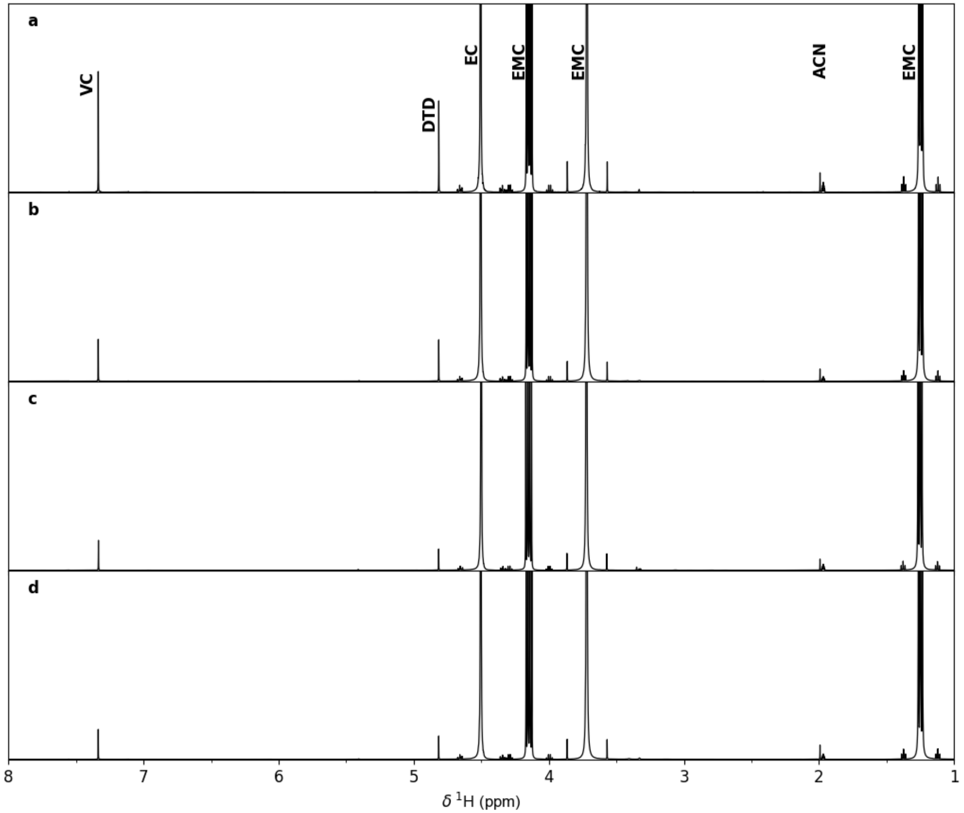


Additional characterization techniques

Ultrasonic transmission



NMR



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