Towards Next Generation Powering Solutions: Cell Assembly and Electrochemical Characterization

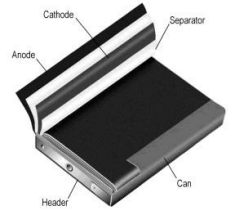
Olli Sorsa

27/10/2021 VTT – beyond the obvious

Contents

- Cell Types
- Cell Assembly
- Electrochemical Methods
  - Cyclic Voltammetry
  - Galvanostatic Cycling
  - Electrochemical Impedance Spectroscopy

Cell Types

Cell Type		Assembly Mode	Capacity / Ah
Coin Cell		Stacking single layers	0.01-0.03
Cylindrical Cell		Winding single sheets	2-6
Prismatic Cell		Winding single sheets	1-4 or 20-300
Pouch Cell		Stacking or winding multiple layers	1-50

https://batteryuniversity.com/learn/article/types_of_battery_cells#:~:text=While%20the%2018650%20has%20a,a%2050%25%20increase%20in%20volume. https://www.epectec.com/batteries/prismatic-pouch-packs.html

Laboratory Scale Cells

- Coin Cells
  - Half-Cell or Full Cell
  - Small and easy to assemble

- Cylindrical Cells or Pouch Cells
  - Full Cell testing
  - Demonstration tests and aging

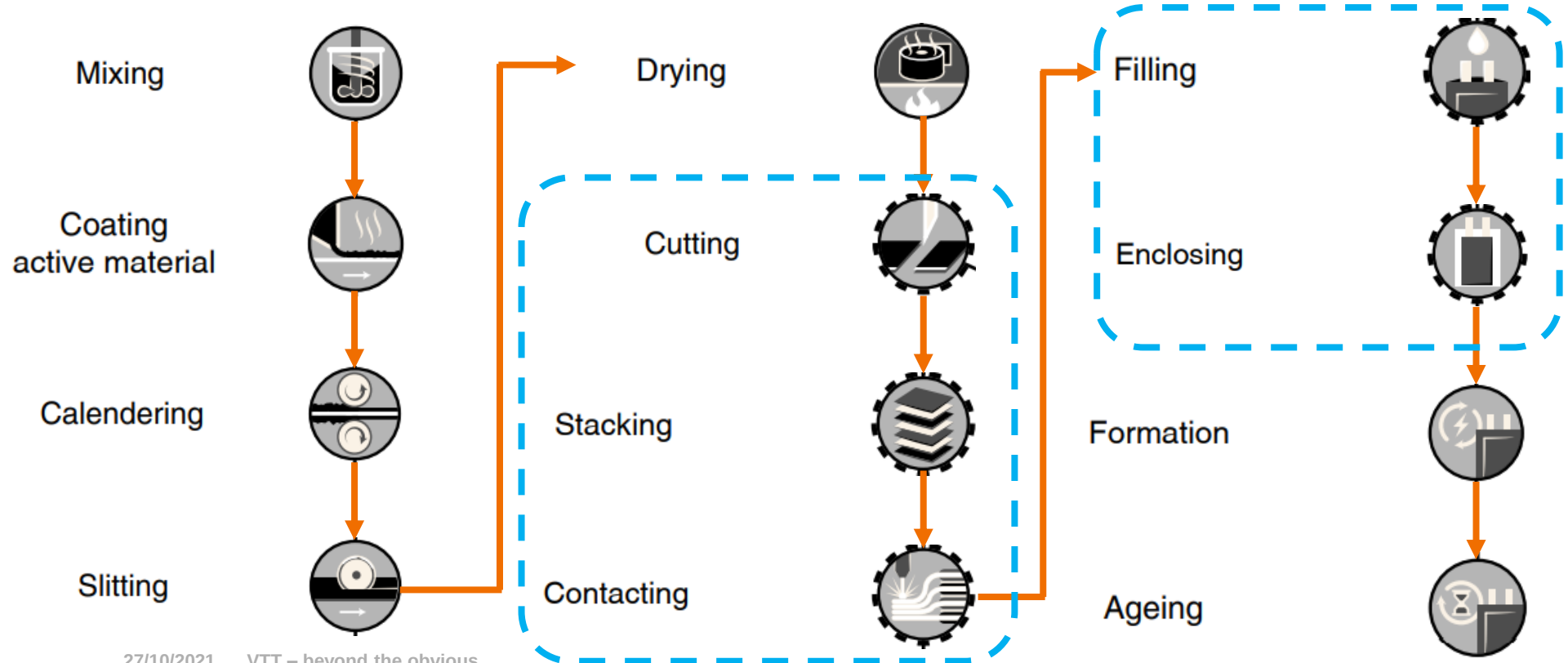
- 3-Electrode Cells
  - More detailed analysis
  - Cyclic voltammetry and Electrochemical impedance spectroscopy of single electrode

https://el-cell.com/products/test-cells/standard-test-cells/

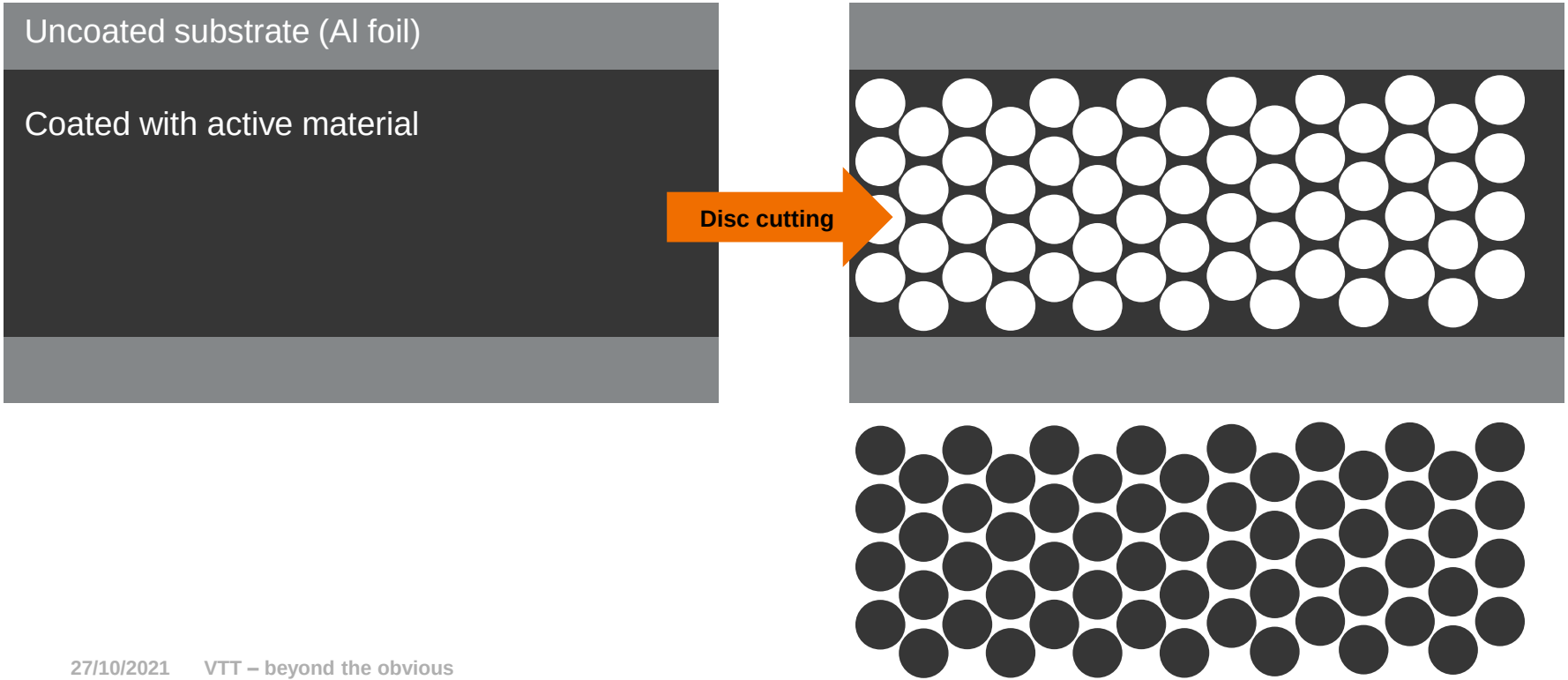
Cell Assembly

Battery Assembly

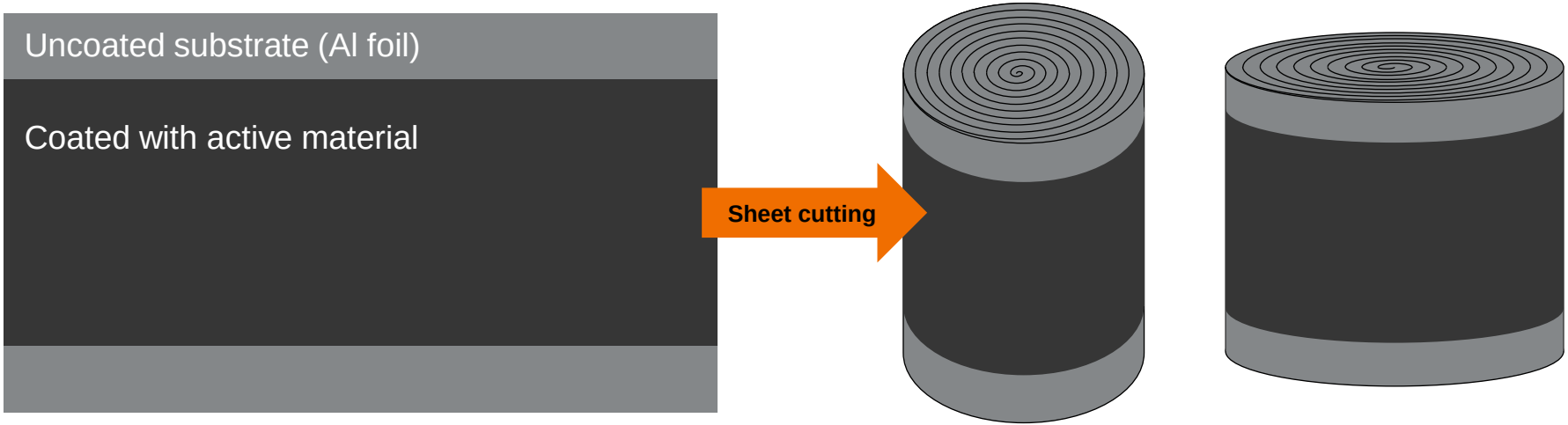
Dry room conditions
Ar glove box



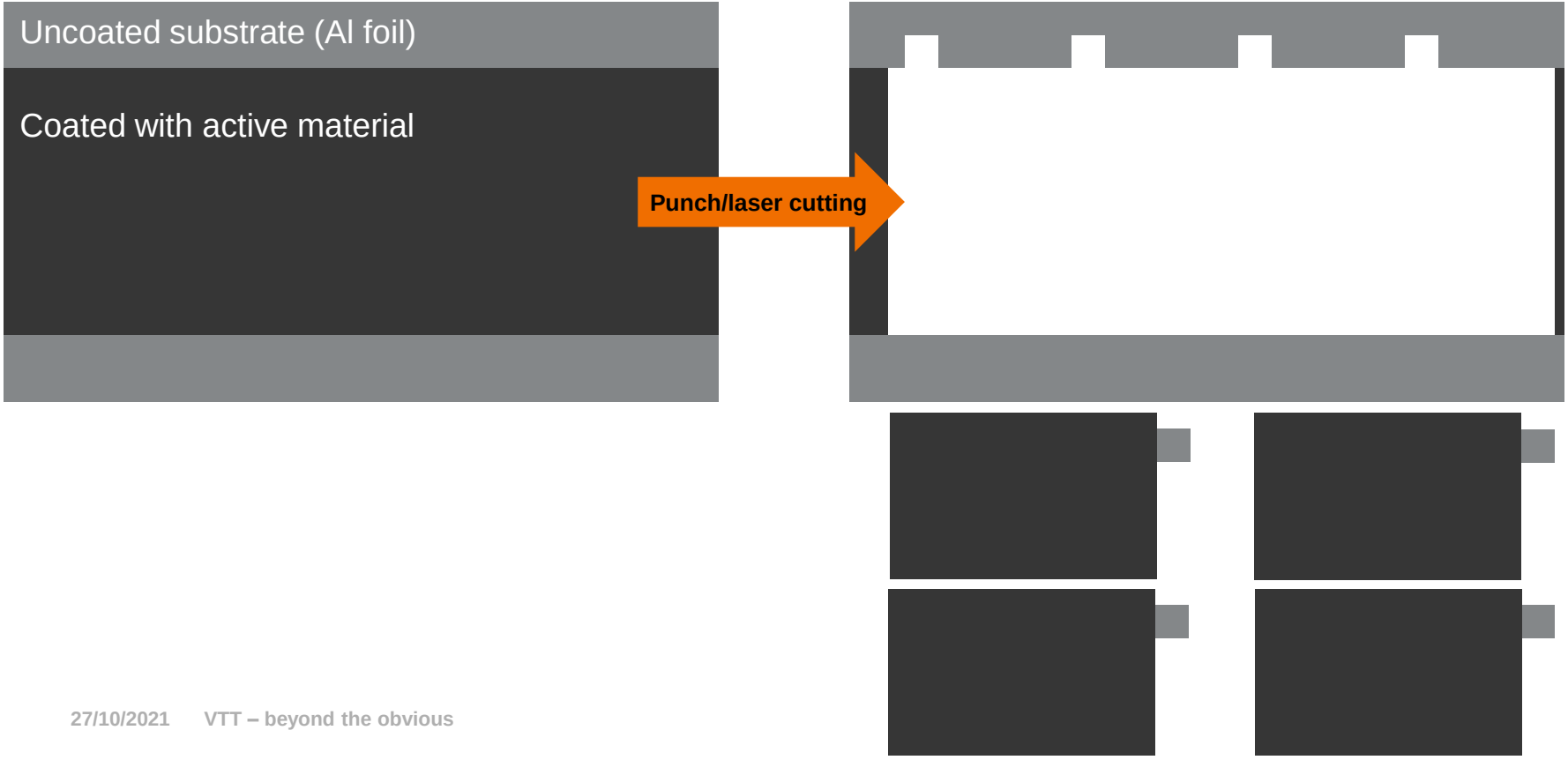
Cutting: Coin Cells



Cutting: Cylindrical & Prismatic Cells



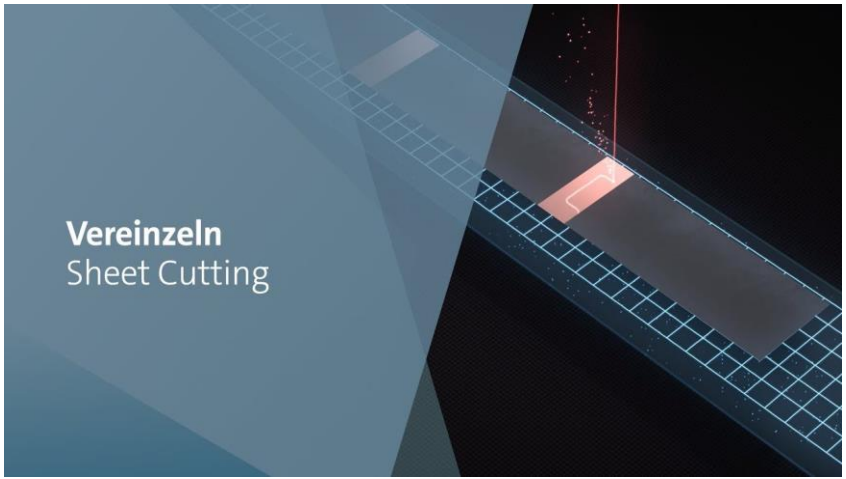
Cutting: Pouch Cells



Cutting

- Punch Cutting
  - Cheap
  - Fast in production line
  - Replaceable blades

- Laser Cutting
  - Expensive
  - Slow in production line
  - Easy to modify
  - No replaceable blades



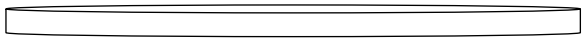
https://www.volkswagenag.com/en/news/stories/2019/09/volkswagen-starts-pilot-production-of-battery-cells.html

Assembly: Coin Cells

- Positive electrode (Cathode)
  - Single-coated NMC on Al foil

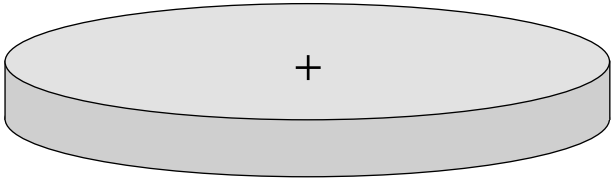
- Electrolyte
  - $LiPF_6$ in carbonate solvents

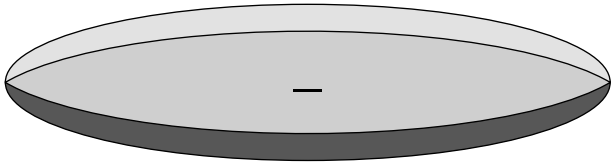
- Separator
  - PP/PE



- Negative electrode (Anode)
  - Single-coated Graphite on Cu foil

- SS CR2016 coin cell
  - 20 mm outer diameter
  - 1.6 mm outer height





Assembly: Coin Cells

- Positive electrode (Cathode)
  - Single-coated NMC on Al foil
- Electrolyte
  - $LiPF_6$ in carbonate solvents
- Separator
  - PP/PE
- Negative electrode (Anode)
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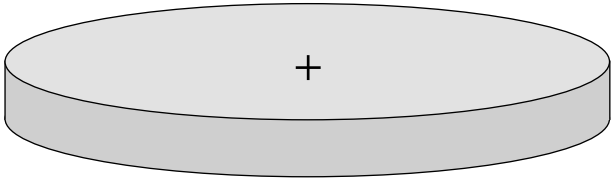
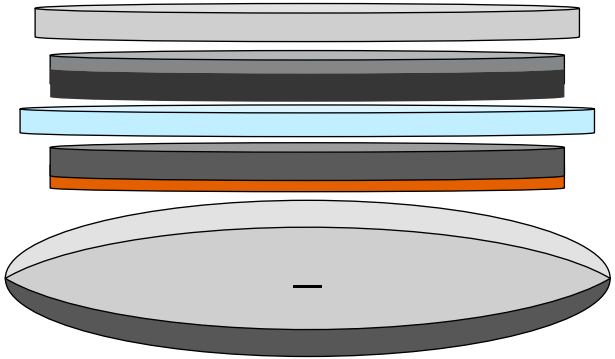


- SS spacer



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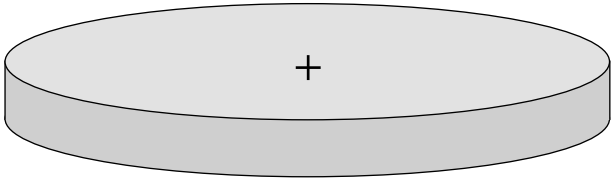
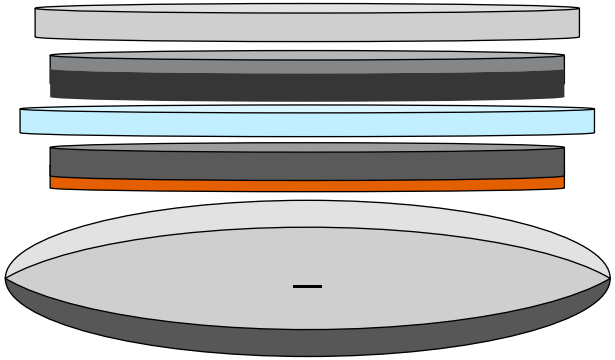


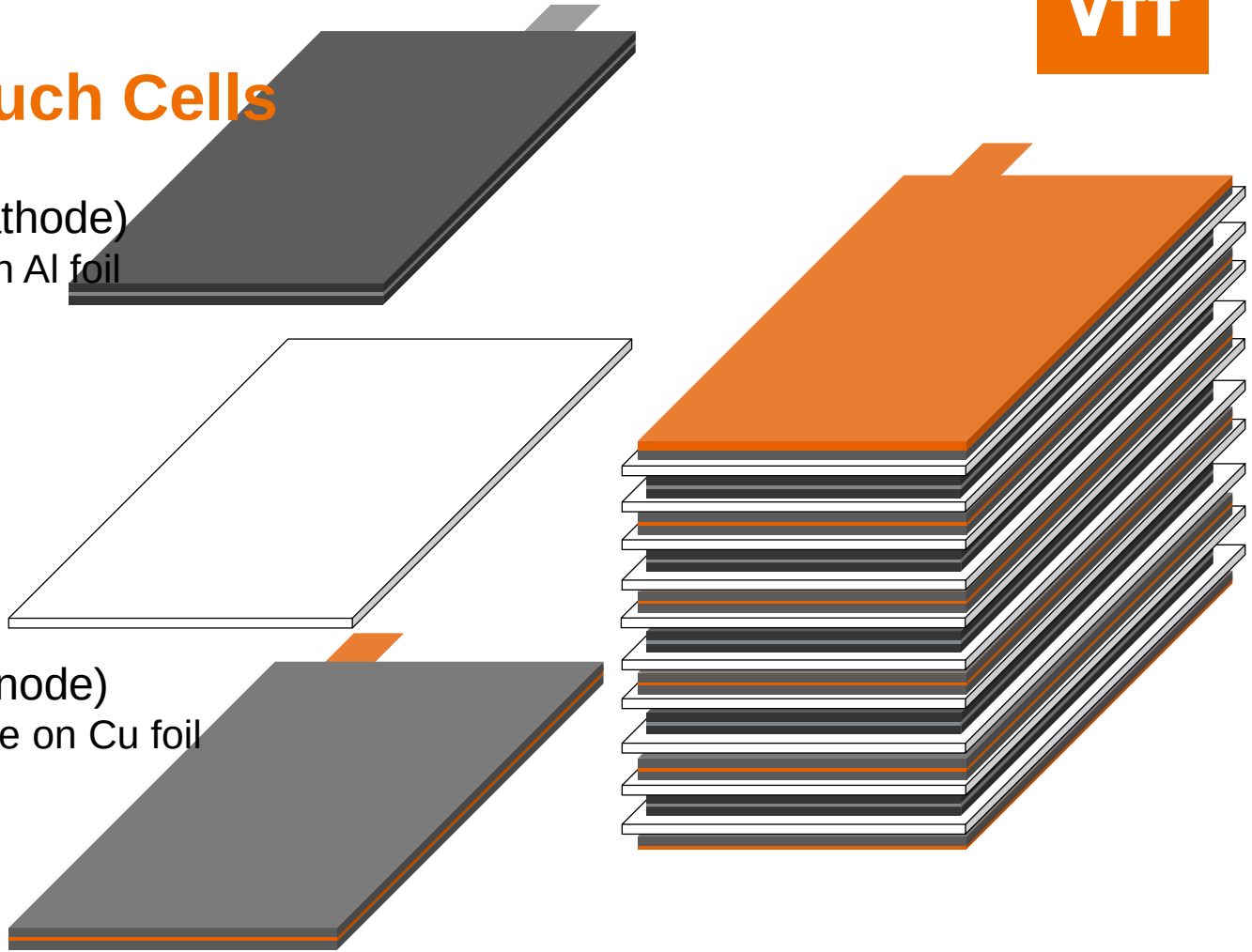
Crimping

- SS spacer



Assembly: Pouch Cells

- Positive electrode (Cathode)
  - Double-coated NMC on Al foil
- Separator
  - PP/PE
- Negative electrode (Anode)
  - Double-coated Graphite on Cu foil



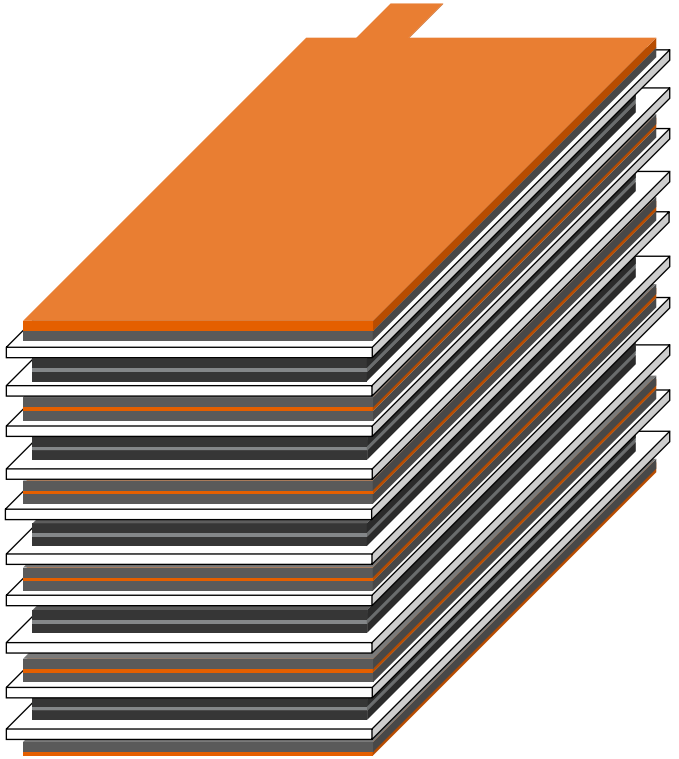
Assembly: Pouch Cells

- If cathode is 5 cm × 10 cm and 2 mAh cm^{-2}

➢ What is the capacity of this cell?

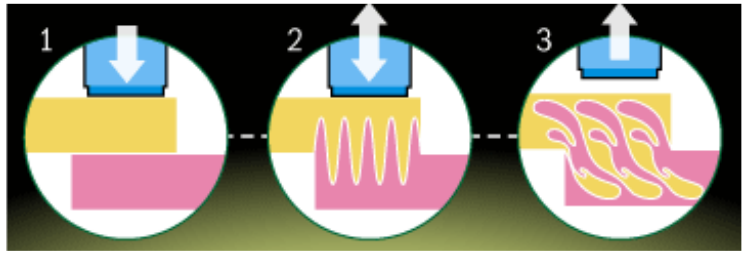
- Capacity per sheet 5 cm × 10 cm × 2 mAh cm^{-2}
  = 100 mAh = 0.1 Ah

- 5 double coated sheets → 10 × 0.1 Ah = <u>1 Ah</u>



Assembly: Pouch Cells: Tab Welding

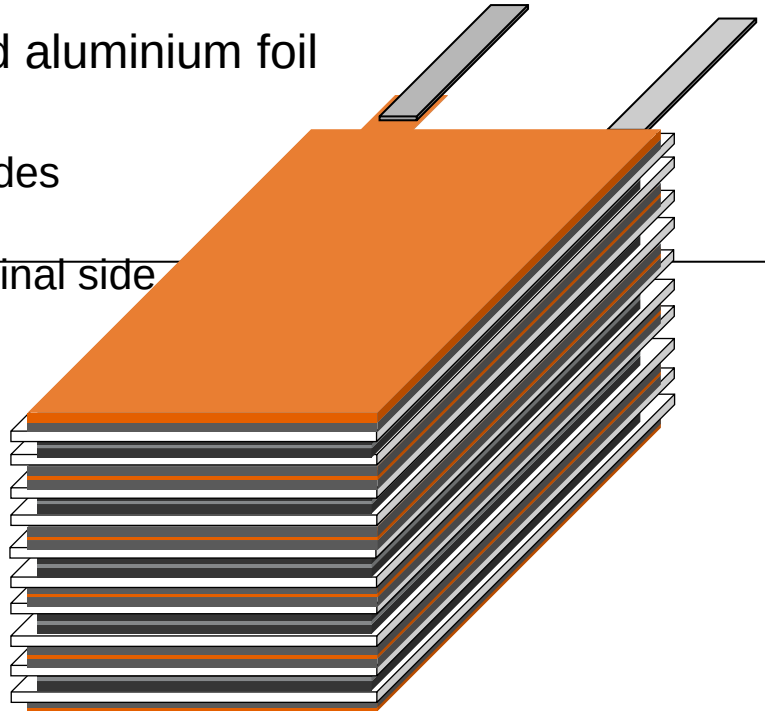
- Supersonic tab welder
- Nickel tabs for anode
- Aluminium tabs for cathode



Assembly: Pouch Cells:

- Casing with laminated aluminium foil

1) Heat sealing for 2 sides
2) Electrolyte filling
3) Vacuum sealing for final side



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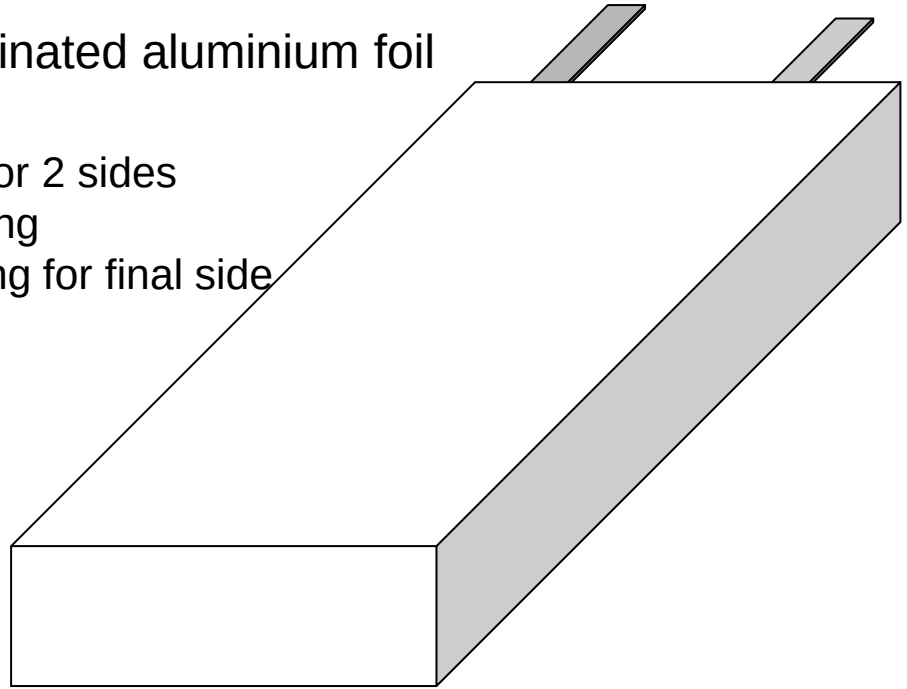
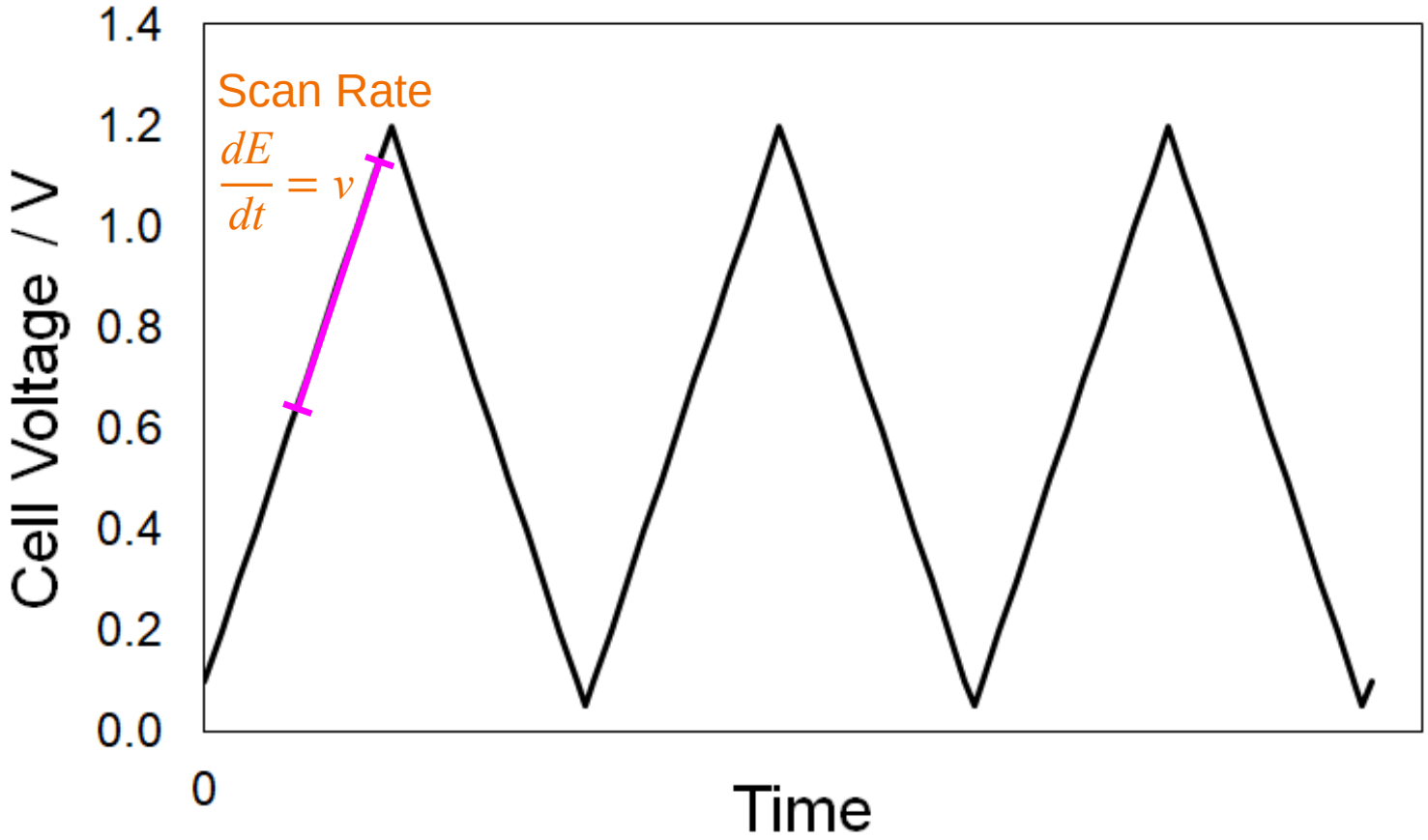


Electrochemical Methods

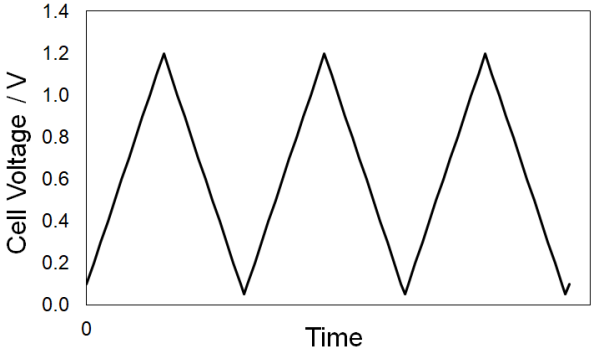
Electrochemical Methods

- Cyclic Voltammetry
- Galvanostatic Cycling
- Electrochemical Impedance Spectroscopy

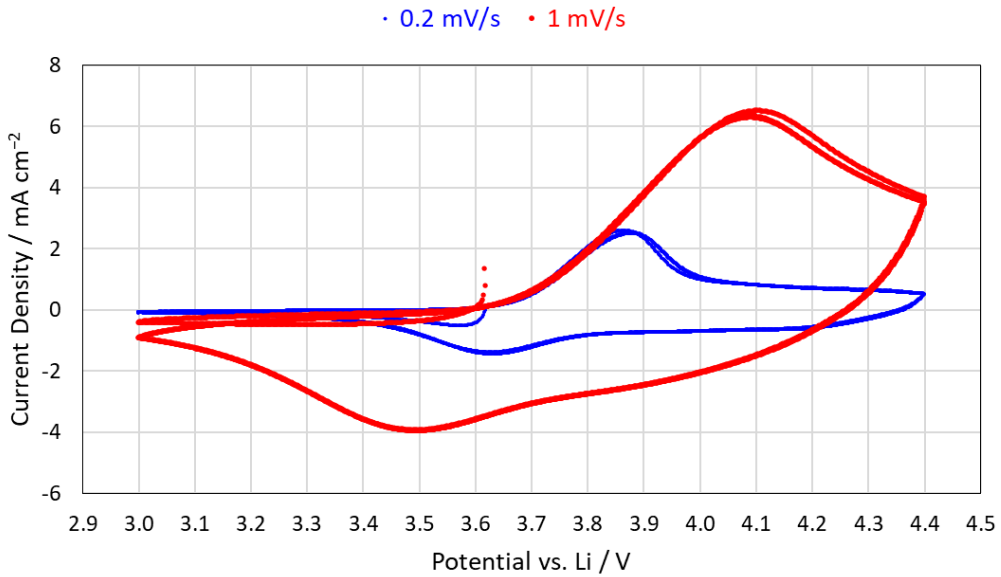
Cyclic Voltammetry



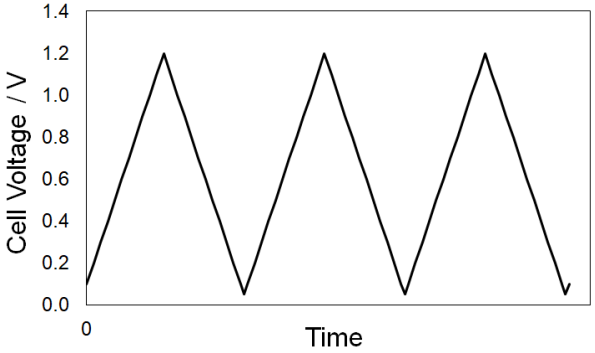
Cyclic Voltammetry



NMC(622)

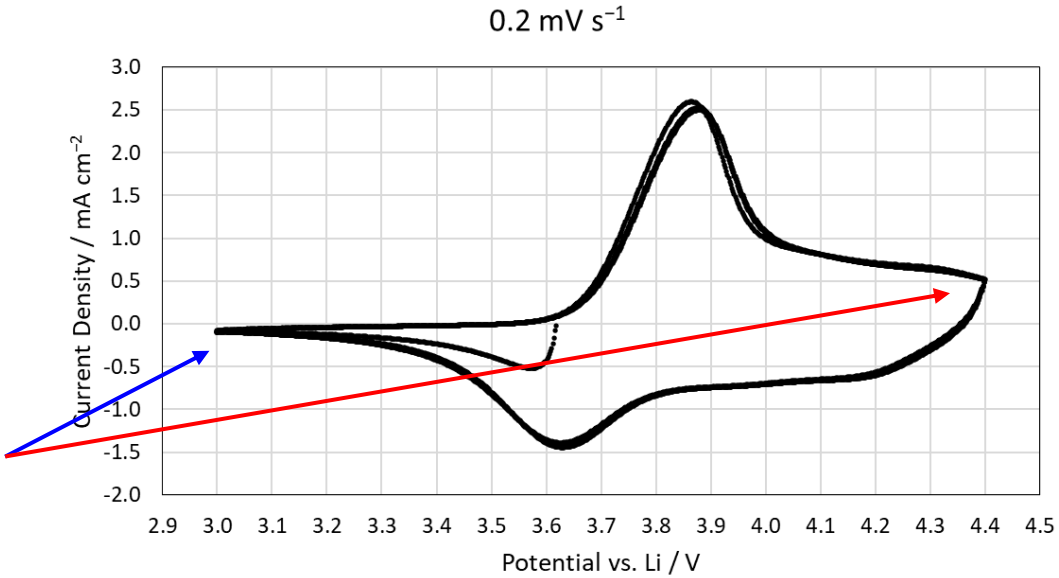


Cyclic Voltammetry



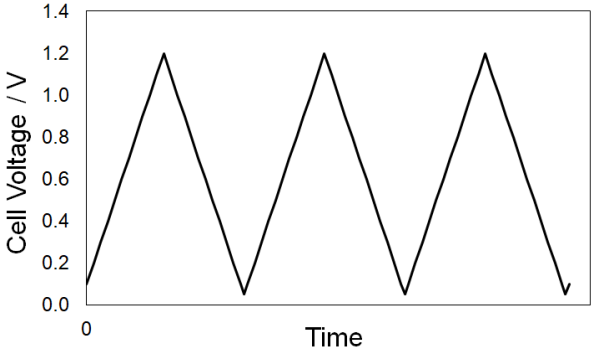
- Electrochemical Stability Window

NMC(622)

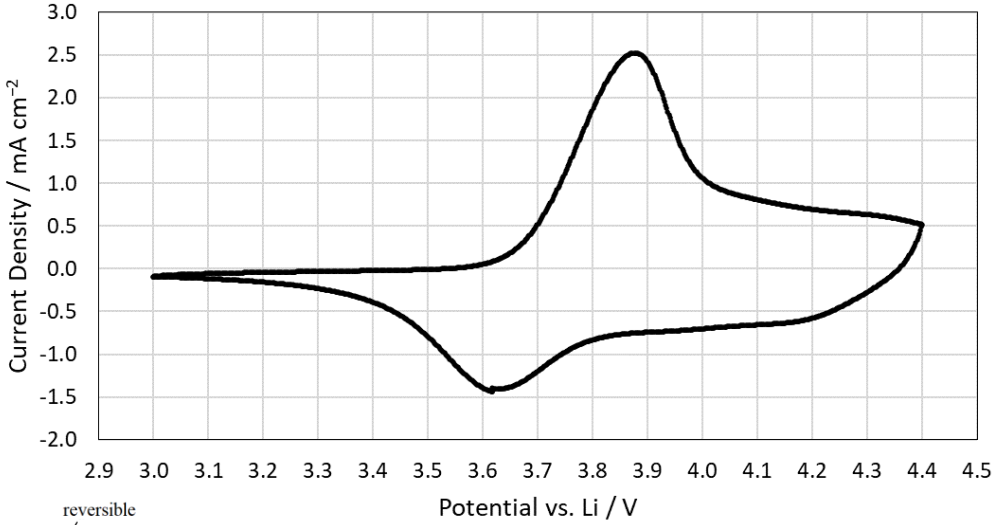


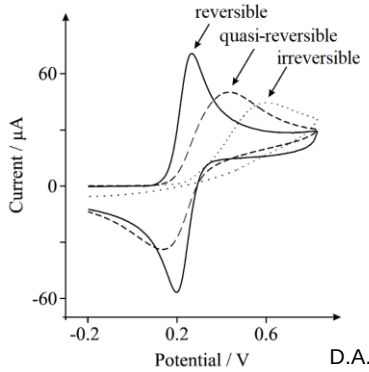
NMC(622)

Cyclic Voltammetry



- Electrochemical Stability Window
- Reversibility of redox reactions





- For reversible reaction ΔE_P = 59 mV

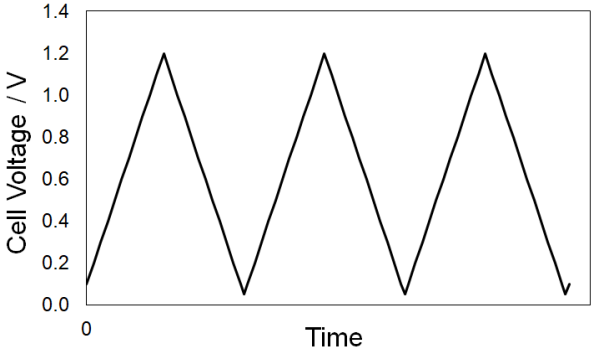
$$I_{P,Rev} = 0.446FAC(FD\nu/RT)^{0.5}$$

- For quasi-reversible reaction $\Delta E_P \propto \nu$

$$I_{P,Irrev} = 0.496(\alpha n')^{0.5}nFAC(FD\nu/RT)^{0.5}$$

D.A.C. Brownson et al. Chem. Soc. Rev. **2012** 41(21)

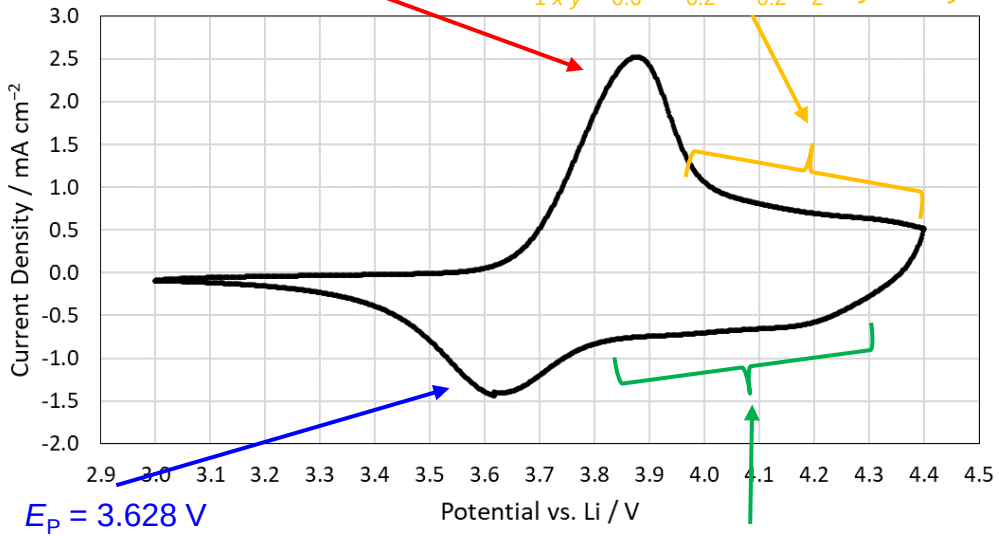
Cyclic Voltammetry



- Electrochemical Stability Window
- Reversibility of redox reactions
- Redox reaction potentials

$Li_{1.0}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2$
→ $Li_{1-x}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2 + xLi^+ + xe^-$
E_P = 3.877 V

$Li_{1-x}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2$
→ $Li_{1-x-y}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2 + yLi^+ + ye^-$

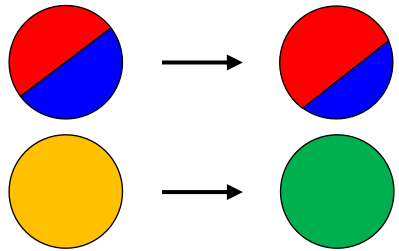


E_P = 3.628 V
$Li_{1-x}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2 + xLi^+ + xe^-$
→ $Li_{1.0}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2$

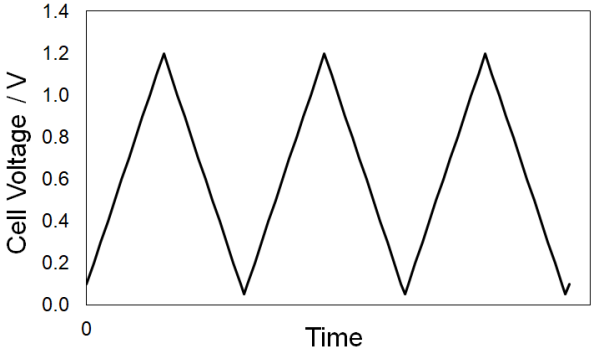
$Li_{1-x-y}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2 + yLi^+ + ye^-$
→ $Li_{1-x}Ni_{0.6}Mn_{0.2}Co_{0.2}O_2$

■ + ■ : intercalation in 2-phase domain

■ + ■ : intercalation in 1-phase domain

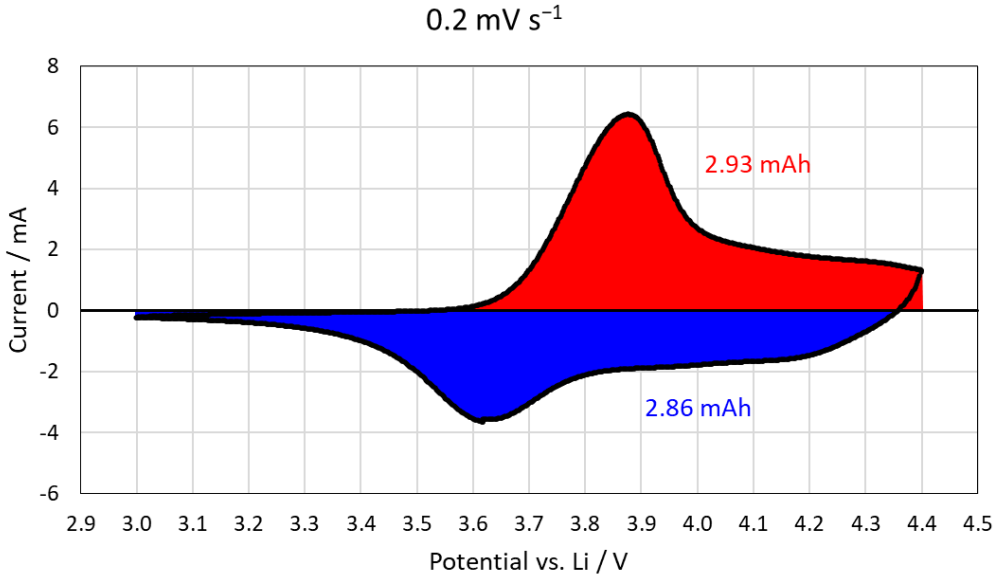


Cyclic Voltammetry



- Electrochemical Stability Window
- Reversibility of redox reactions
- Redox reaction potentials
- Capacity of the material by integration

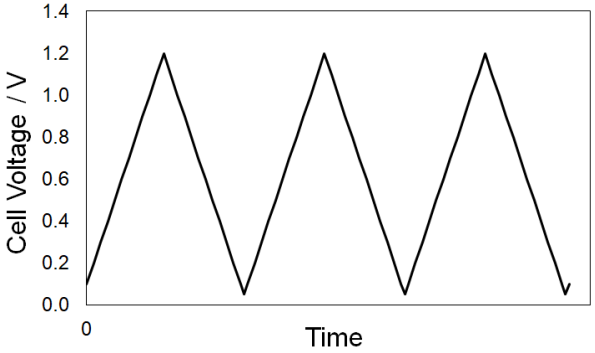
NMC(622)



$$C(F/g) = \int_{E_1}^{E_2} i(E)dE / 2(E_2 - E_1)mv$$

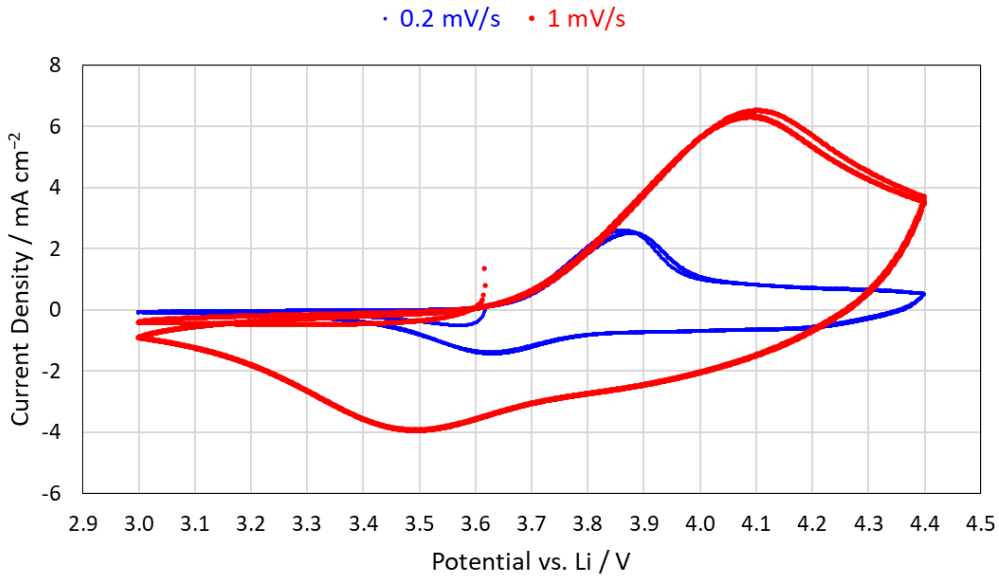
Coulombic Efficiency: 2.86 mAh / 2.93 mAh = 98%

Cyclic Voltammetry



- Electrochemical Stability Window
- Reversibility of redox reactions
- Redox reaction potentials
- Capacity of the material by integration
- Mass transport information (Randles-Ševčík)

NMC(622)



$$I_p^{Rev} = \pm(2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2}$$

Diffusion Coefficient Scan Rate

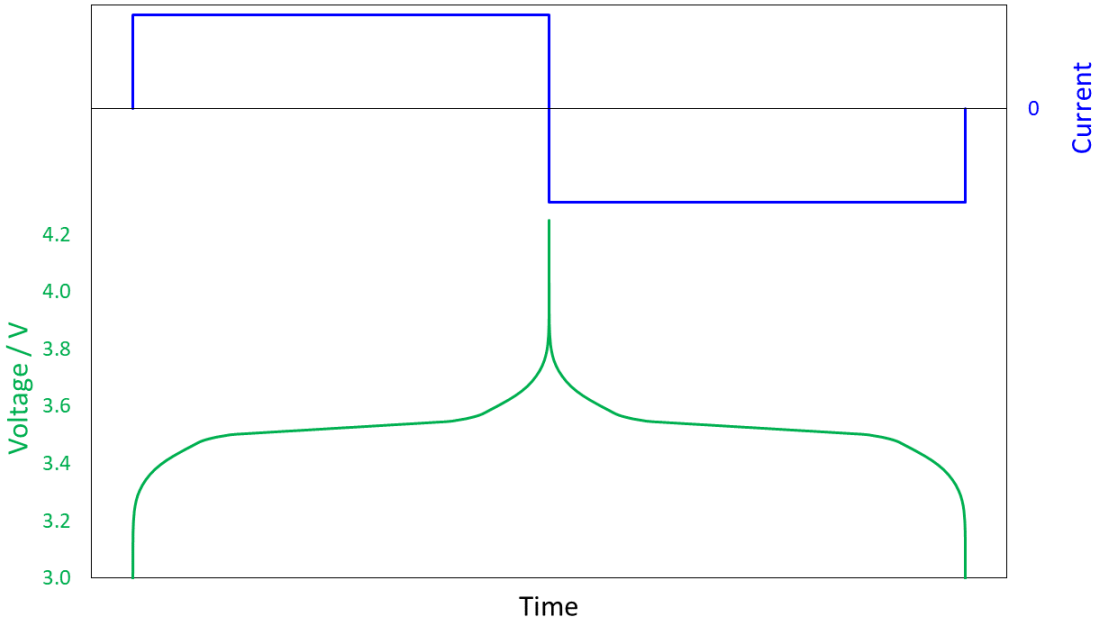
Electrochemical Methods

- Cyclic Voltammetry
- Galvanostatic Cycling
- Electrochemical Impedance Spectroscopy

Galvanostatic Cycling

The cell is charged and discharged at specific condition until a specific cut-off

- Constant current
  - Voltage cutoff
  - Charge/time cutoff
- Constant voltage
  - Current cutoff
  - Time cutoff
- Constant power
  - Voltage cutoff
  - Charge/time cutoff
- …



Galvanostatic Cycling

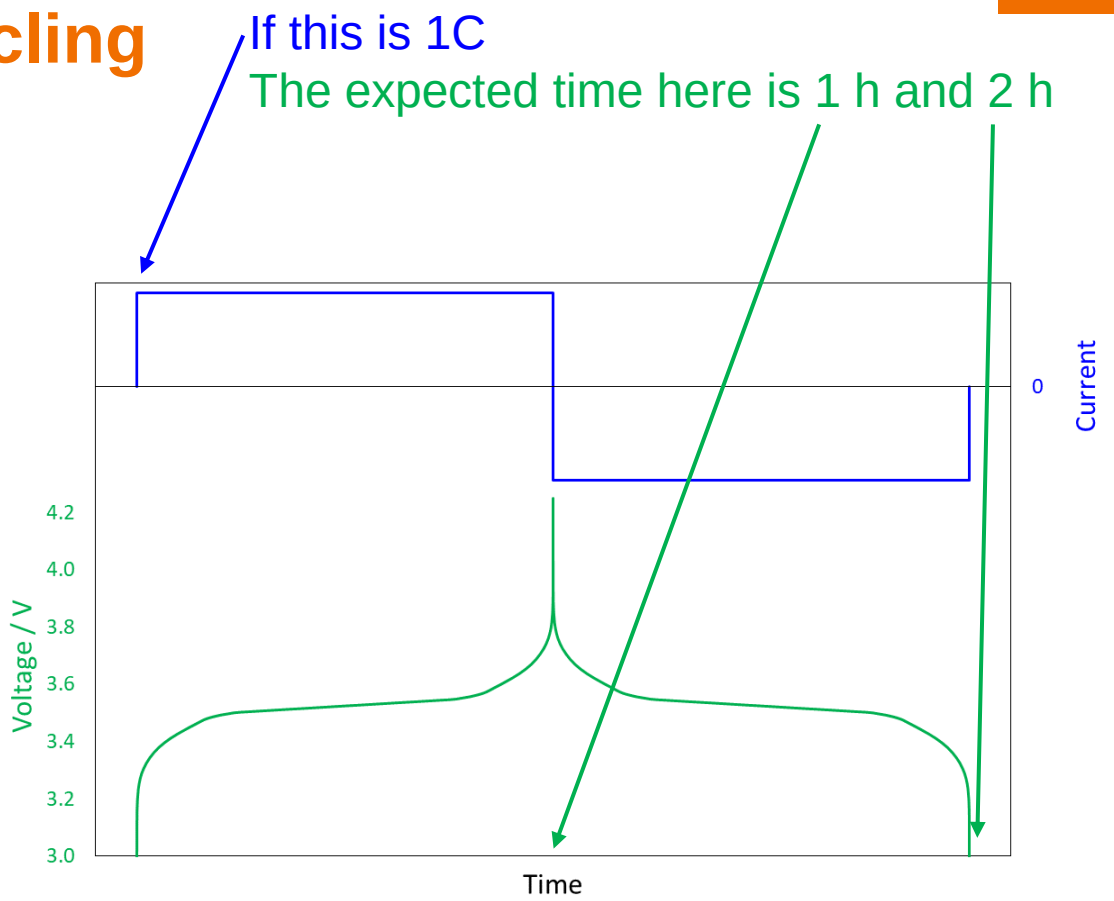
C-rate

1C current for a 100 mAh cell is 100 mA

→ 2C current 200 mA
= ~0.5 h charging/discharging

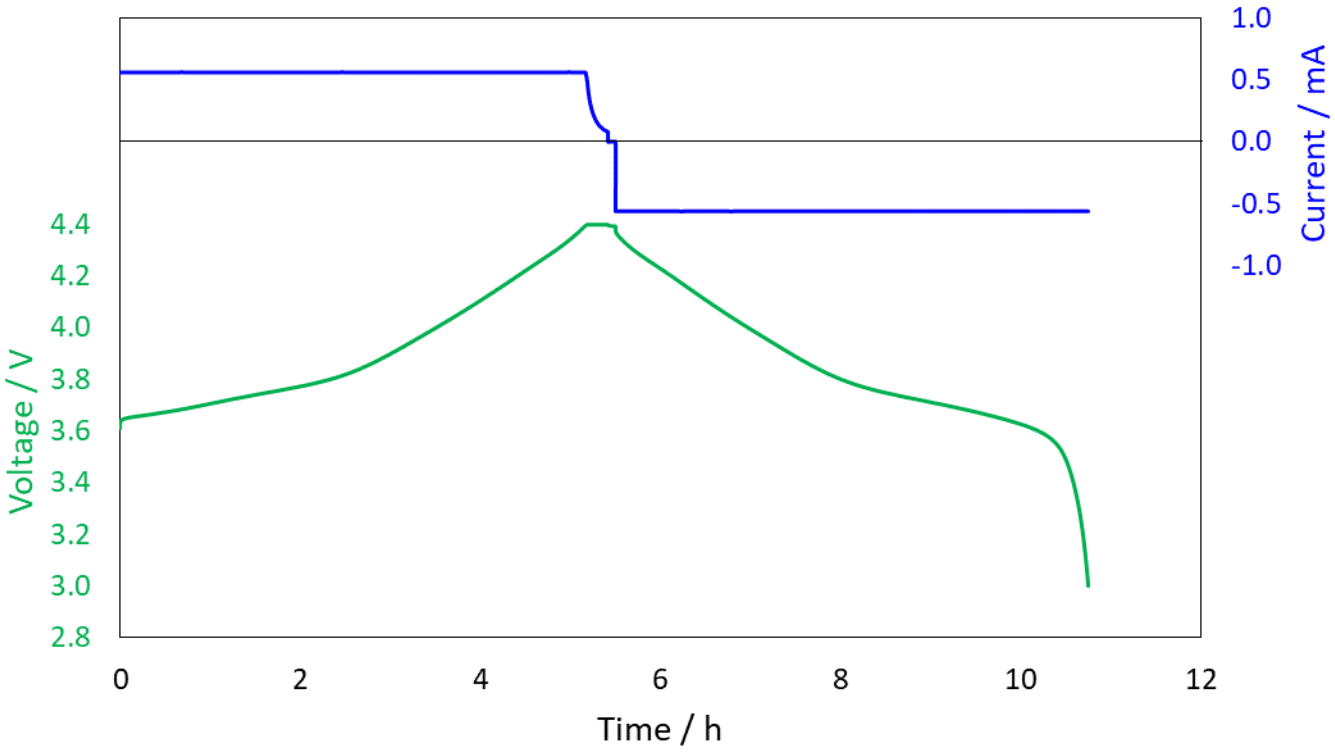
→ 0.5C current 50 mA
= ~2 h charging/discharging

…



Galvanostatic Cycling

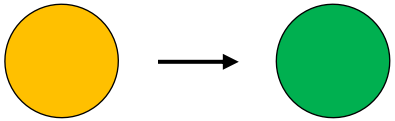
- NMC(622)
- CCCV mode for charging
- Rate is 0.2 C → 5 h

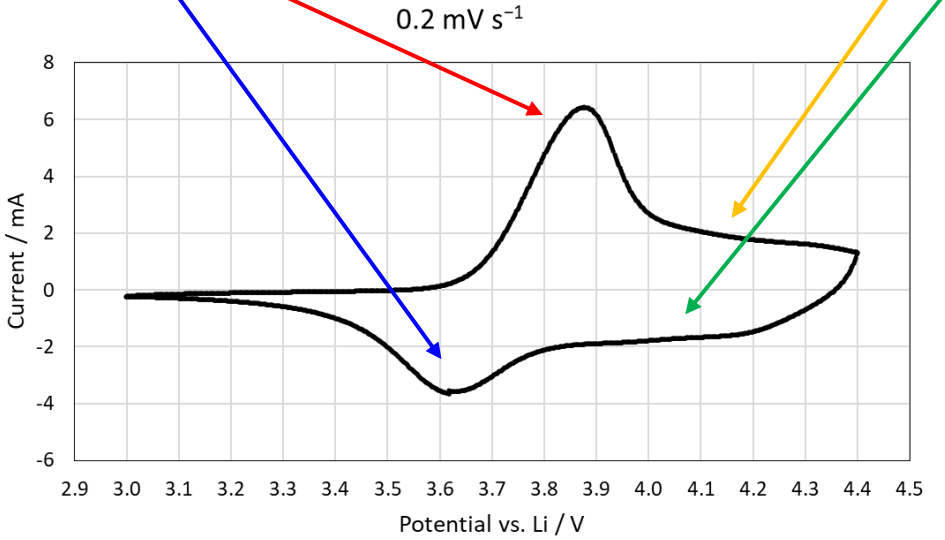


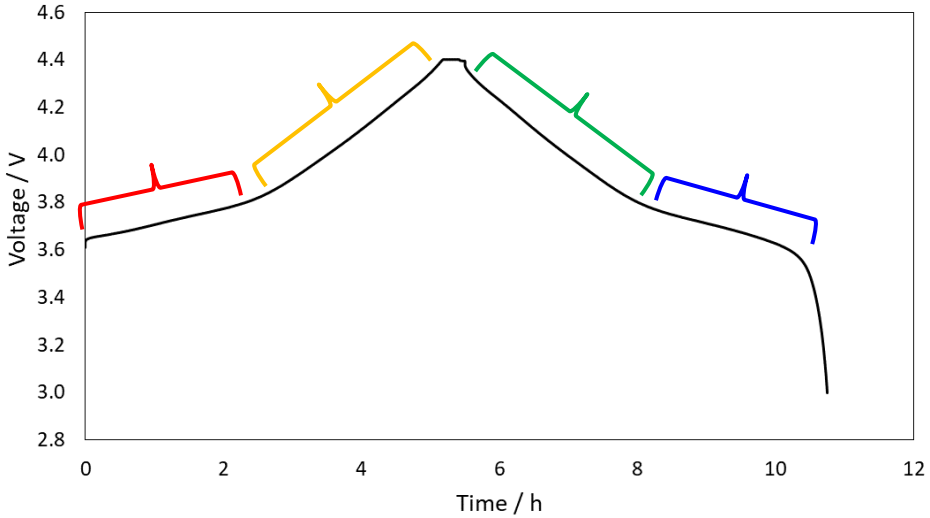
Galvanostatic Cycling

+ : intercalation in 2-phase domain

+ : intercalation in 1-phase domain

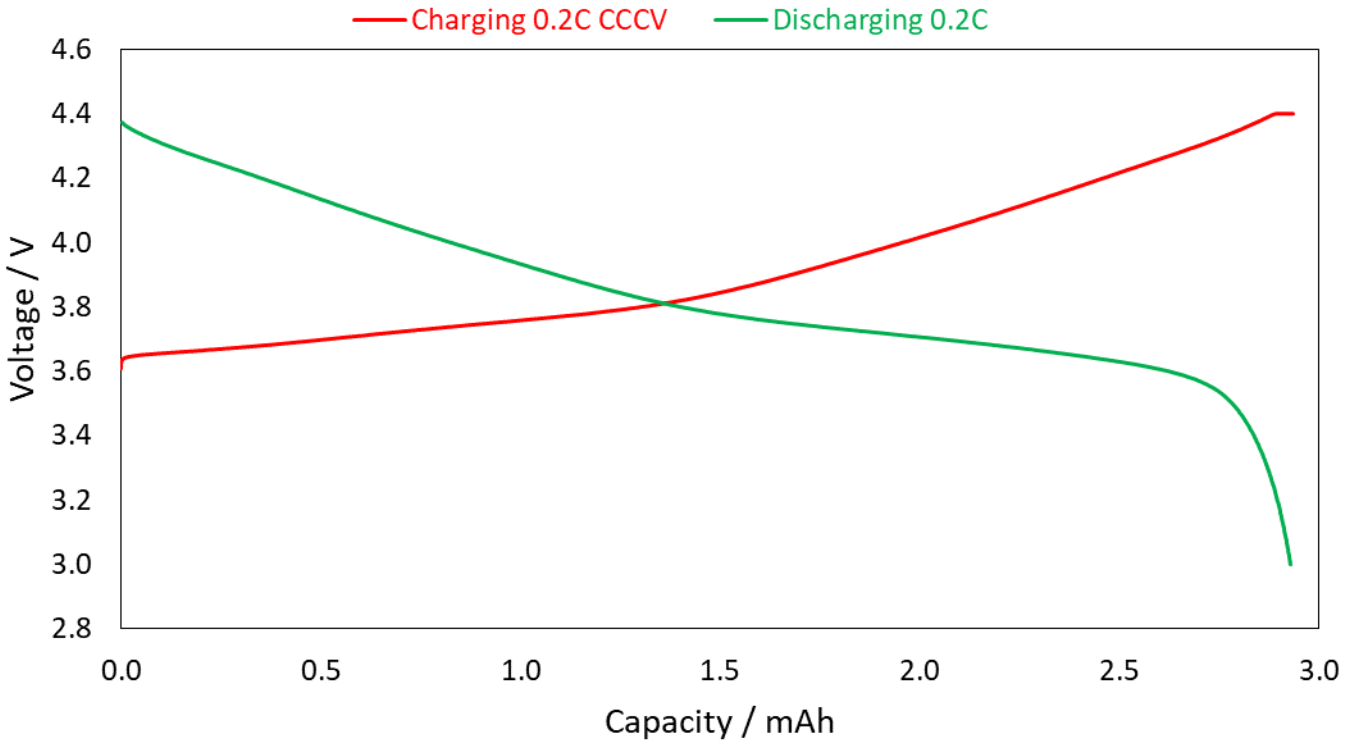






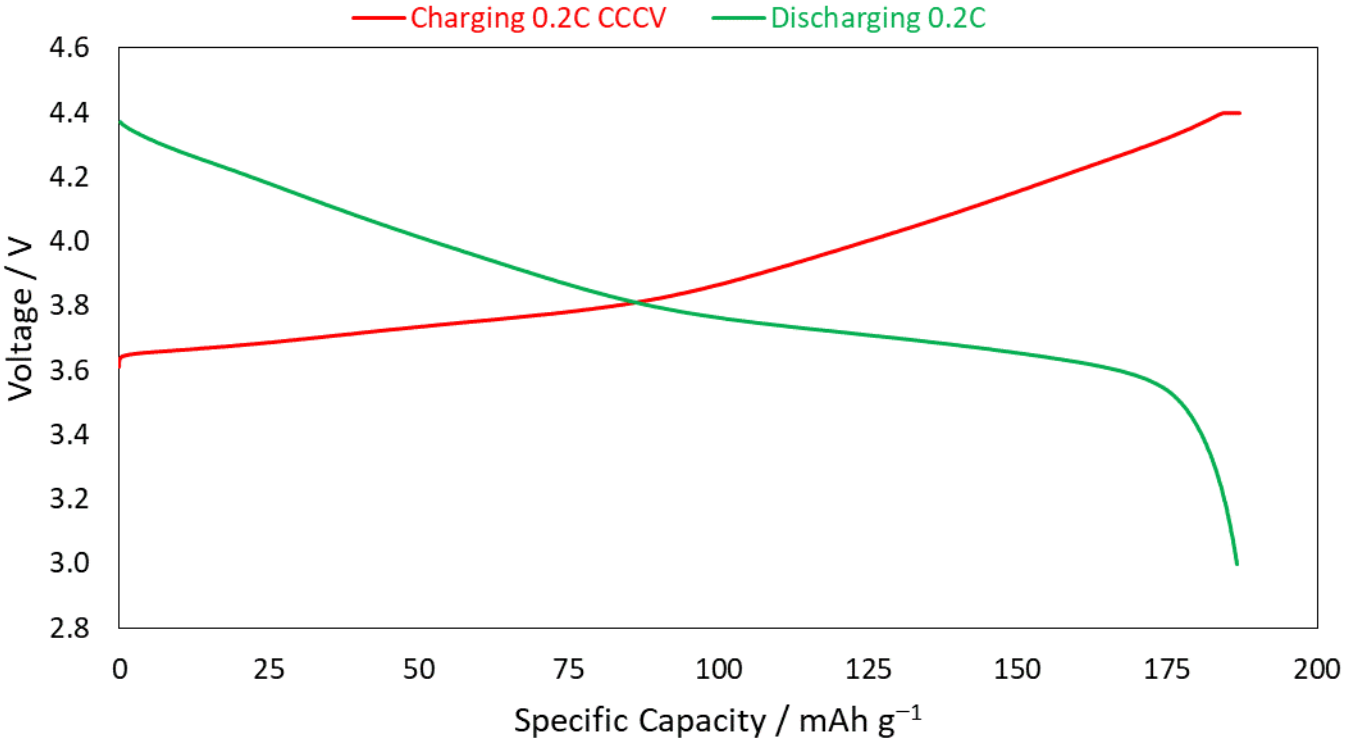
Galvanostatic Cycling

- NMC(622)
- Capacity



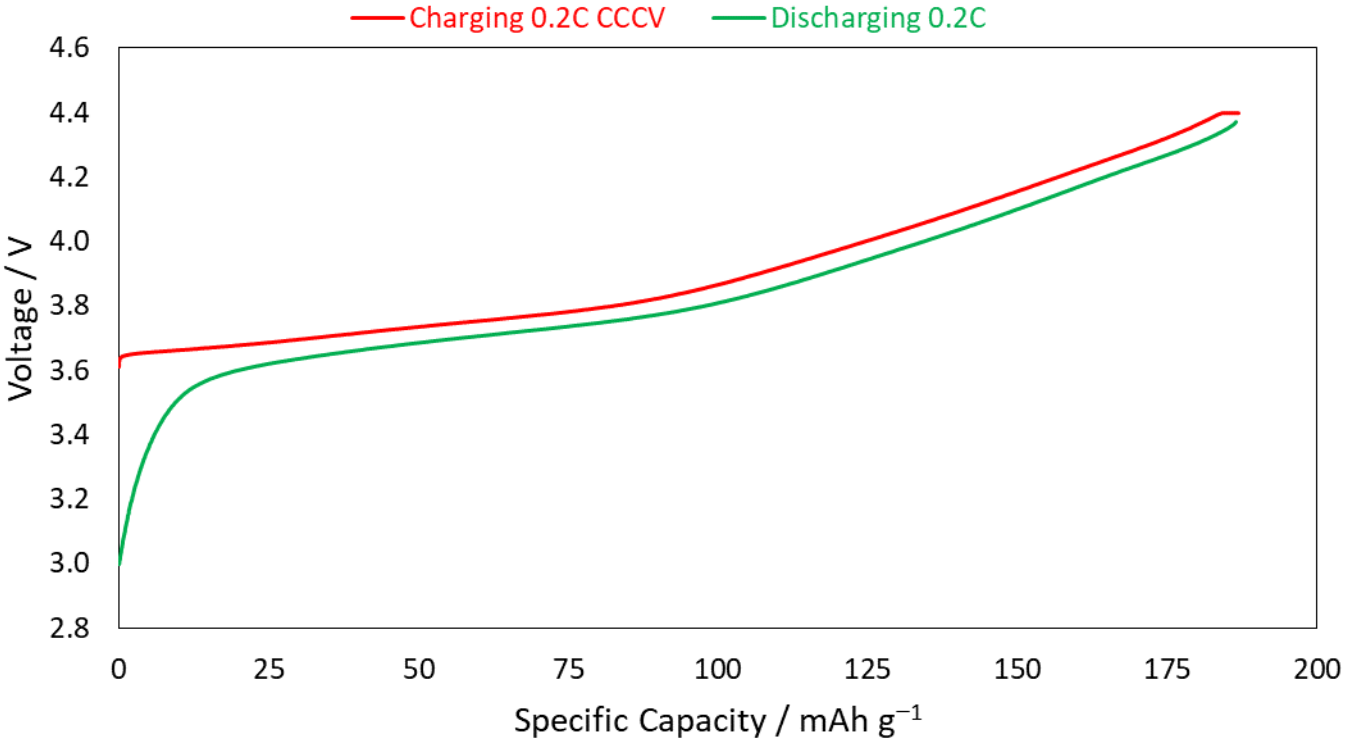
Galvanostatic Cycling

- NMC(622)
- Capacity
- Normalization



Galvanostatic Cycling

- NMC(622)
- Capacity
- Normalization
- Inversion



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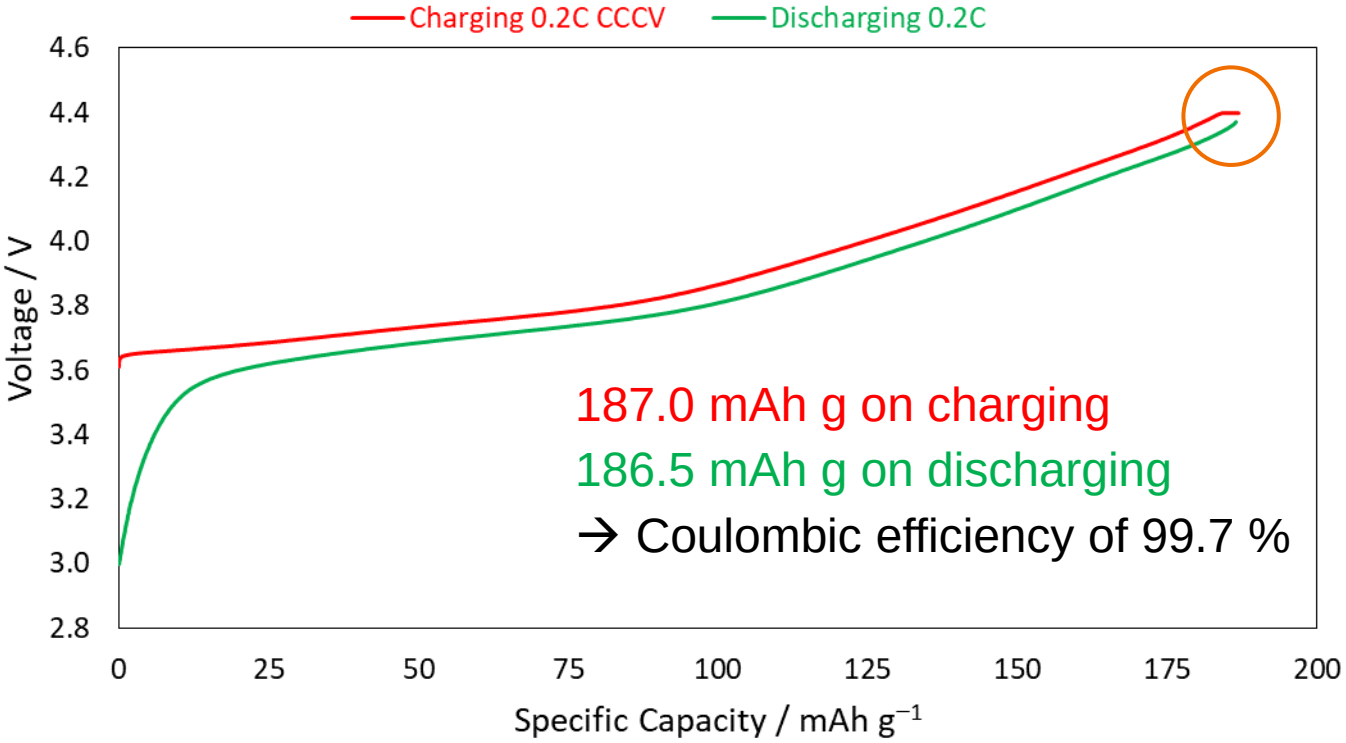

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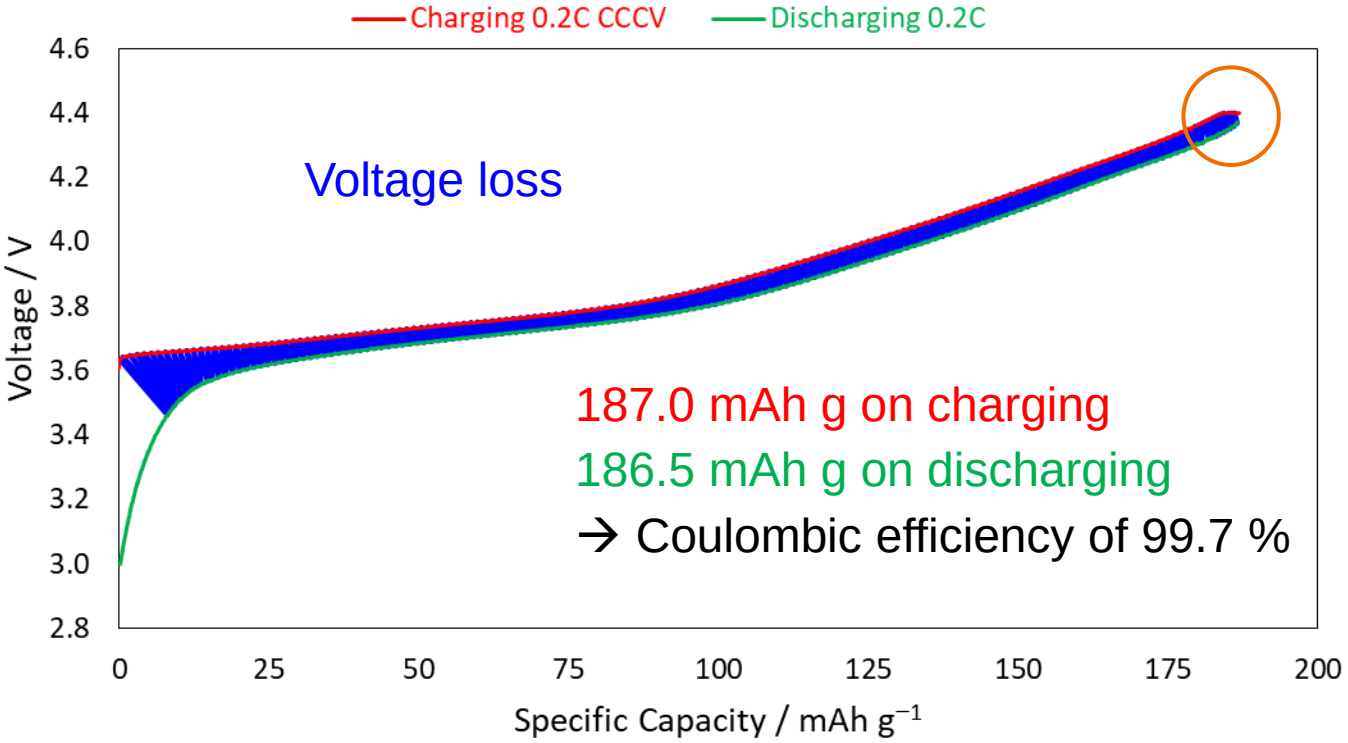
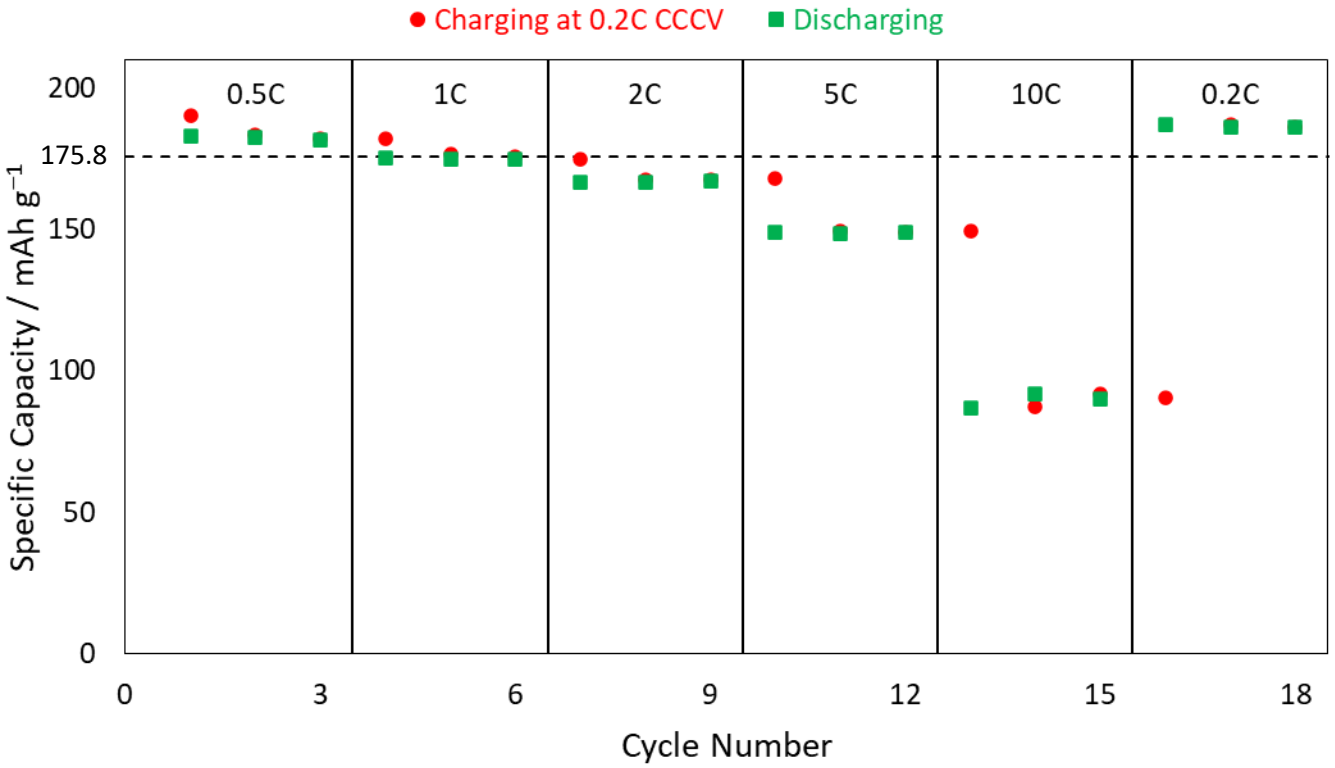


Galvanostatic Cycling

Rate capability

- CCCV mode
- NMC(622)
  - 175.8 mAh g^{-1}



Electrochemical Methods

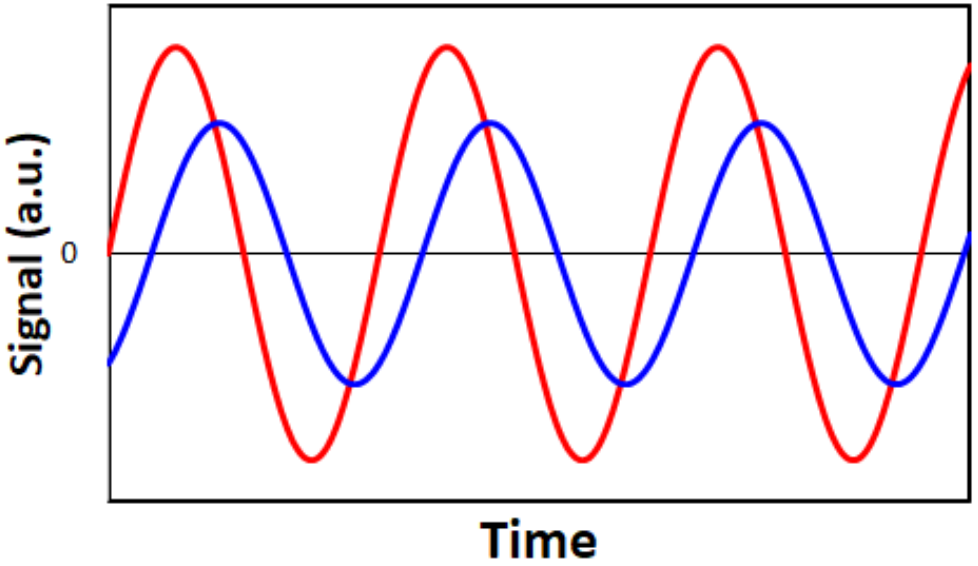
- Cyclic Voltammetry
- Galvanostatic Cycling
- Electrochemical Impedance Spectroscopy

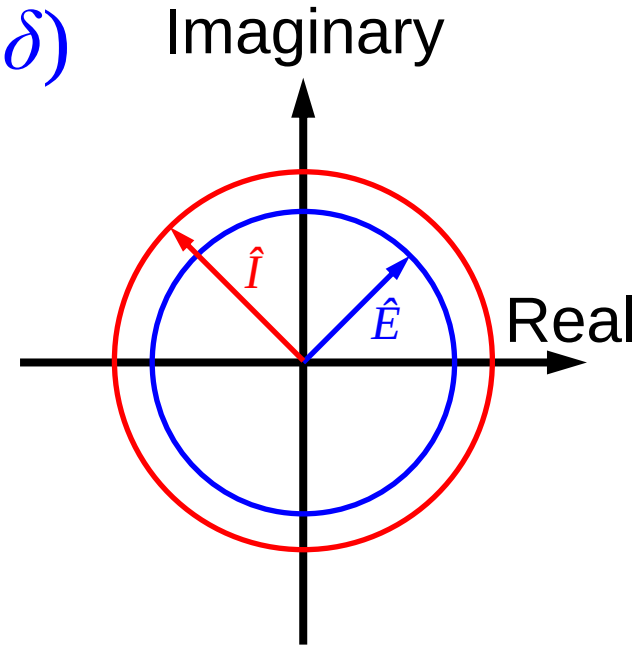
Electrochemical Impedance Spectroscopy

Input → System → Output

$I = \hat{I}\sin(\omega t)$

$E = \hat{E}\sin(\omega t+\delta)$





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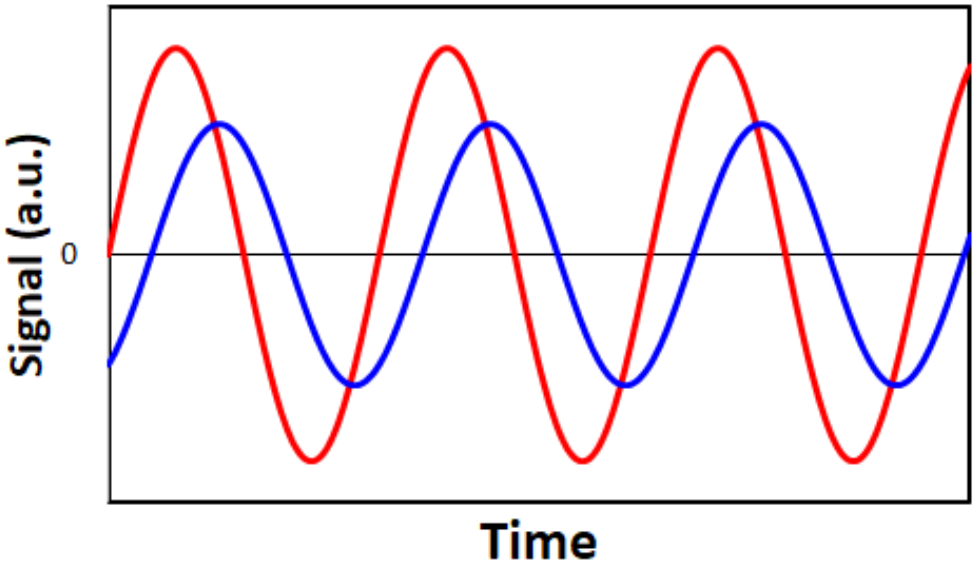
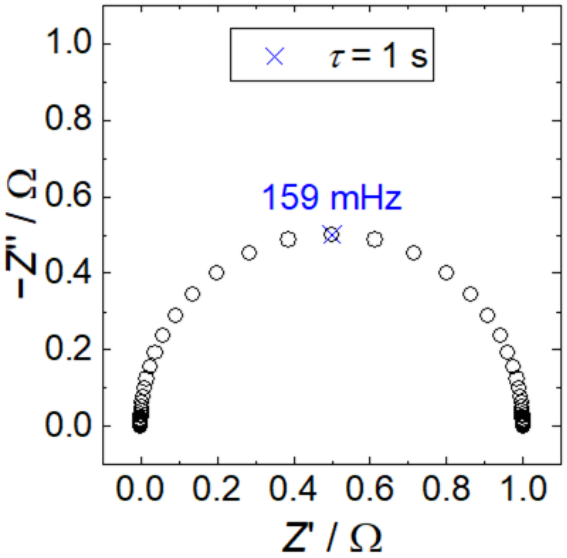


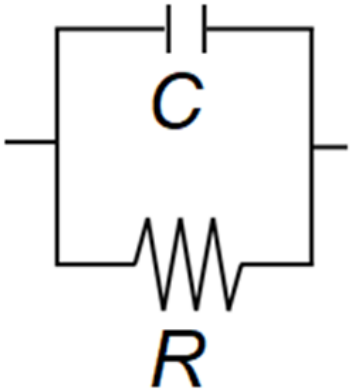
Impedance Z

$$Z = \frac{\hat{E}e^{i\omega t}}{\hat{I}e^{i(\omega t+\delta)}}$$

→ Complex number

Electrochemical Impedance Spectroscopy





Impedance Z

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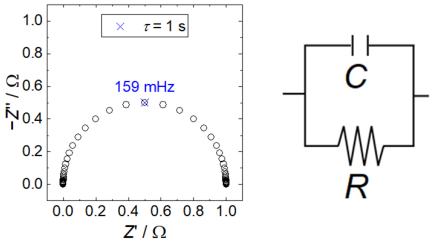
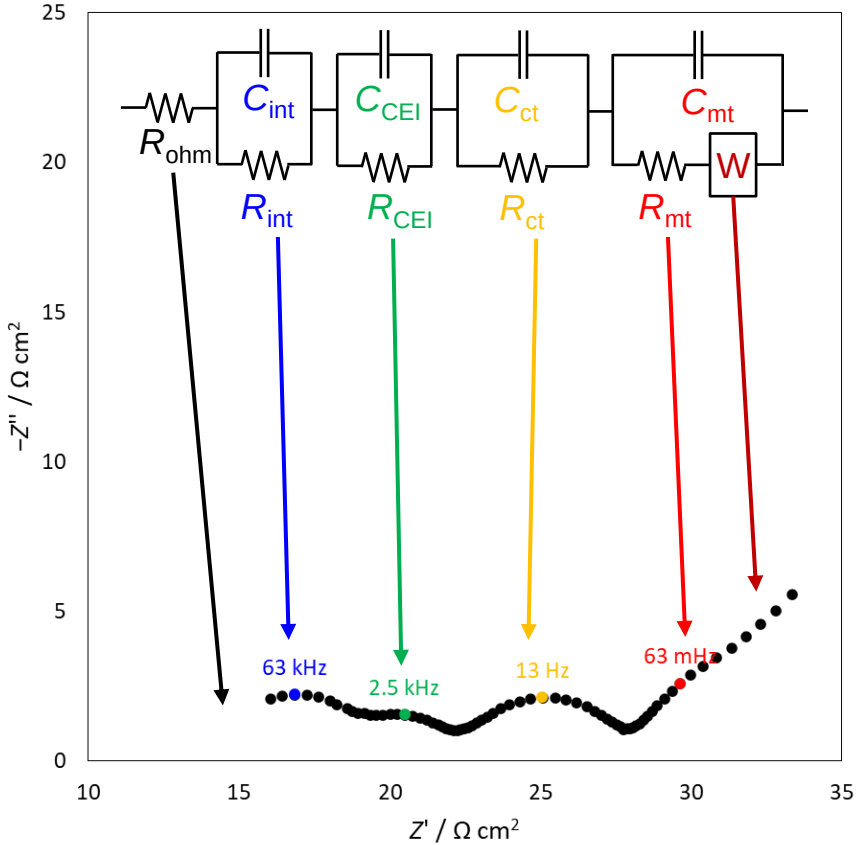
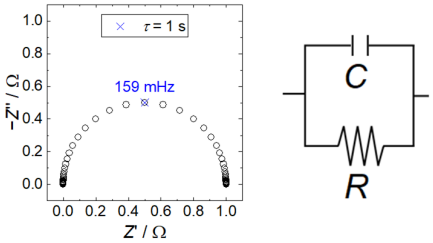
Electrochemical Impedance Spectroscopy



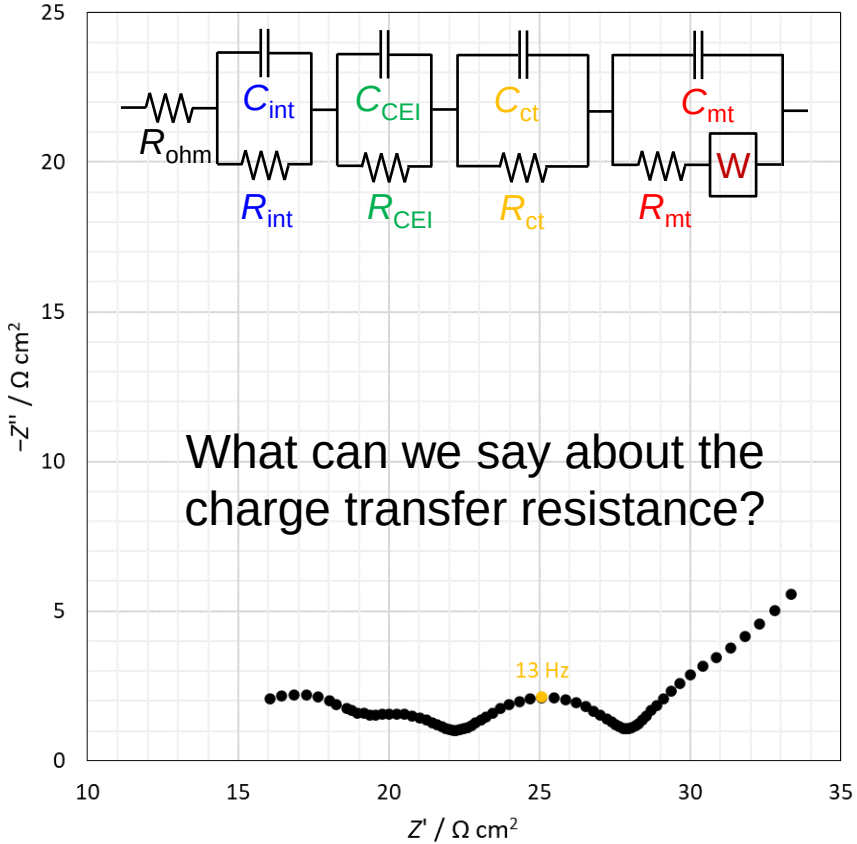
- Distribution of losses



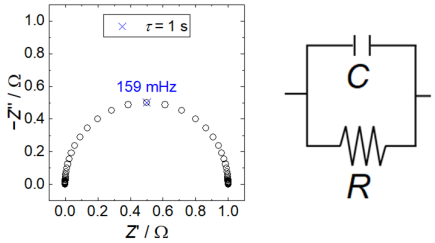
Electrochemical Impedance Spectroscopy



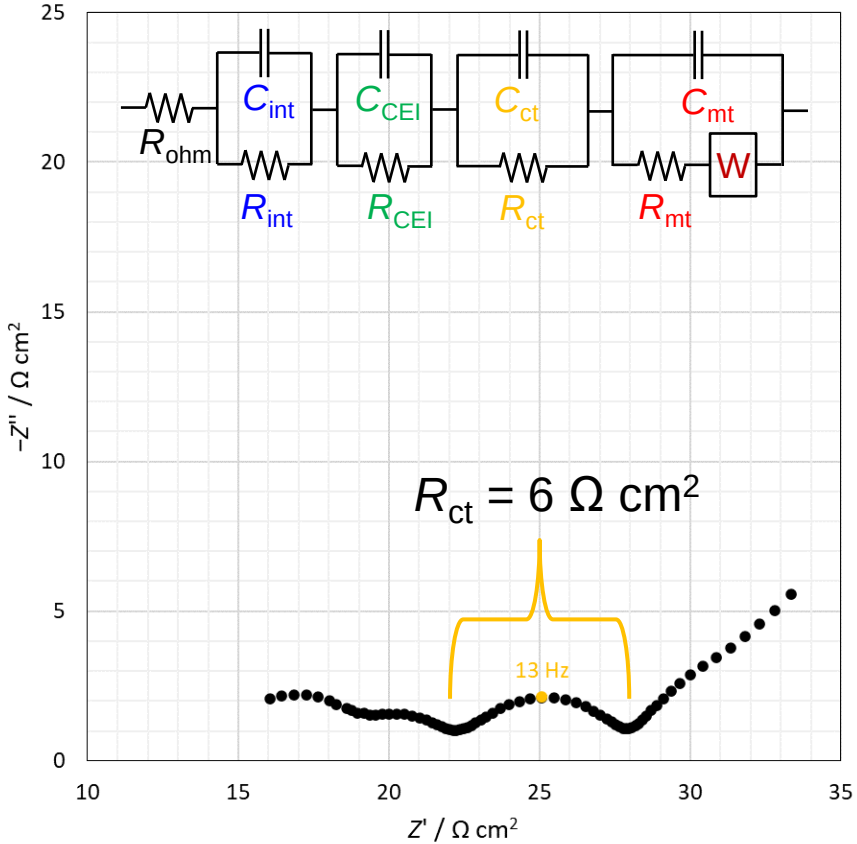
- Distribution of losses



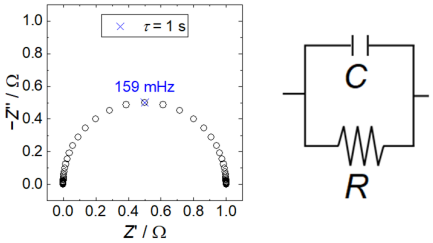
Electrochemical Impedance Spectroscopy



- Distribution of losses



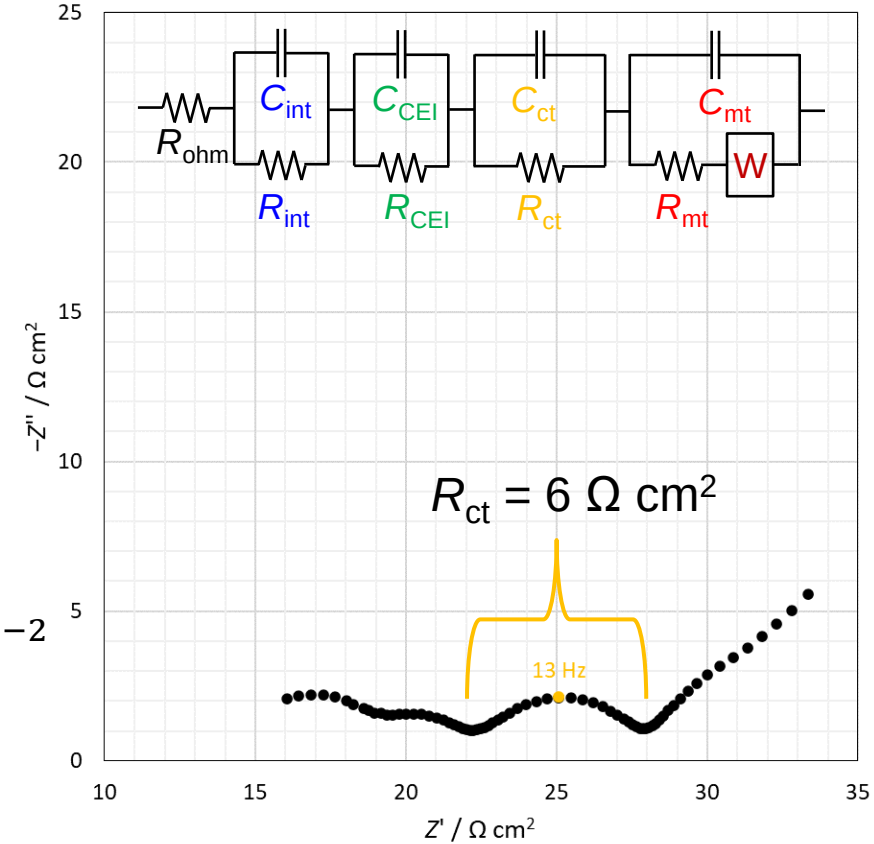
Electrochemical Impedance Spectroscopy



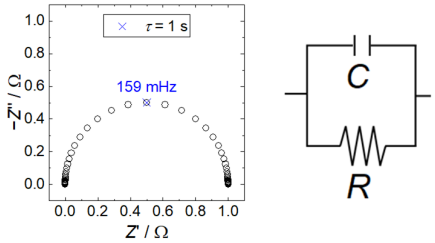
- Distribution of losses

$$\tau_{ct} = R_{ct}C_{ct} = \frac{1}{2\pi f_{TO}}$$

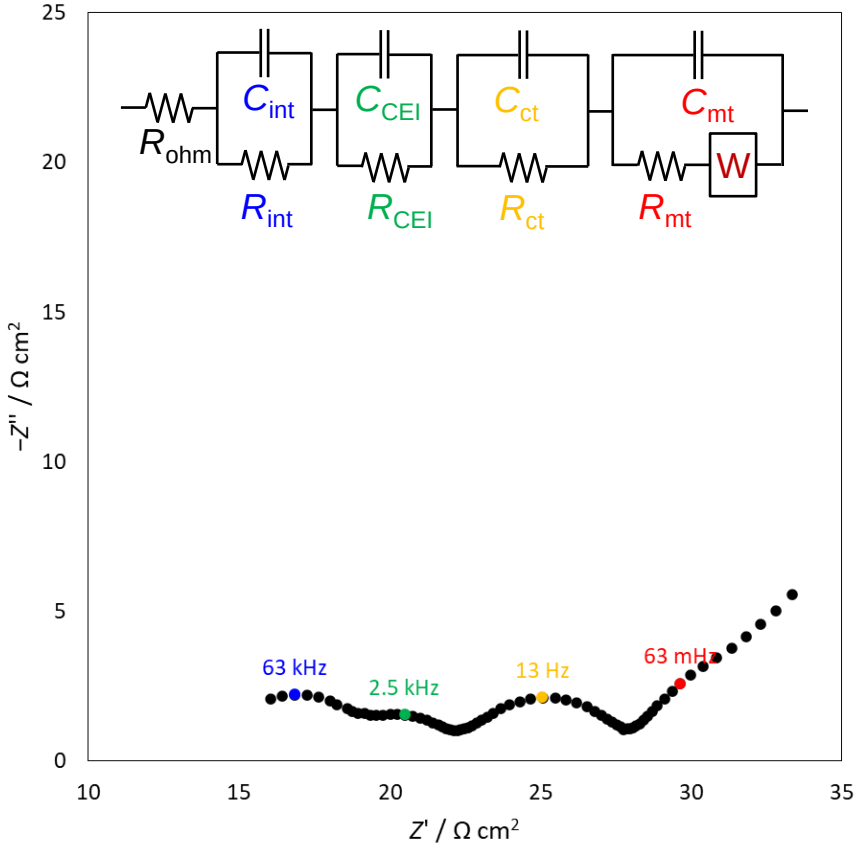
$$\rightarrow C_{ct} = \frac{1}{2\pi f_{TO} R_{ct}} = 2\ \mathrm{mF\ cm^{-2}}$$



Electrochemical Impedance Spectroscopy



- Distribution of losses
- Vs. State of Charge
- Vs. Aging



VTT

beyond

the obvious

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