Electrochemical Impedance Spectroscopy (EIS) of Lithium Ion Cells

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Electrochemical Impedance Spectroscopy (EIS)

- Advantages
  - Non-destructive
    - Low Perturbations (Linear polarization regime)
    - Fast, reproducible and convenient
  - Ability to quantitatively segregate processes with different rate constants.

- Disadvantages
  - Difficult to interpret
  - Non-ideal behavior
    - Complicated by surface films and adsorbed species and porous electrodes
Electrochemical Impedance Spectroscopy (EIS)

Charge transfer Process with mass transfer effects

Nyquist Plot

Randles Circuit

Charge transfer Process (with mass transfer effects) on Film-covered electrodes

Z'(Ohms)

Z'' (Ohms)

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Electrochemical Impedance Spectroscopy (EIS)

Generalized equivalent circuit of a battery or cell
(Subscripts and c denote anode and cathode, respectively)
EIS of Carbon Anode in a Li Ion Cell

MCMB Carbon-LiNiCoO$_2$ Cell
Li Metal Reference Electrode

1.0 M LiPF$_6$ EC+DMC (30:70)

Anode
EIS of LiNi\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{2} Cathode

MCMB Carbon-LiNiCoQ Cell
Li Metal Reference Electrode

- 1.0 M LiPF\textsubscript{6} EC+DMC (30:70)

\begin{center}
\begin{tikzpicture}
\draw (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw (0.5,0.5) circle (0.2);
\node at (0.5,0.5) {$C_f$};
\draw (0.75,0.5) -- (0.75,0.3) -- (0.75,0.3);\node at (0.75,0.3) {$C_{dl}$};
\draw (0.5,0.25) -- (0.5,0.25) -- (0.5,0.25);\node at (0.5,0.25) {$R_c$};
\draw (0.25,0.25) -- (0.25,0.25) -- (0.25,0.25);\node at (0.25,0.25) {$R_f$};
\node at (0.5,0.75) {$R_e$};
\end{tikzpicture}
\end{center}

Cathode

\begin{center}
\begin{tikzpicture}
\draw (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw (0.5,0.5) circle (0.2);
\node at (0.5,0.5) {$C_f$};
\draw (0.75,0.5) -- (0.75,0.3) -- (0.75,0.3);\node at (0.75,0.3) {$C_{dl}$};
\draw (0.5,0.25) -- (0.5,0.25) -- (0.5,0.25);\node at (0.5,0.25) {$R_c$};
\draw (0.25,0.25) -- (0.25,0.25) -- (0.25,0.25);\node at (0.25,0.25) {$R_f$};
\node at (0.5,0.75) {$R_e$};
\end{tikzpicture}
\end{center}
EIS of a Li Ion Cell

MCMB Carbon-LiNiCoO₂ Cell
Li Metal Reference Electrode

- Anode Measurement
- Cathode Measurement
- Total Cell Measurement
- Sum of anode and cathode

Temperature = 23°C
DC Polarizations in Li Ion Cell

- MCMB Carbon - LiNiCoO₂ Cell
- Li Reference Electrode
- 1.0 M LiPF₆ EC+DEC+DMC (1:1:1)
- Temperature = 23°C

- Cathode
- Anode

Current (Amps)
Cathode Potential (V vs Li⁺/Li)
Anode Potential (mV vs Li⁺/Li)
EIS of Carbon Anode at LT

MCMB Carbon-LiNiCoO₂ Cell
Li Metal Reference Electrode

- 1.0 M LiPF₆ EC+DMC (30:70)
Temperature = 23°C

Anode

Z' (Ohms)

Z'' (Ohms)

MCMB Carbon-LiNiCoO₂ Cell
Li Metal Reference Electrode

- 1.0 M LiPF₆ EC+DMC (30:70)
Temperature = 0°C

Z' (Ohms)

Z'' (Ohms)

MCMB Carbon-LiNiCoO₂ Cell
Li Metal Reference Electrode

Temperature = -20°C

Z' (Ohms)

Z'' (Ohms)

MCMB Carbon-LiNiCoO₂ Cell
Li Metal Reference Electrode

Temperature = -40°C

Z' (Ohms)

Z'' (Ohms)
EIS of Oxide Cathode at LT

Temperature = 23°C

Temperature = 0°C

Temperature = -20°C

Temperature = -40°C
EIS of Li Ion cell at LT

Temperature: 23°C

- Z' (Ohms)
- Z" (Ohms)

MCMB Carbon-LiNiCoO₂ Cell
Li Metal Reference Electrode

△ Anode Measurement
■ Cathode Measurement
△ Total Cell Measurement

Temperature = 23°C

Temperature: 0°C

- Z' (Ohms)
- Z" (Ohms)

MCMB Carbon-LiNiCoO₂ Cell
Li Metal Reference Electrode

Temperature = 0°C

△ Total Cell Measurement
● Anode Measurement
△ Cathode Measurement

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EIS of Li Ion cell at LT

Temperature: -20°C

MCMB Carbon-LiNiCoO₂ Cell
Li Metal Reference Electrode

- Anode Measurement
- Total Cell Measurement
- Cathode Measurement

Temperature = -20°C

Temperature: -40°C

MCMB Carbon-LiNiCoO₂ Cell
Li Metal Reference Electrode

- Anode Measurement
- Cathode Measurement
- Total Cell Measurement

Temperature = -40°C

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EIS During High Temp. Storage

Stored at 60°C for 1 week

Carbon Anode

Li$_x$(NiCo)O$_2$ Cathode

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EIS During High Temp. Storage

**Carbon Anode**

<table>
<thead>
<tr>
<th>Solvent Type</th>
<th>SEI Resistance, Ohms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1:1 (EC:DEC:DMC)</td>
<td>0.16</td>
</tr>
<tr>
<td>1:1:1 (EC+DMC+EMC)</td>
<td>0.14</td>
</tr>
<tr>
<td>High (EC)</td>
<td>0.12</td>
</tr>
</tbody>
</table>

**Li\(_x\)(NiCo)O\(_2\) Cathode**

<table>
<thead>
<tr>
<th>Solvent Type</th>
<th>SEI Resistance, Ohms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1:1 (EC:DEC:DMC)</td>
<td>1.40</td>
</tr>
<tr>
<td>1:1:1 (EC+DMC+EMC)</td>
<td>1.20</td>
</tr>
<tr>
<td>High (EC)</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Stored at 60°C for 1 week
Cycling (100% DOD) at 25°C

Temp = 23°C

1.0 Amp Charge current (C/5) to 4.1 V
Taper Cut-Off at 0.100 A (C/50)
1.0 Amp Discharge Current (C/5) to 3.0 V
EIS During Cycling

Cell Fully Charged Prior To Measurements
OCV = \sim 4.07\text{V}

23\text{C}

- Z'' (Ohms)

Z' (Ohms)

200 Cycles
100 Cycles
5 Cycles

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The graph shows the discharge capacity (Ah) plotted against cycle number for different temperatures and cell types. The cycle number is along the x-axis, ranging from 0 to 300. The discharge capacity is along the y-axis, ranging from 0 to 7.

- **23°C**: The line shows a steady decrease in discharge capacity with increasing cycle number. The capacity at cycle 1 is around 5.825 Ah.
- **40°C**: The line also shows a decrease in discharge capacity with cycle number, but at a higher rate compared to 23°C.
- **-20°C**: The line indicates a slower decrease in discharge capacity compared to 23°C.

- **Cell Y500 (4.1 V @ 40°C)**: The line for Cell Y500 starts at a higher capacity and shows a significant decrease over cycles.
- **Cell Y513 (4.0 V @ 40°C)**: The line for Cell Y513 starts at a lower capacity than Cell Y500.

Additional notes:
- 45.6% of initial RT capacity.
- 19.0% of initial RT capacity.

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EIS During Cycling

23°C

- Cell 500z10
- Cell 513z10

After 4.0V cycling at 40°C (Cycle 105)
After 4.1V cycling at 40°C (Cycle 105)

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EIS During Cycling

Effect of Variable Temperature Cycling
Cell Charged to 4.1V During All Cycling
Alternating Temperatures: -20 °C and 40 °C
10 Cycles at Each Temperature

23 °C

- Cell 500z2
- Cell 500z6
- Cell 500z10

After 55 Cycles
After 15 Cycles
After 135 Cycles

Z' (Ohms)

Z'' (Ohms)

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EIS vs. SOC

- $Z'$ (Ohms)
- $Z''$ (Ohms)

- Y011z2 (25% SOC)
- Y011z4 (75% SOC)
- Y011z5 (100% SOC)
- 50%SOC

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Summary

- Electrochemical impedance Spectroscopy is a useful technique to follow the interfacial changes in a Li ion cell.
- Cathode contributes significantly to the overall cell impedance.
- The SEI resistance of both anode and cathode increase
  - At low temperatures
  - During storage
  - During cycling