Time Effective Testing and Compact Modeling of Electrochemical Impedance Spectroscopy (EIS) for Lithium Ion Batteries

Rapid, Reliable, and Repetable, EIS (R^3EIS),

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Ignition for the research and development

Motivating Question from Industrial partner

- We build high quality battery packs but they are expensive
- High quality cells are needed for high quality packs and they are expensive
- We want to change supplier and ensure that the cells and packs are of high quality
- How can we quickly and non destructively test and qualify cells suppliers?
- Can we sort cells based on quality to build better packs?

Requirement Specification – Desirable properties of the tester

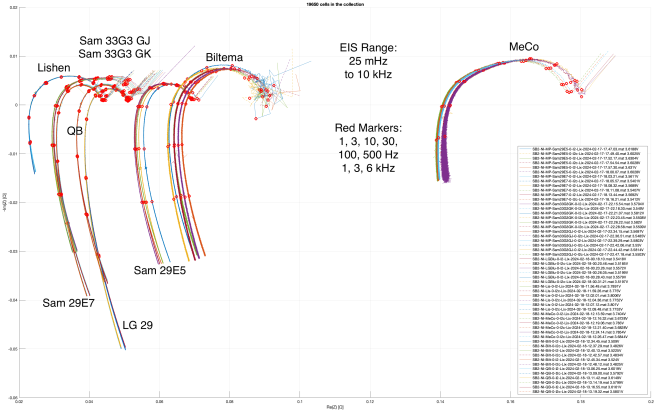
- Fast – Production line compatibility
- Non destructive – with high information content
- Repeatable – same result every time
- Cost effective – low cost per test

Fundamental question: What is the quality/properties/status of a cell?

Battery resistance (impedance) → Some hints

Electrochemical Impedance Spectroscopy (EIS)

EIS → More detailed fingerprint of cell quality.



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Spectroscopy - Determine response

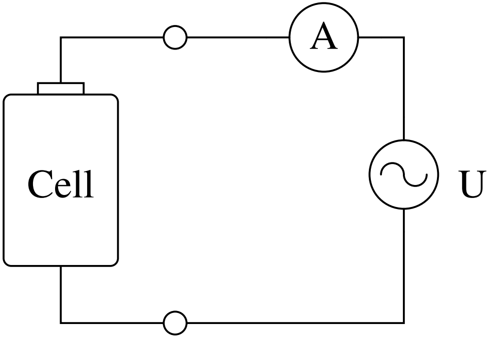
Measure U(ω) and I(ω) and calculate $Z(\omega) = \frac{U(\omega)}{I(\omega)}$

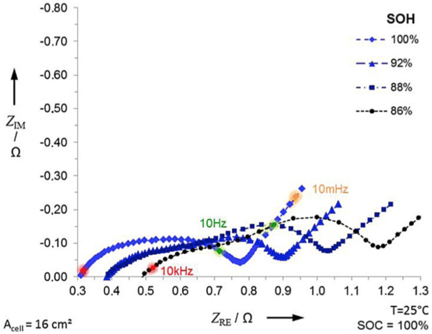
Keep track of amplitude and phase - as complex number $Z(\omega)$.

Plot the complex impedance $Z(\omega)$, with negative imaginary axis

- Nyquist plots

Note arc/circle shapes





Impedance plot from Westerhoff et al. (2016).

The Fingerprint,

Interpreting the – Equivalent Circuit Models (ECM)

Ohms Law, Resistance, R

U = R · I

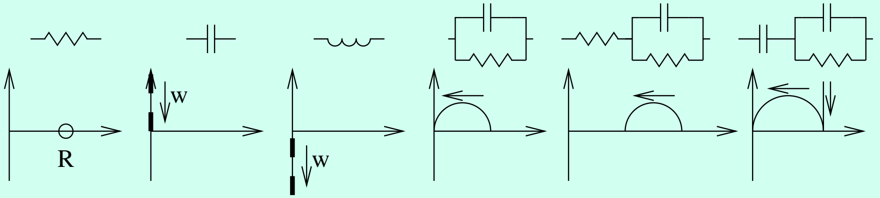
Assymptotic properties and frequencies

	R	C	L
short circuit	0	$\omega \to \infty$	$\omega \to 0$
open circuit	∞	$\omega \to 0$	$\omega \to \infty$

Complex Impedance, Z

U = Z · I

- Resistance $Z_R = R$
- Capacitor $Z_C = \frac{1}{j\omega C}$
- Inductor $Z_L = j\omega L$



Causes for impedances in a battery cell

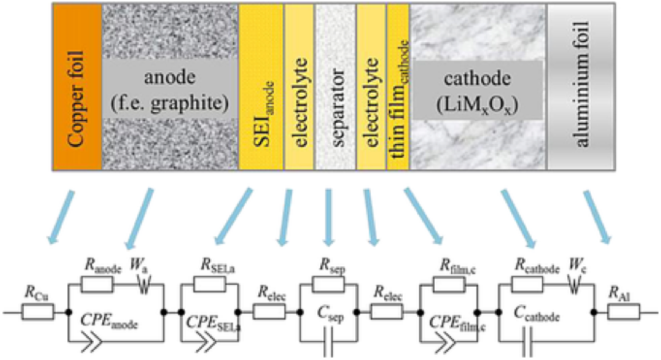


Figure from Westerhoff et al. (2016).

Material properties and physical processes like diffusion.

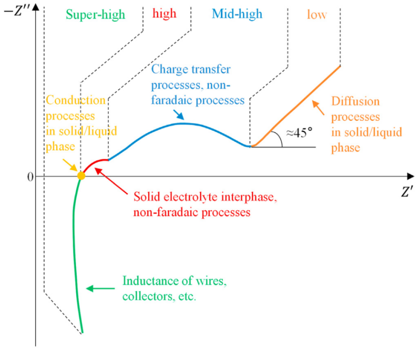


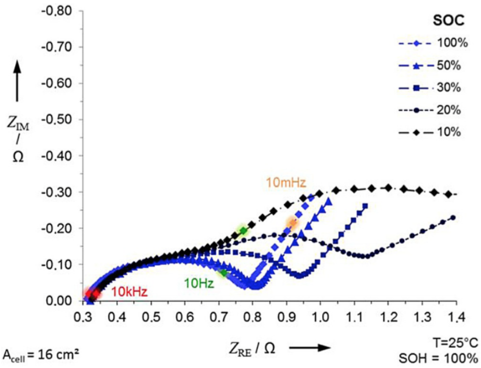
Figure from Wang et al. (2021)

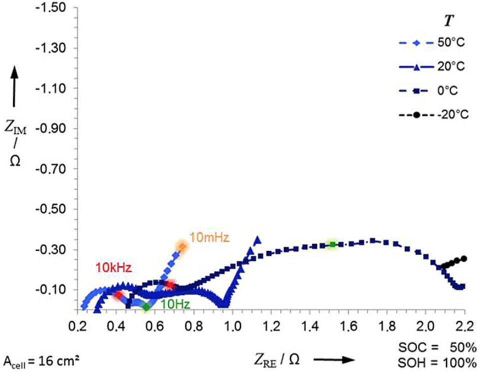
Why is EIS interesting?

The impedance is rich in information

- More detailed information than resistance measurements.
  - Get a detailed fingerprint of the internal properties
- Non invasive test that exposes internal cell properties
  - State of charge – SOC
  - Temperature
  - State of health – SOH
  - Solid Electrolyte Interphase Size
  - Diagnostics
    - Internal Short - Dendrite connections
    - Thermal Runaway
    - Overcharge/Overdischarge
  - Production variations
- There is a vast knowledge base
- EIS, SOH and Battery search – More than 300 Scientific publications

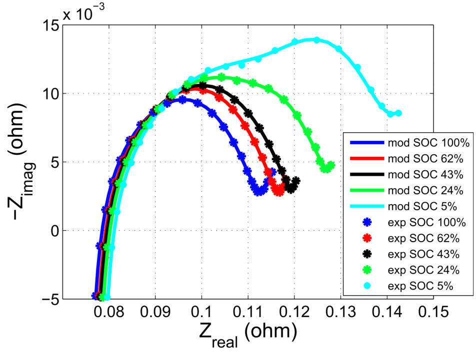
Spectroscopy – Shape depends on battery conditions SOC Temperature

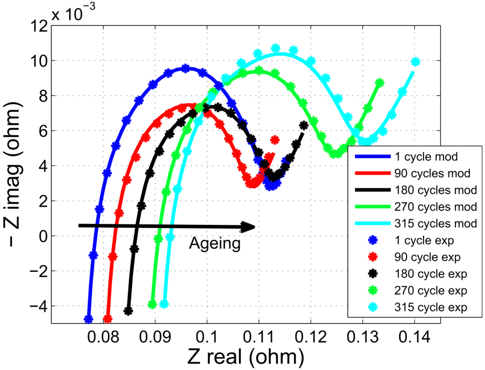




Impedance plots from Westerhoff et al. (2016)

Nyquist Diagram - Varying SoC and SoH





Impedance plots from Galeotti et al. (2015).

Much information in the fingerprint.

Shows that it is possible to decouple different internal properties effects.

Over rated charging and discharging

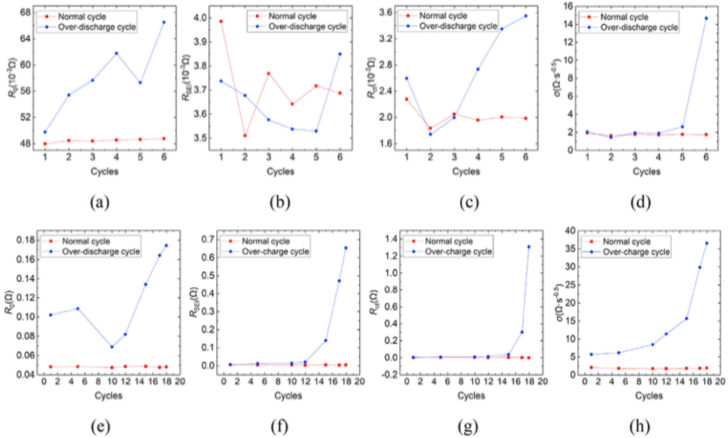


Fig. 19. Changes of (a) (e) ohmic resistance R_0, (b) (f) SEI film resistance R_{SEI}, (c) (g) charge transfer resistance R_{ct}, and (d) (h) Warburg coefficient σ when the battery is over-discharged/charged.

Equivalent circuit parameters from Wang et al. (2021).

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The Challenges and Path to a Solution

My Spark ⚡ – The Challenge of Alelion

- Would like to buy cheaper cells.
- Ensure production of high quality batteries.

General Challenges for Battery Quality

- The weakest link in a chain limits the chain strength.
  - Extends to batteries too
  - The weakest cell will limit the battery.
  - The weakest cell will be more stressed in use.
  - A weak cell degrades faster than the rest of the pack.
- Ensure all cells in a pack have equal performance.
  - Eliminate weak links.
  - Select cells that have equal or similar properties.
  - Equalizes aging of cells.

Towards a Solution

- Need a powerful tool for quality assessment of cells
- Electrochemical Impedance Spectroscopy (EIS)
  - A lot of information about a cell in the result.
  - Give input stimuli and measure response.
  - Normal test with stimuli, timeconsuming.
- In an assembly line: short time-slots for measurements.
  - Challenge to extract information.
  - Solution: multi-spectral input signal.

Basic differences – Traditional EIS and R^3EIS Principle

Traditional EIS – Used by PhDs

- Equilibrate the cell before measurement
- One single frequency at a time
- Measure steady state response
- Small signal amplitude
- Frequency sweep over the desired range
- Time consuming
- Battery can drift during measurement

R^3EIS Principle

- No equilibration – In operando
- Multiple frequencies simultaneously
- Measure transient response
- Sum of signal amplitude
- Designed multi-sine signal
- Fast measurement
- Snapshot of battery state

Signal design for maximum information in minimum time

Many frequencies simultaneously – Limited Amplitude – Compile a smart signal
Not trivial – Requires expertise in signal processing and battery EIS
Many possible designs – Trade-off between time, resolution and accuracy

The goal and challenges for an EIS tester implementation

Challenge and limits

- Goal: How can we extract as much information as possible in a given time?
- What are the limits?
- Testing time sets the limit, on the lowest frequency. (Physics)
  $f_{min} = \frac{1}{T}$ Hz, where T is the test time.
- Data Acquisition (DAQ) sets the limit on the highest frequency. (Nyquist theorem)
  $f_{max} = \frac{f_s}{2}$ Hz, where f_s is the sampling frequency.
- Practical implementations have to obey these limits.
- Improvements in quality are possible by not going to the limits.

Limits in implementation – The frequency box

- $f_{min} = \frac{3}{T}$ Hz, due to an initial transient. (T is tuneable.)
- $f_{max} \leq \frac{f_s}{2}$ Hz, f_s limited by hardware (current $f_{max} = 10$ kHz, but tested up to 50 kHz).

Signal design – Implementation

Frequency selection

- Base frequency: $f_0 = \frac{1}{T}$
- First used frequency: $f_1 = k_1 f_0$, $k_1 = 3$
- Avoid spread spectrum by separating frequencies

$$k_{n+1} \geq k_n + 10$$

  except first 3 (use 3,7,13)
- Avoid harmonics by using k_n prime numbers

Amplitude selection

- Define amplitude levels for each frequency, focus on the most important regions
- Ensure total amplitude stays within limits. Optimal phase developed by Schroeder (1970)

Theoretical limits

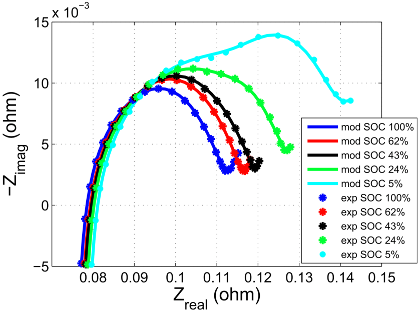
10 kHz @ 2 min → 60131 frequencies
50 kHz @ 5 min → 670000 frequencies
Extreme number of frequencies
signal-to-noise ratio not optimal

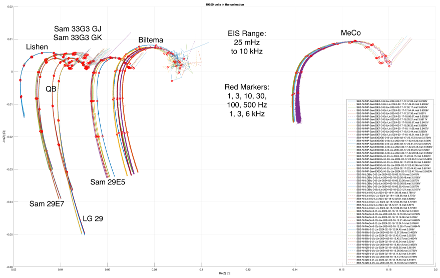
Introduce logspace (600 freq)

- Use logarithmic spacing for frequency selection
- Reduces the number of frequencies while maintaining coverage
- Improves signal-to-noise ratio

Low frequencies as dense as theory allows, high frequencies more sparse.

Nyquist Diagrams – Traditional EIS and R^{3}EIS Prototype





Traditional EIS 60 frequencies, 20 minutes.

R^{3}EIS Prototype, 60131 frequencies, 2 minutes.

10 000 more data points per time units.
Users impressed by the resolution, repeatability and quality of the EIS results.

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First Steps Towards Analysis of EIS Data with ECM

Compact frequency domain modeling of equivalent circuits in Matlab

- Using anonymous functions in Matlab to define components
- Define rules for combining components in series and parallel

```
%%              Definitions of components and connections.
cap = @(C,w) 1./(i*w.*C);
res = @(R,w) R;
ind = @(L,w) L.*i.*w;
cpe = @(a,C,w) 1./((i*w).^a.*C);
cpeL= @(a,L,w) L.*(i*w).^a;
par = @(x,y) 1./(1./x+1./y);
ser = @(x,y) x + y;
ser3= @(x,y,z) x+y+z;
```

Building System Models

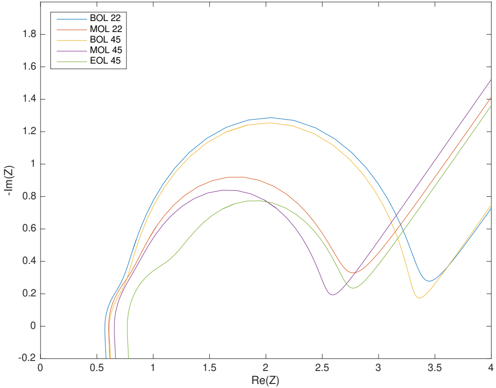
```
%   Impedance models for Batteries from Literature
threeComp = @(p,w) ser(res(p.R_O,w),...
                       par(cap(p.C_SEI,w),...
                           res(p.R_CT,w)));
fiveComp  = @(p,w) ser(res(p.R_O,w),...
                       par(cap(p.C_SEI,w),...
                           ser(res(p.R_SEI,w),...
                               par(cap(p.C_DL,w),res(p.R_CT,w)))));
sixComp   = @(p,w) ser(res(p.R_O,w),...
                       par(cap(p.C_SEI,w),...
                           ser(res(p.R_SEI,w),...
                               par(cap(p.C_DL,w),...
                                   ser(res(p.R_CT,w),cap(p.C_W,w))))));
% adding inductance and constant phase elements
sevenComp = @(p,w) ser3(cpeL(.95,1e-7,w),res(p.R_O,w),...
                       par(cap(p.C_SEI,w),...
                           ser(res(p.R_SEI,w),...
                               par(cap(p.C_DL,w),...
                                   ser(res(p.R_CT,w),cpe(.5,p.C_W,w))))));
```

Generating EIS Cell Signatures - Frequency

```
EOL45_0.R_CT=1.18e-3;
EOL45_0.R_SEI=.70e-3;
EOL45_0.C_DL=214.5;
EOL45_0.C_SEI=50.1;
EOL45_0.C_W=12.20e3;

%%            Define Frequency Range
omega=logspace(-3,5,100);

%%            Do some plots
figure(1); clf
plot(sixComp(BOL22_0,omega)'*1e3)
hold on
plot(sixComp(MOL22_0,omega)'*1e3)
plot(sixComp(BOL45_0,omega)'*1e3)
plot(sixComp(MOL45_0,omega)'*1e3)
plot(sixComp(EOL45_0,omega)'*1e3)
axis([0 4 -.2 2])
legend('BOL 22','MOL 22','BOL 45',...
       'MOL 45','EOL 45','Location','NorthWest')
ylabel('-Im(Z)')
xlabel('Re(Z)')
```



Batixt in Canada – Business Sweden – Supporting JAS 39 Gripen Export

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Thank you for your attention!

–Questions?
–Discussion.

References

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