Electrochemical Impedance Spectroscopy: Low Z Systems

GAMRY INSTRUMENTS

Electrochemical Impedance Spectroscopy (EIS)

- Very wide frequency range 10µHz to 1MHz i.e. time scales of 1µs to ~28hours
- Non-destructive. Small variations from the equilibrium condition.
- Can be done on the device under test with own electrodes. No other probe necessary
- EIS can measure subcomponent properties with the system intact!

EIS Relevance to Energy Storage and Conversion (ESC)

- Materials research before building ESC devices give plenty of information before the device is assembled.
- Information about the individual parts “in service” allows identifying processes and points out what failed.
- Once a device is assembled into the final form, EIS can still get materials properties without the device disassembled.

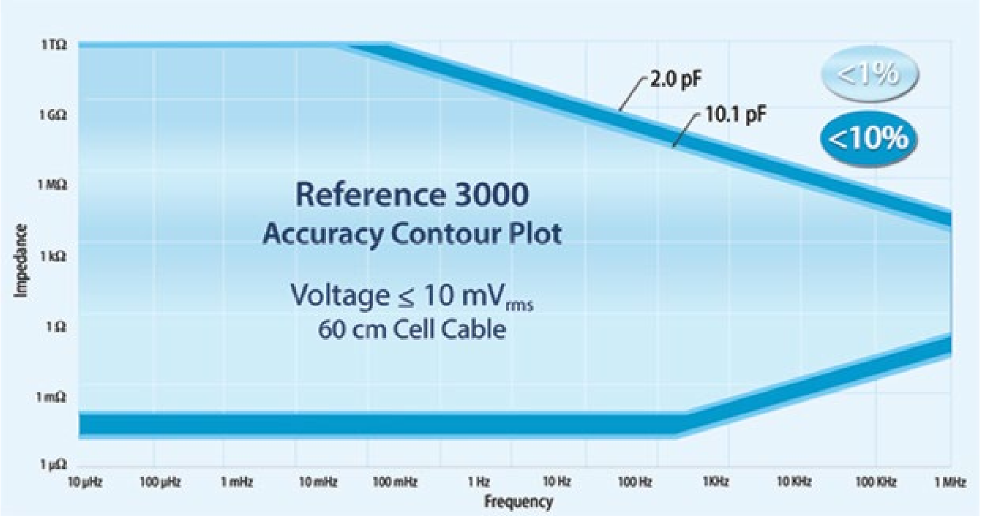
EIS of ESC Devices

- ESC Devices are not all the same!
  But there are some relevant similarities…

- ESC Devices are low impedance (μΩ to a few Ω)
- Whole Device is [often] measured
- Some systems have high DC offset current requirements
- Porous electrodes complicate modeling
- EIS is useful to determine
  - Equivalent Series Resistance (ESA)
  - Leakage current
  - Charge transfer impedances
  - Capacitance
  - Device failures

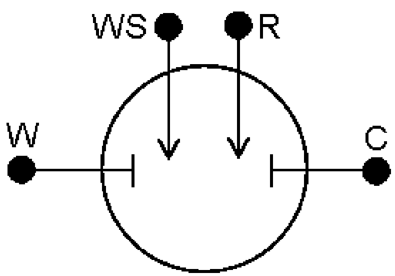
Measuring Low Impedance

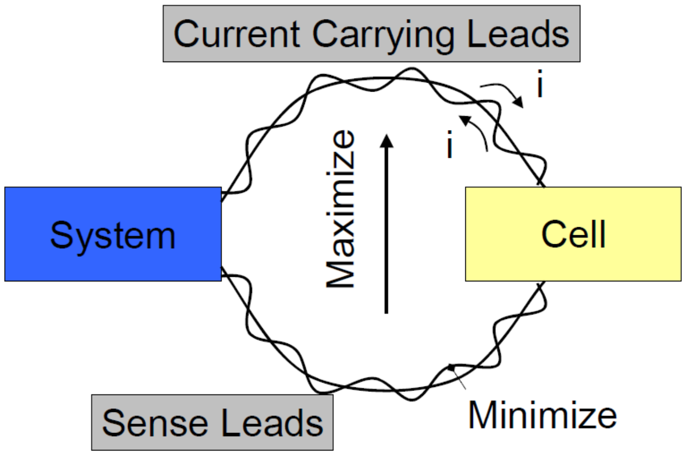
- Small impedances translate to small voltages and large currents
  - 100mA x 10µΩ = 1µV
- Because of the way the instrument is constructed, applying small potentials is much harder than measuring small potentials.
- Potentiostatic vs. Galvanostatic
  - Control “larger” signal, measure “smaller”
  - Small polarization = small AC potential
  - Instrumentation limits



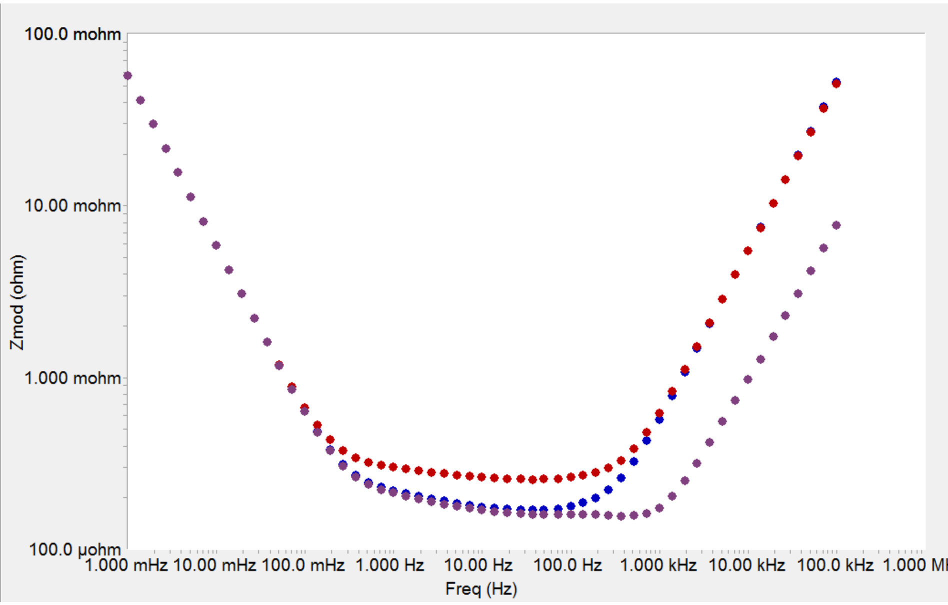
Measuring Low impedance

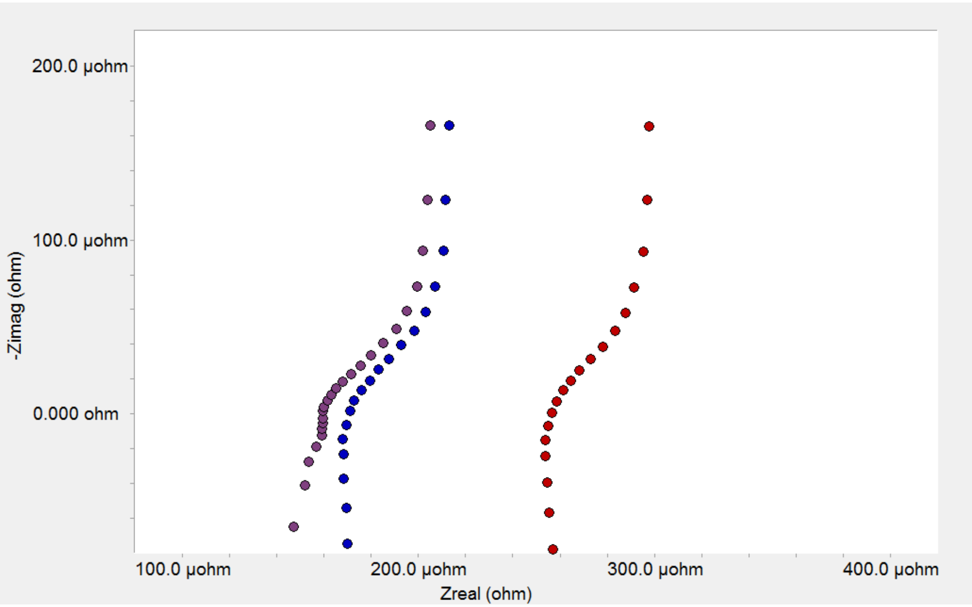
- Utilize 4-probe design
- Minimize cable inductance
- Know your system's limits
  - Measure background with low Z dummy (surrogate or shorted lead)





4 Terminal Measuremens and Minimizing Cable Inductance

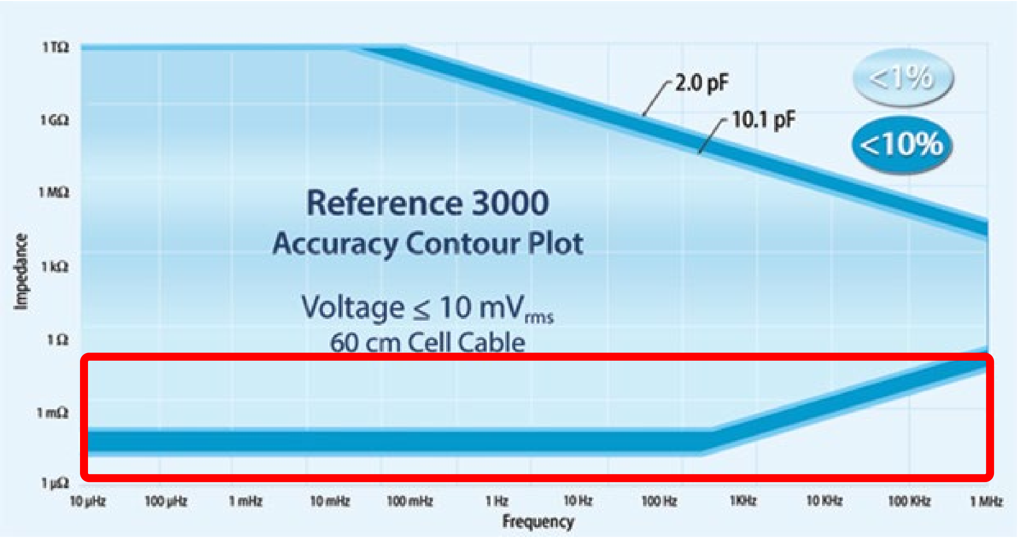


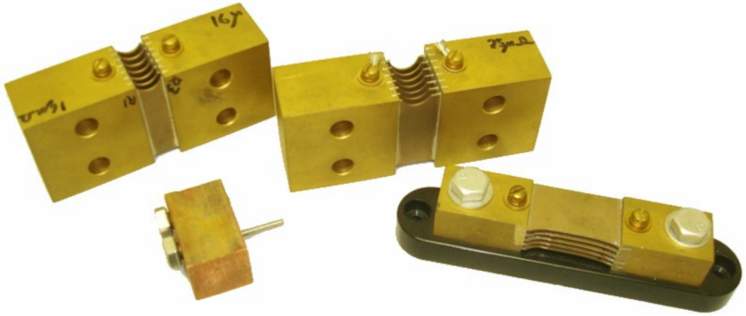


	L	ESR	C
2 electrode, 2 terminal	90 nH	250 µΩ	2700 F
2 electrode 4 terminal	90 nH	165 µΩ	2700 F
mimimized inductance (baseline measurement)	16 nH	150 µΩ	2700 F

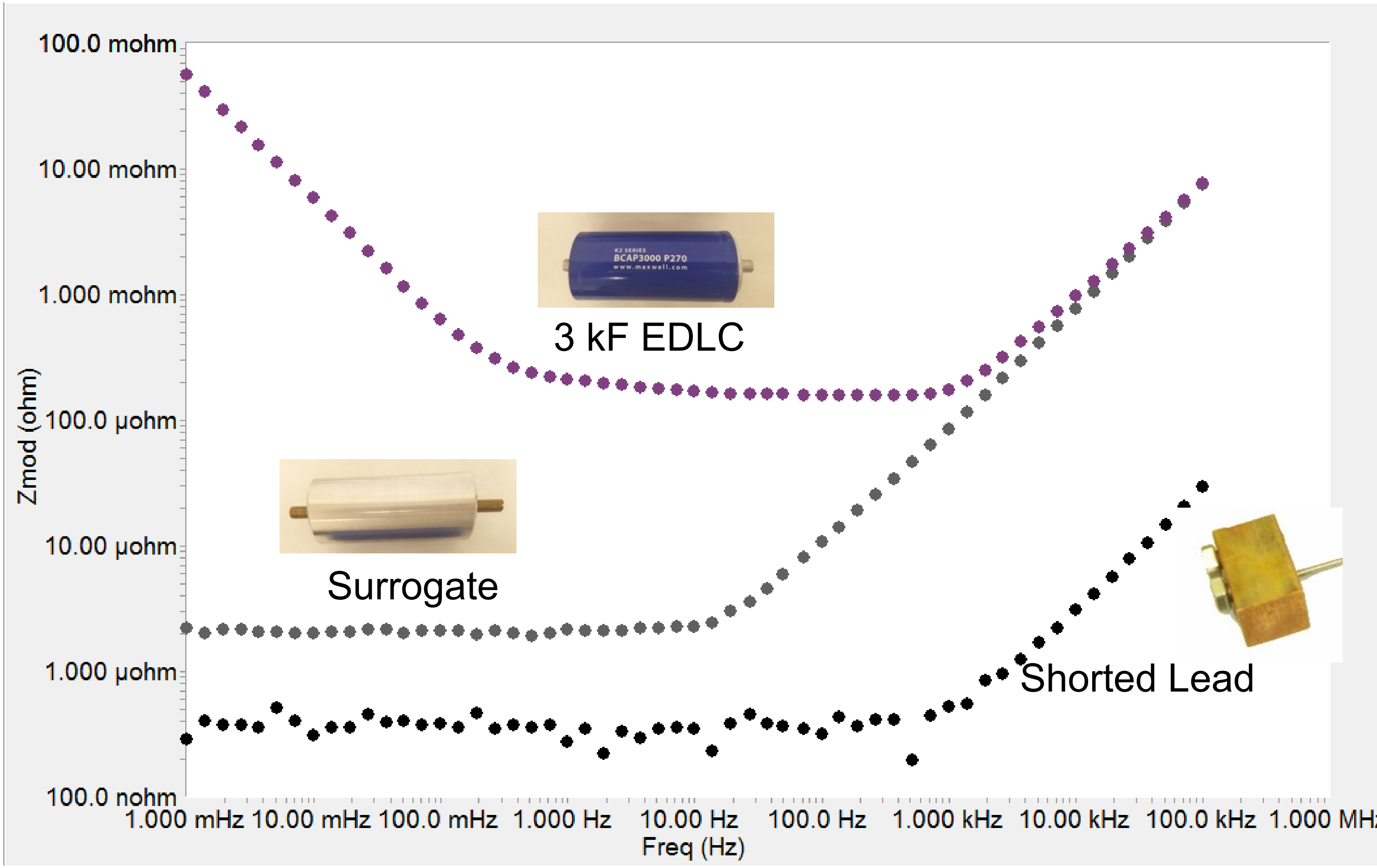
Identify Your System's Limits

- Accuracy Contour Plot (ACP)
- Measure Low Z dummy
  - Shorted Lead/Surrogate

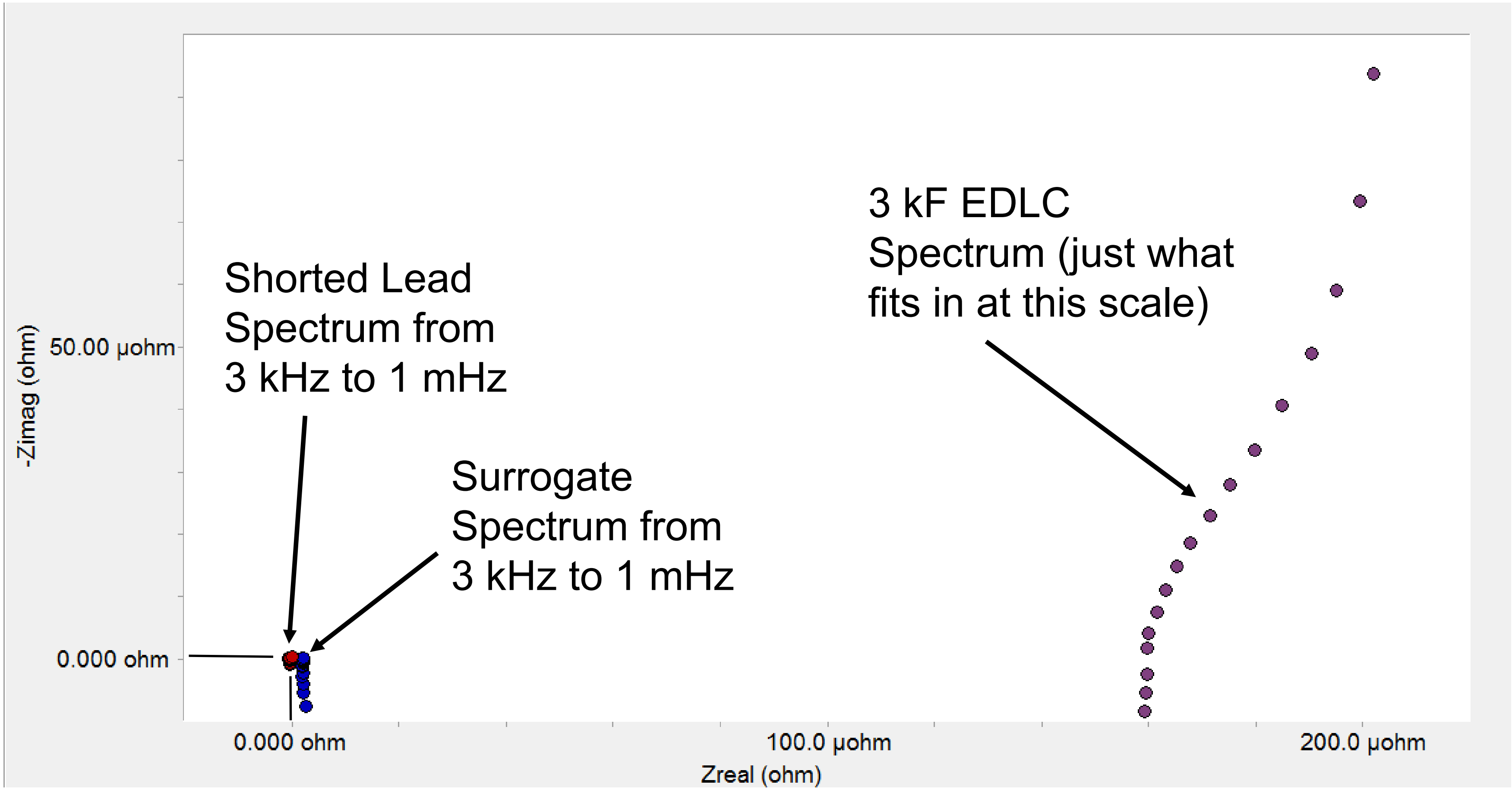




Cell, Surrogate, & Shorted Lead

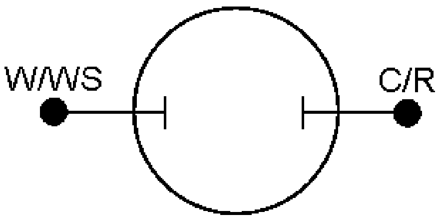


Cell, Surrogate, & Shorted Lead

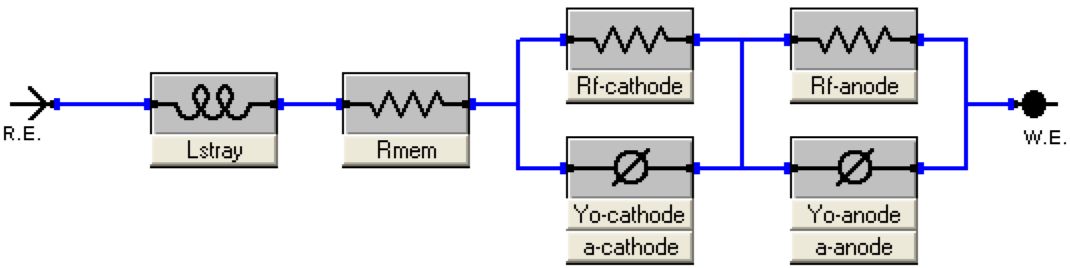


Measuring Complete Devices

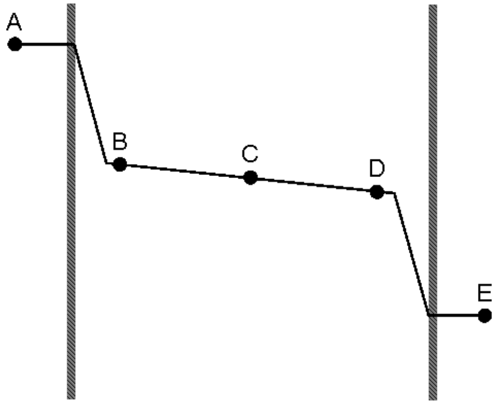
- Cathode/Membrane/Anode
- 2-Electrode mode
- More complex model



2-electrode cell connections

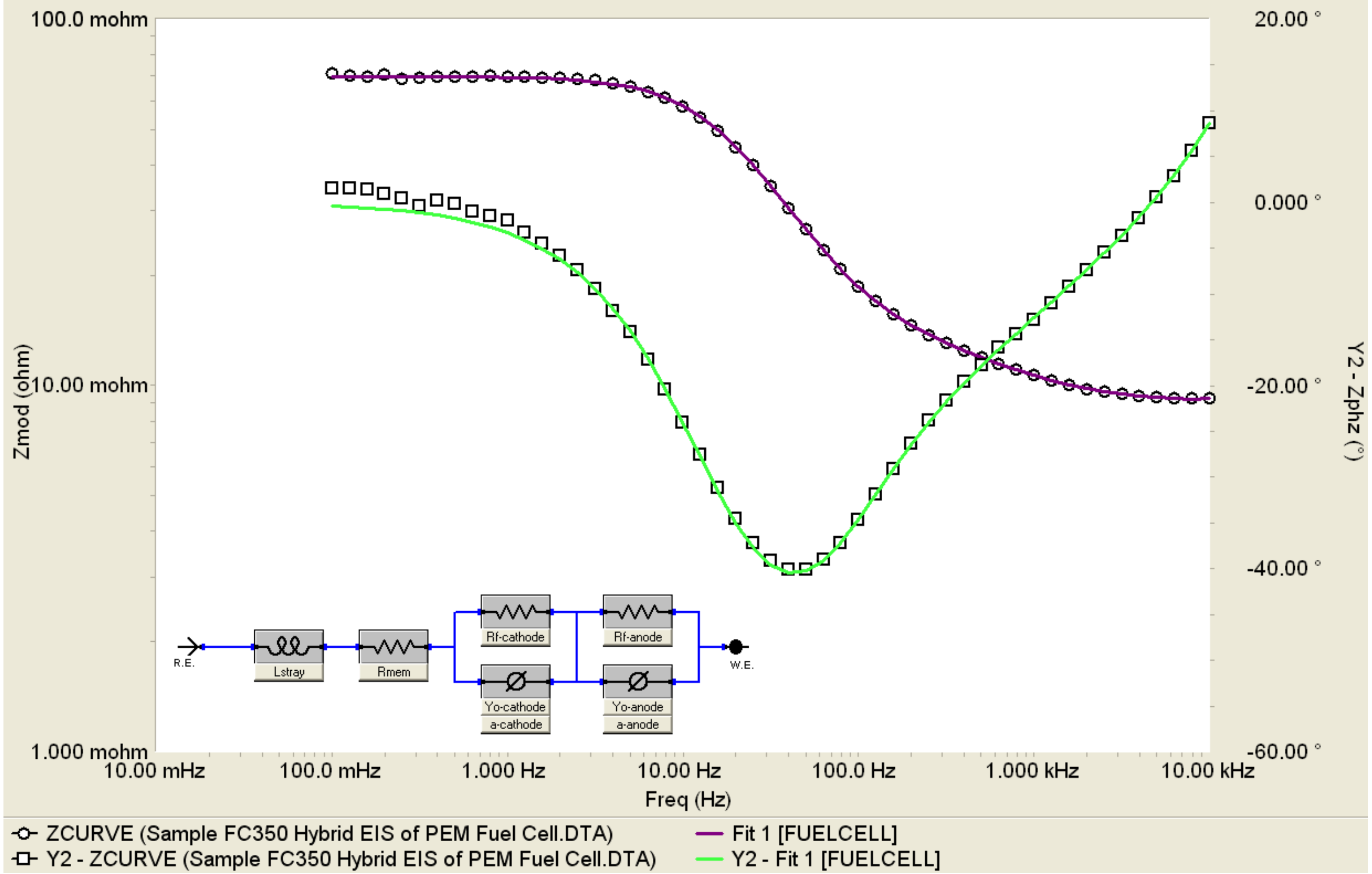


Simple equivalent circuit model for a complete device



Voltage across cell
A and E are cathode and anode

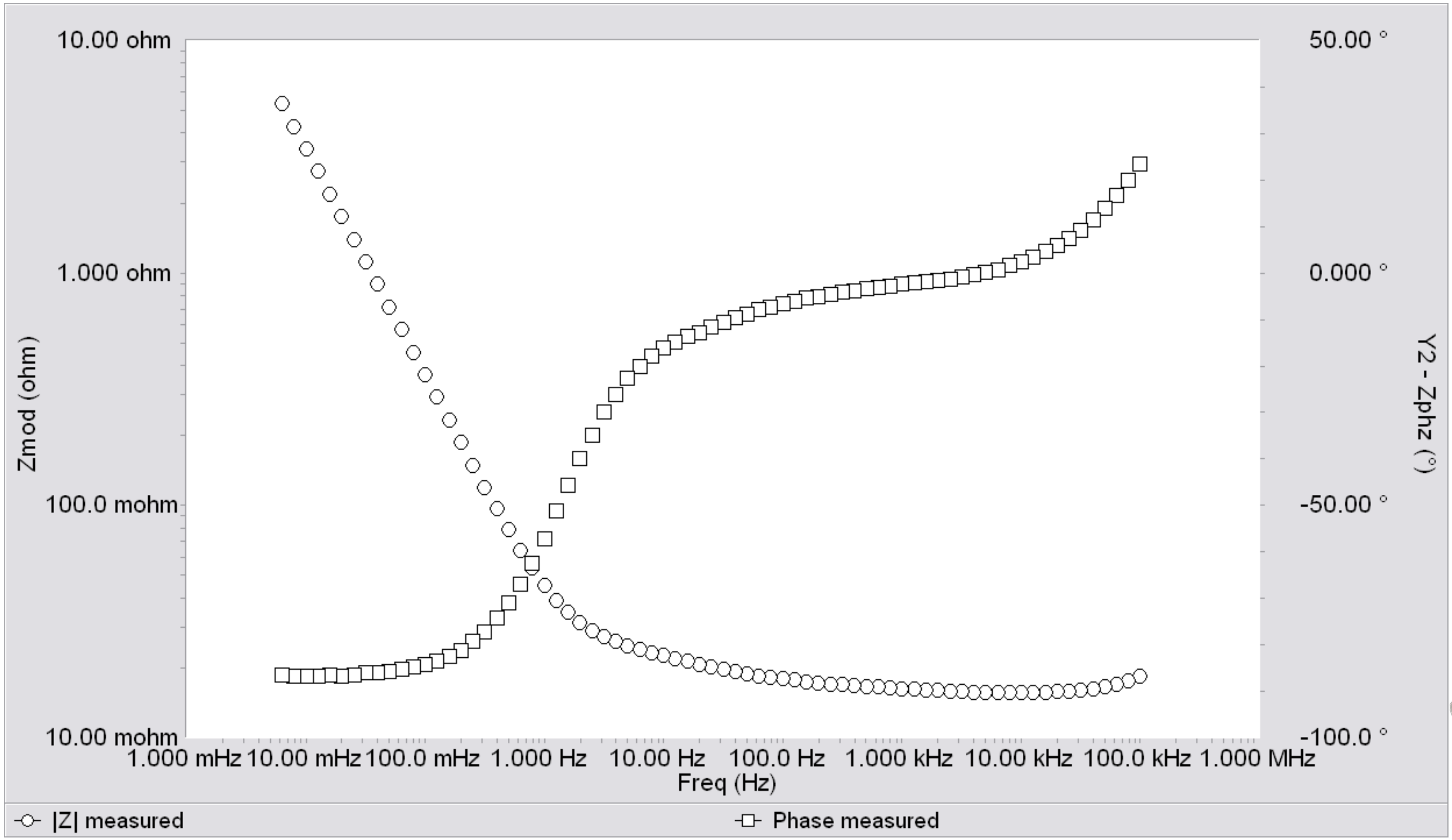
Measuring Complete Fuel Cell

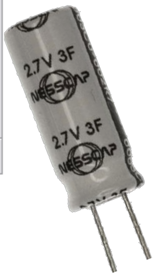


EIS on Operating Devices

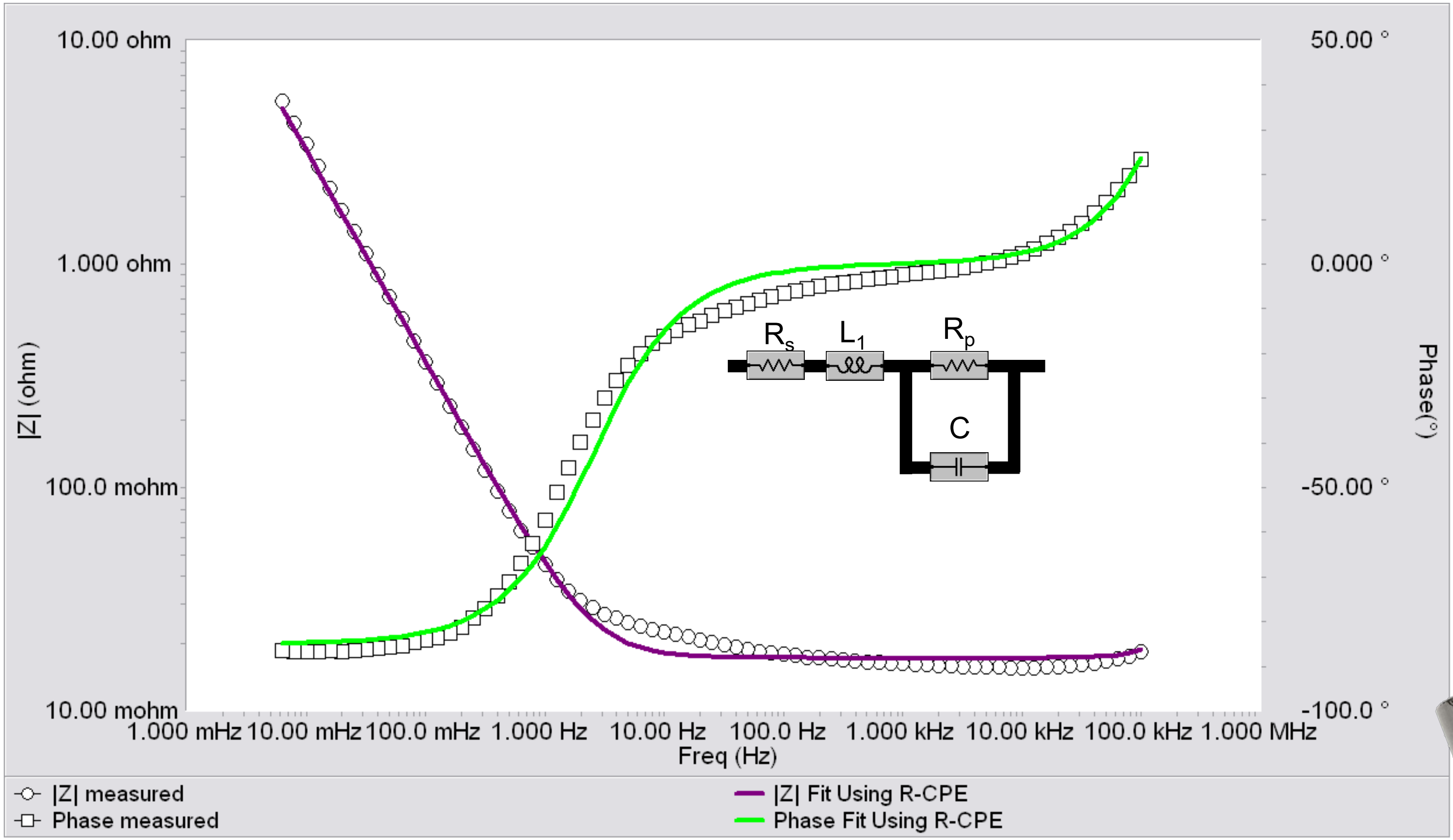
- Addition of small AC signal to a large DC offset
  - Electronic Load or Booster
  - Separation of resulting signal from offset
- Drift of storage devices (batteries) an issue
  - Faster EIS is helpful
    - Low frequency data is high information
    - Low frequency data is slow to obtain
    - Multi-Sine EIS

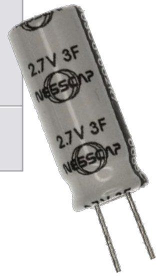
Porous Electrodes – Modeling with Transmission Lines





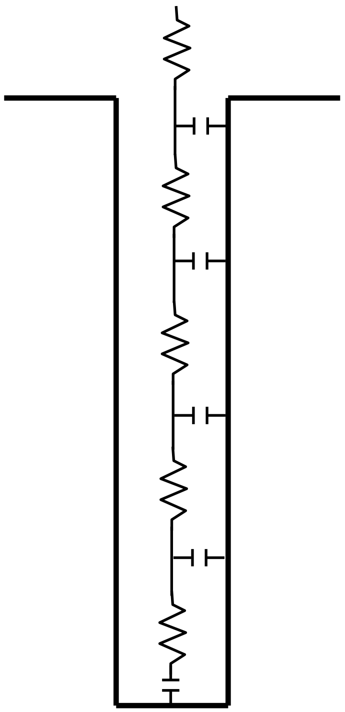
Porous Electrodes – Modeling with Transmission Lines



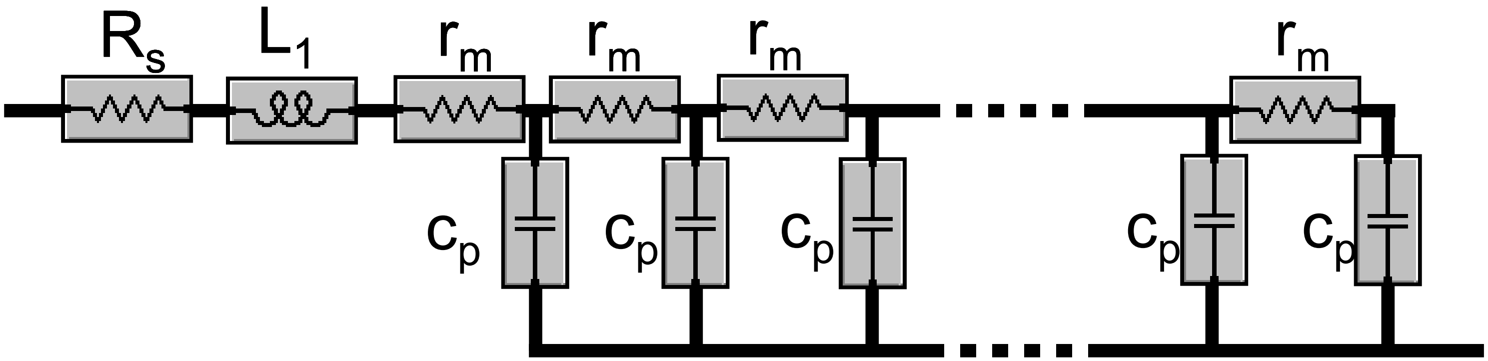


Porosity

- Given most energy storage and conversion mechanisms are interfacial, a high surface area to volume/weight ratio is beneficial.
- Porous electrodes are the logical choice.
- Porous electrodes complicate the analysis of impedance spectra due to the distributed nature.



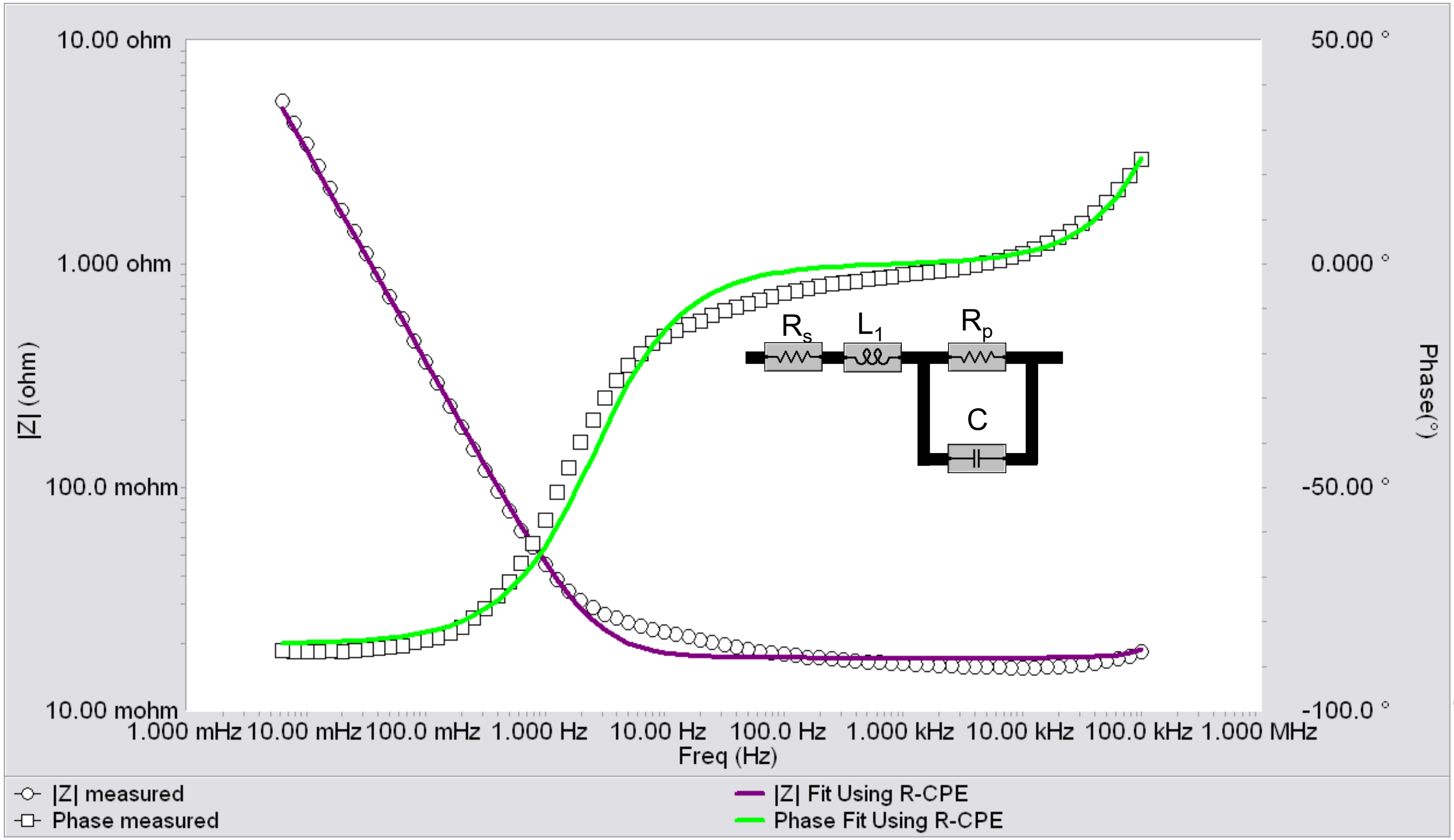
Model & Information content

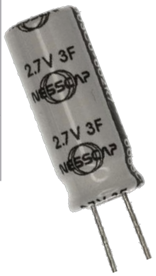


- The impedance data contain information about:
  - Equivalent series resistance (ESR)
  - Capacitance

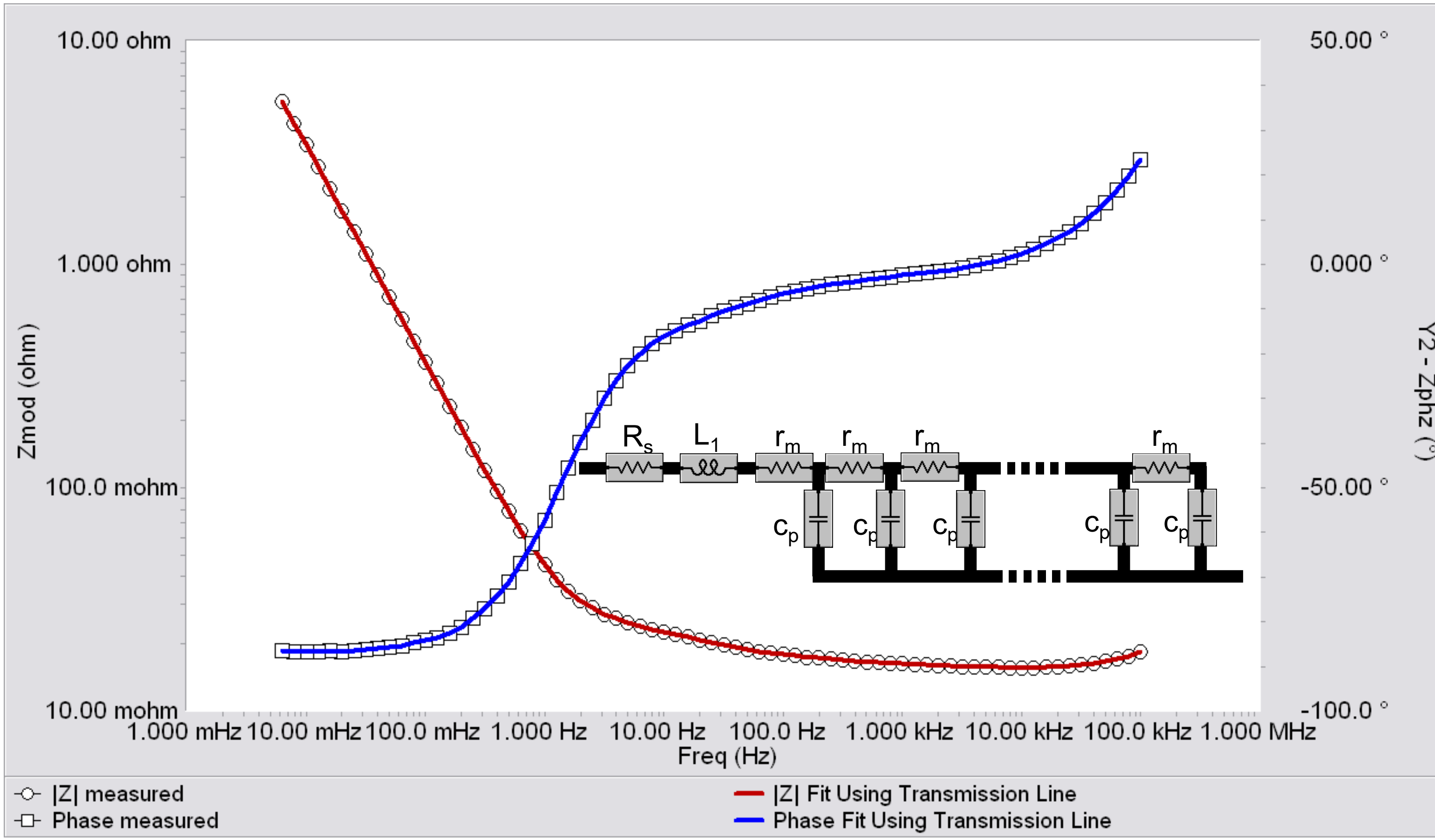
The details of the supercapacitor analysis can be found in:
https://www.gamry.com/assets/Uploads/Demystifying-Transmission-Lines-10-20-2015.pdf

Porous Electrodes – Modeling with Transmission Lines

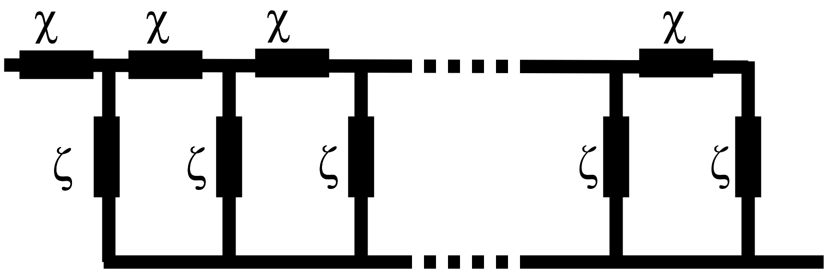




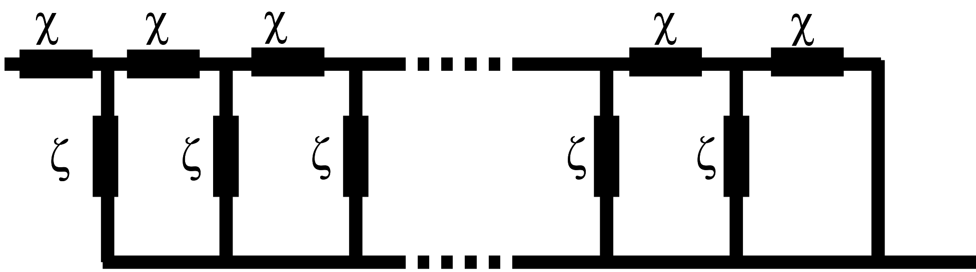
Porous Electrodes – Modeling with Transmission Lines



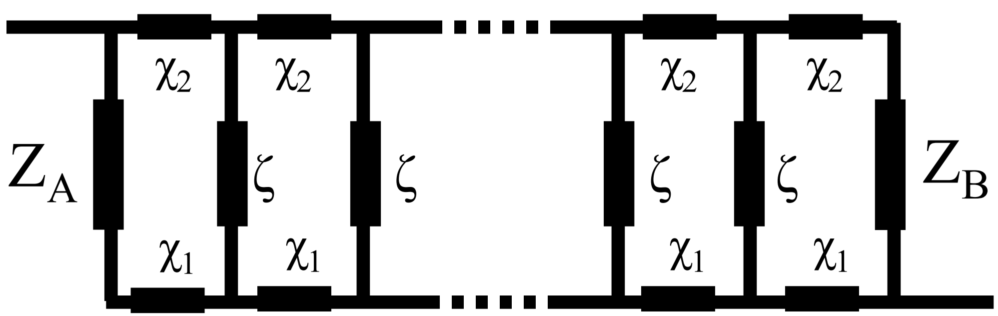
Parametric Transmission Lines



Open Circuit Terminated



Short Circuit Terminated

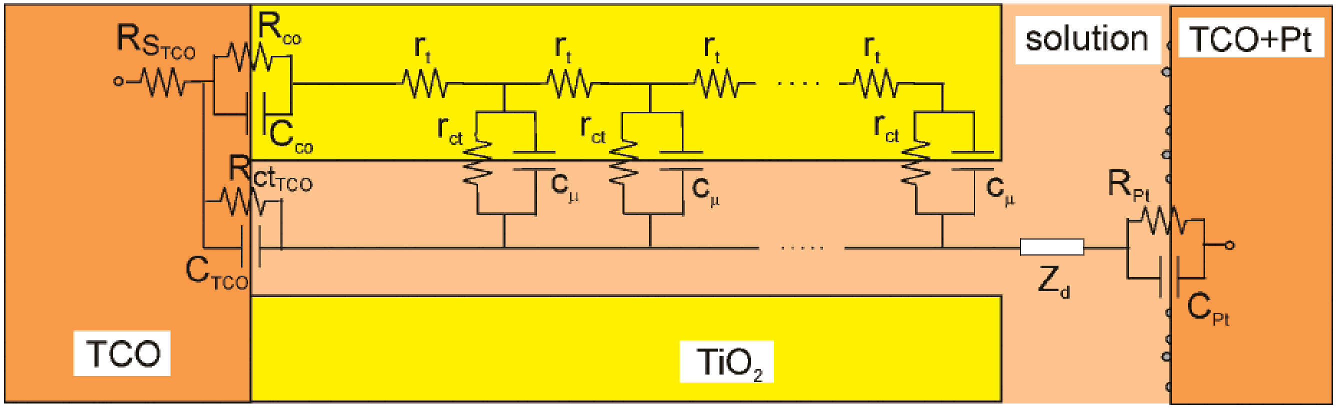


Unified

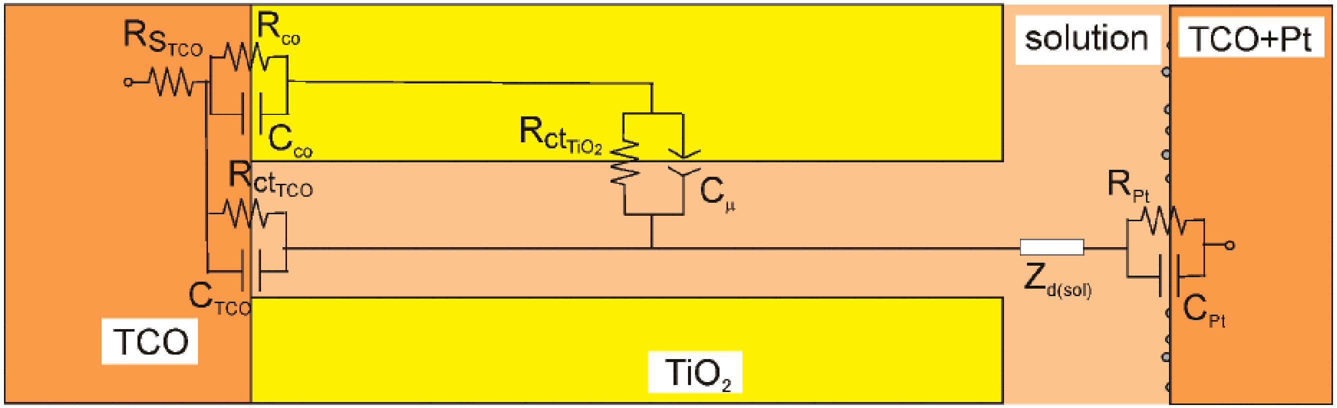
Bisquert, J. & Fabregat-Santiago F.

Dye Sensitized Solar Cells

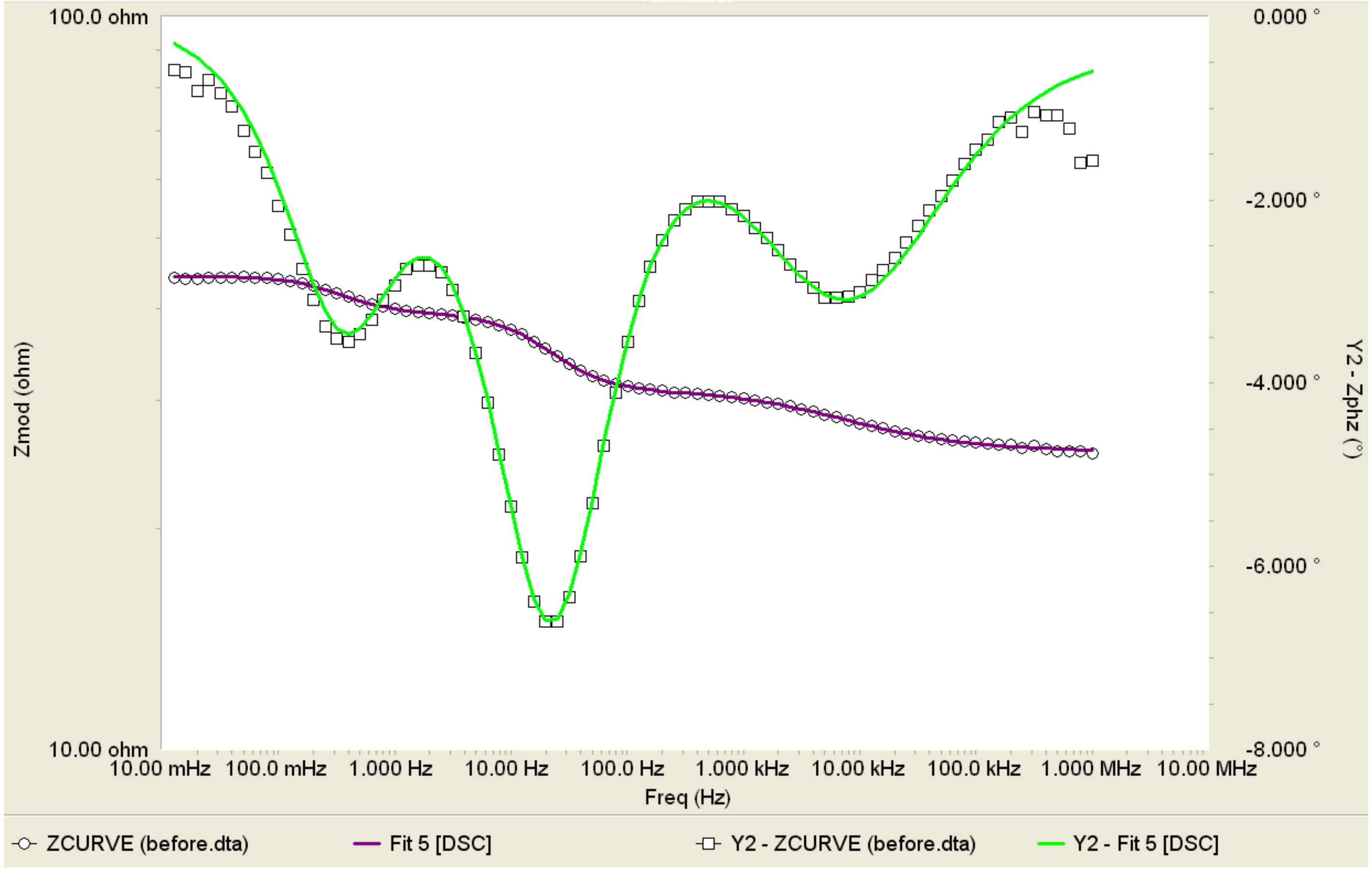
(a)



(b)

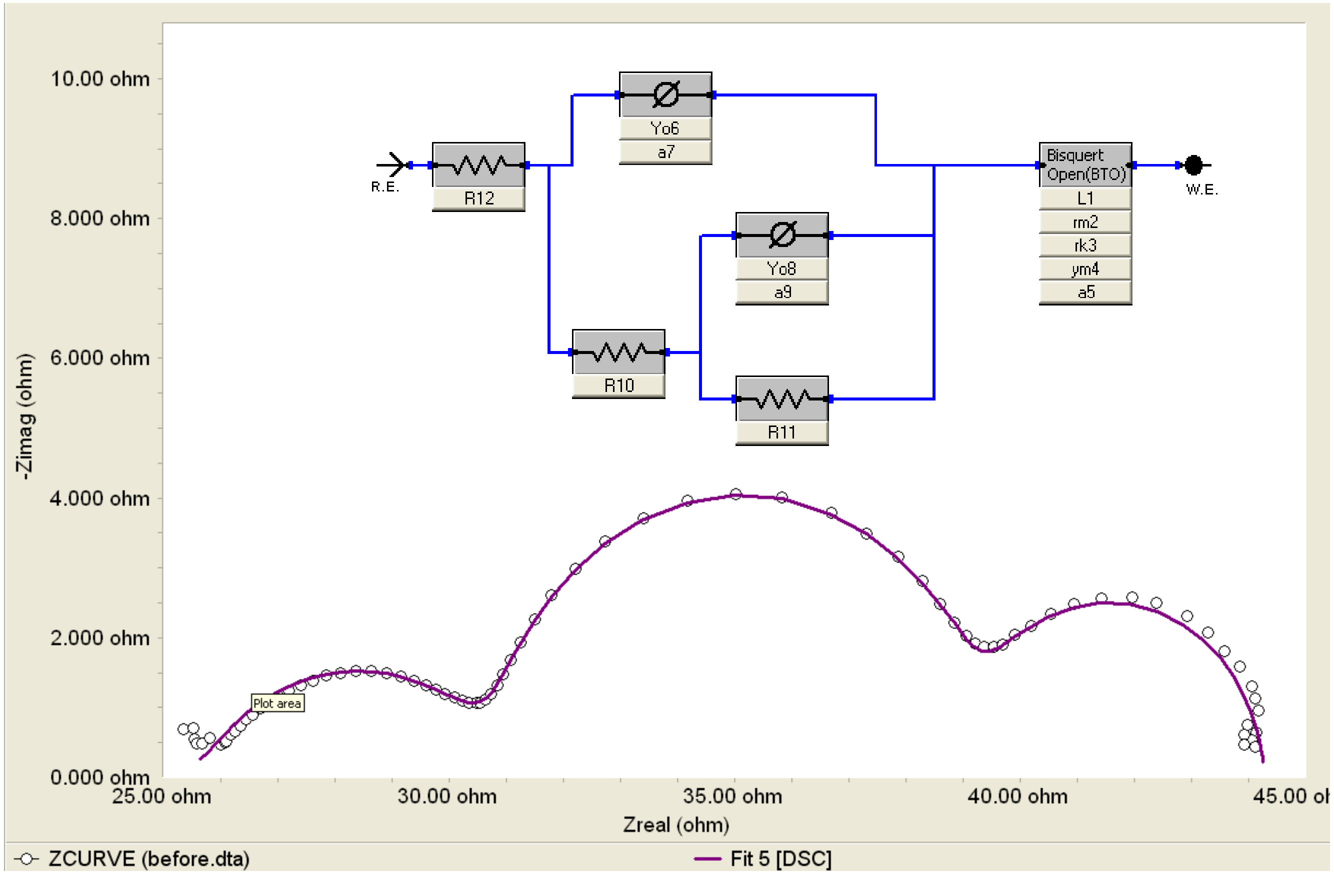


Dye Sensitized Solar Cells



Yiying Wu, et al., Ohio State University, Dept of Chemistry

Dye Sensitized Solar Cells



Yiying Wu, et al., Ohio State University, Dept of Chemistry

Criteria For Valid EIS

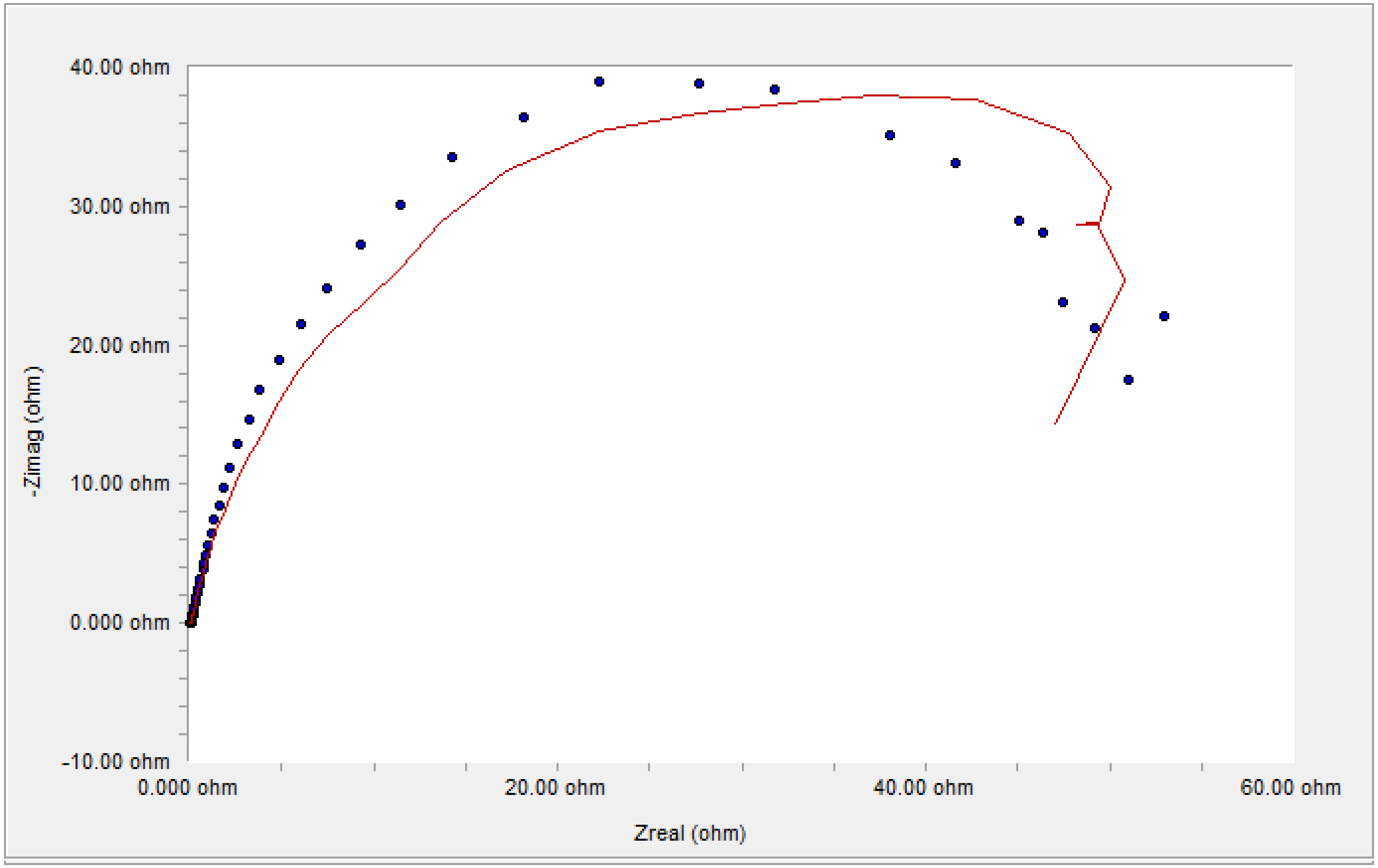
Linear – Stable - Causal

- Linear: The system obeys Ohm's Law, $E = iZ$. The value of Z is independent of the magnitude of the perturbation. If linear, no harmonics are generated during the experiment.
- Stable: The system does not change with time and returns to its original state after the perturbation is removed.
- Causal: The response of the system is due only to the applied perturbation.

Warning about Kramers Kronig

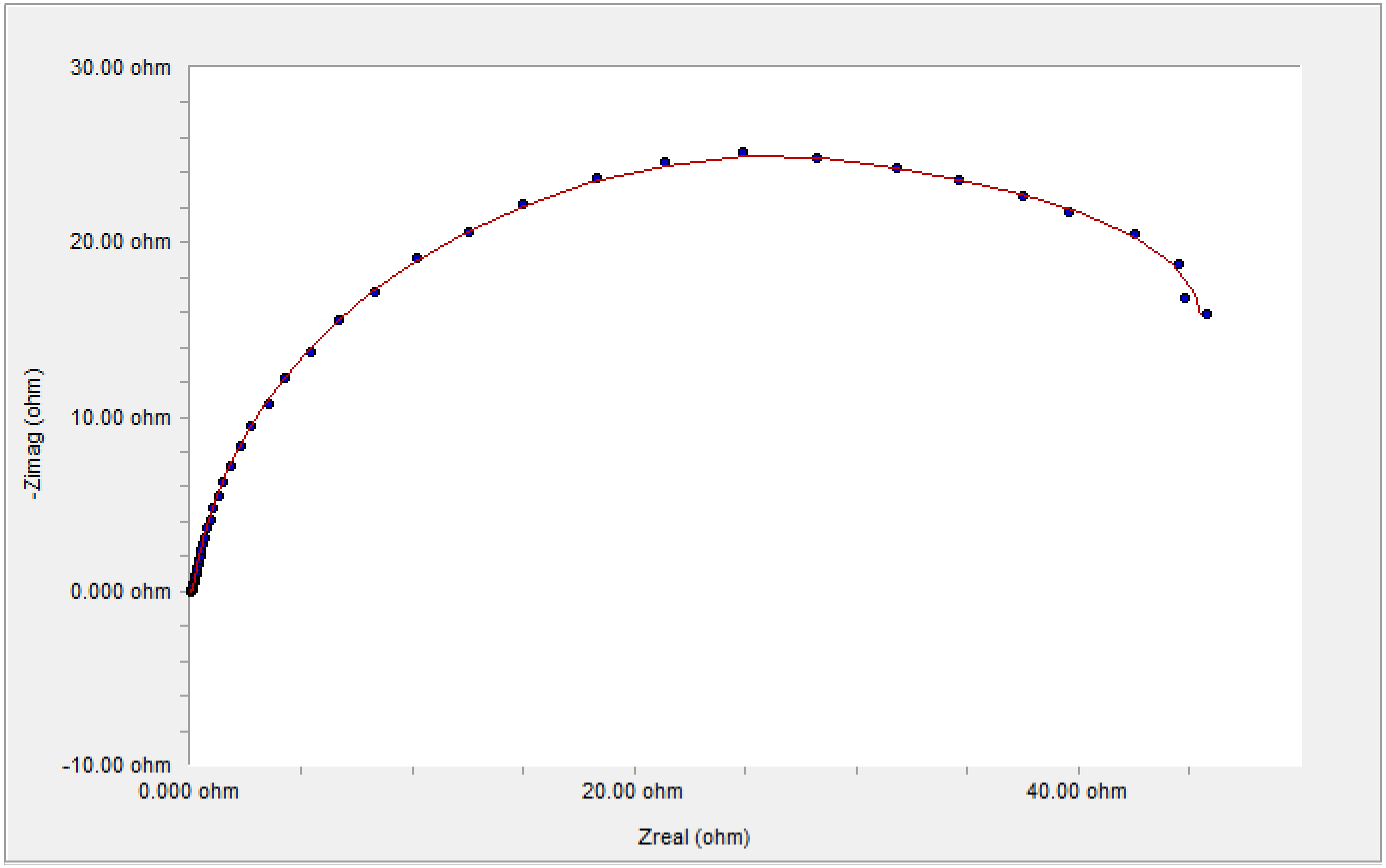
- First, if KK fails, the data is bad. Do NOT attempt to fit it. It will NOT fit. The circuit model components are KK transformable.
- If KK passes, there is still no guarantee that the data is useful. Things like instrumental artifacts will pass KK but will not yield any useful data.
- KK will fail if the data is either not causal, not linear or not stable

NiCd – Bad KK



40.00 ohm
30.00 ohm
20.00 ohm
10.00 ohm
0.000 ohm
-10.00 ohm
-Zimag (ohm)
0.000 ohm
20.00 ohm
40.00 ohm
60.00 ohm
Zreal (ohm)

Lowering the AC Amplitude



Assuming we have good data

- We can obtain information about:
  - Equivalent Series Resistance (ESR / internal resistance)
  - Various capacitances
  - Leakage?
  - Inductance?

ESR

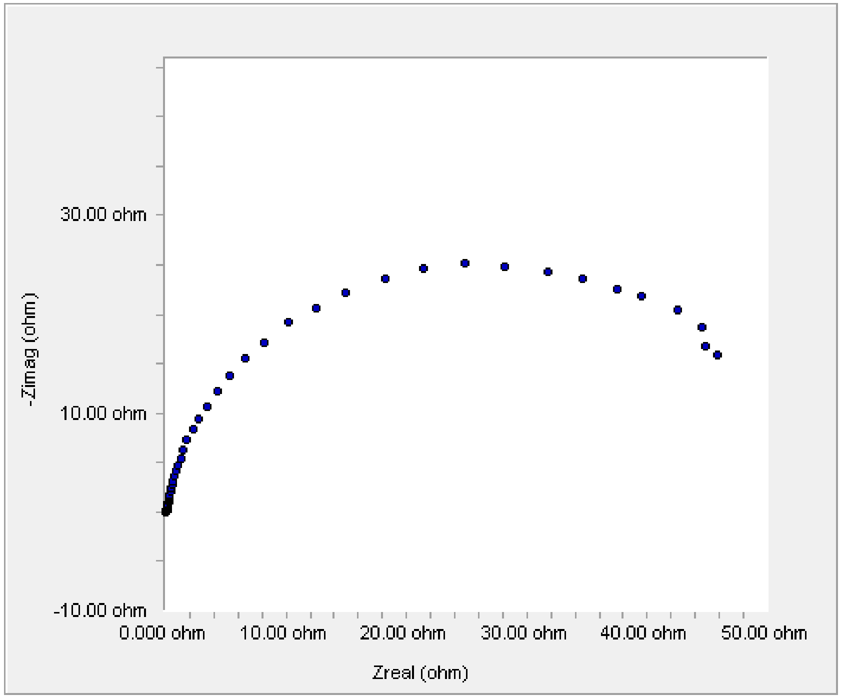
- Equivalent Series Resistance (ESR), High Frequency Resistance (HFR), Internal resistance are all the same number
- The easiest parameter to read off the Nyquist
  - Reading the high freq. x intercept gives the ESR on the Nyquist

Inductance

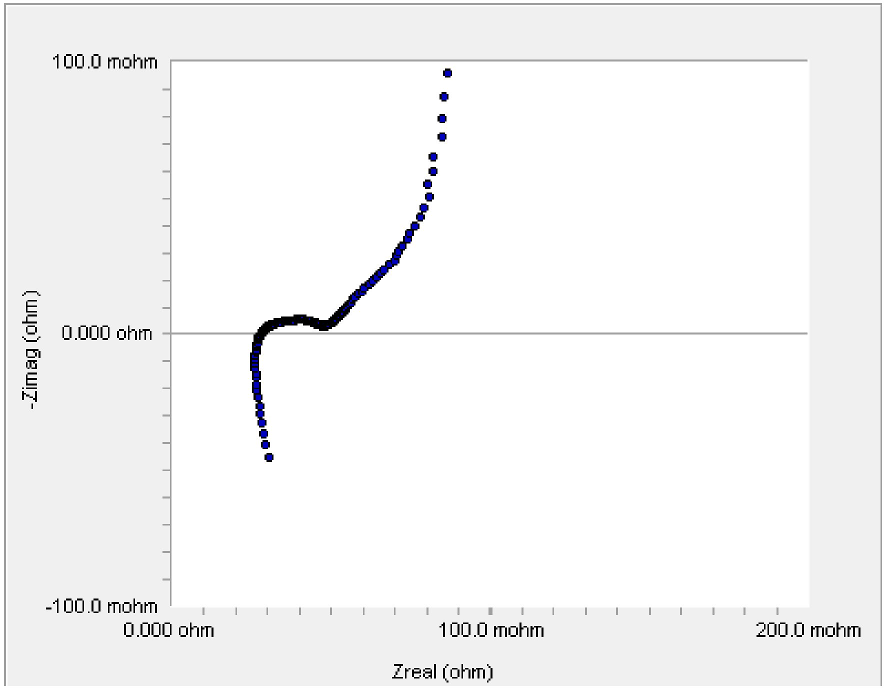
- Almost always instrumental and therefore useless.
- Related to cabling, may be related to cell geometry. Hard to decouple from instrumental issues.

Typical Data for Batteries

Commercial NiCd Cell

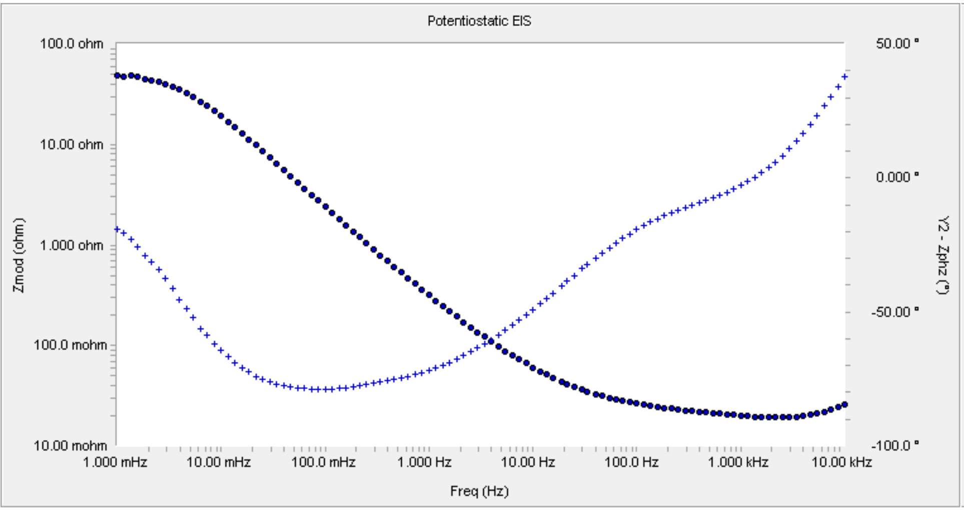


Commercial 18650 Li Ion cell

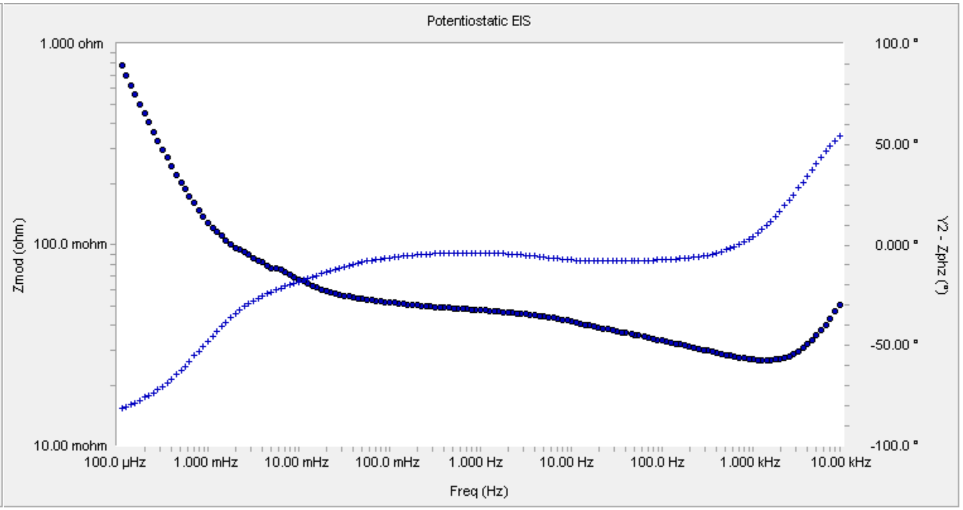


Bode Plot

Commercial NiCd Cell

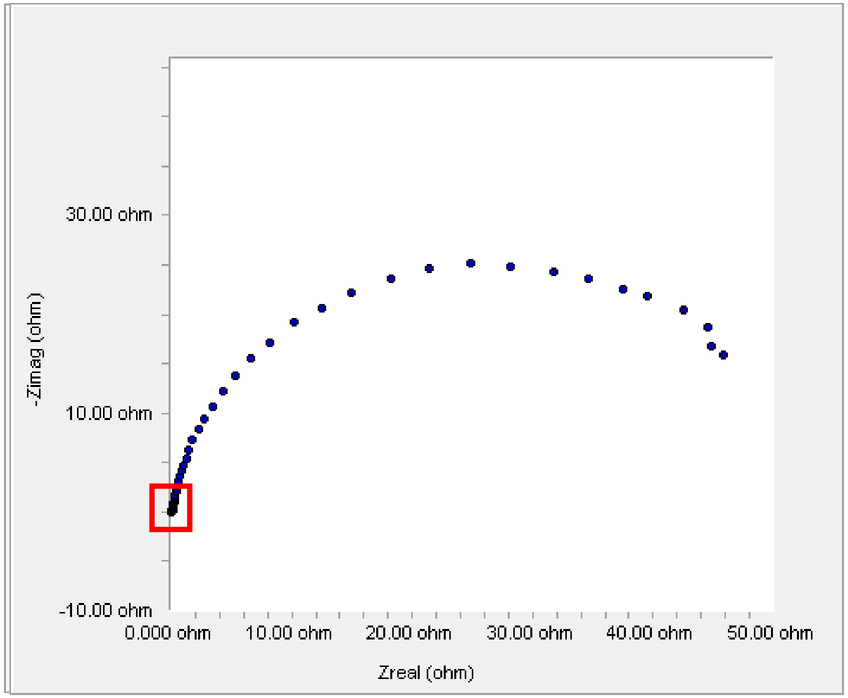


Commercial 18650 Li Ion cell

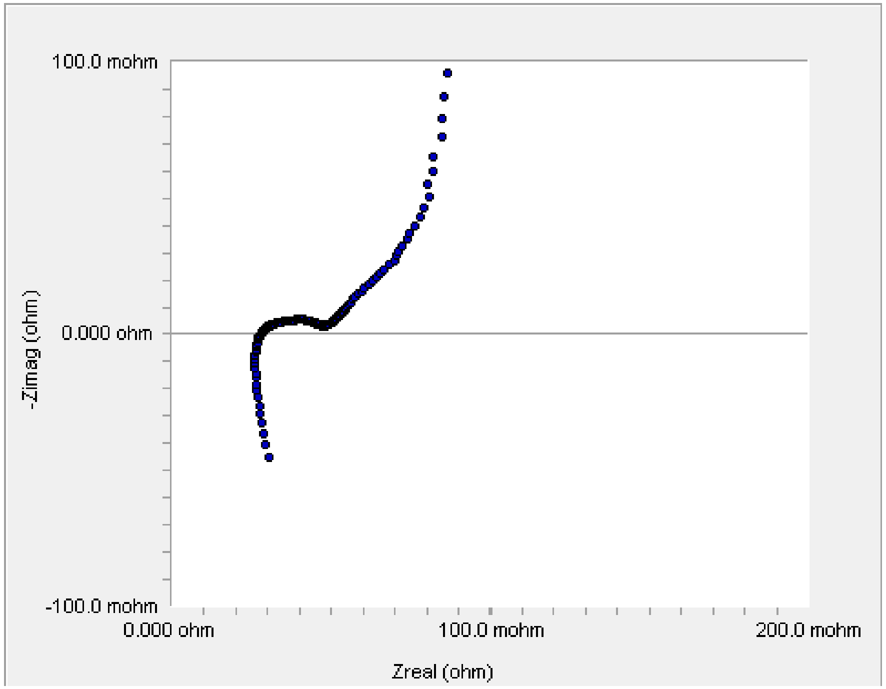


Nyquist / ESR

Commercial NiCd Cell

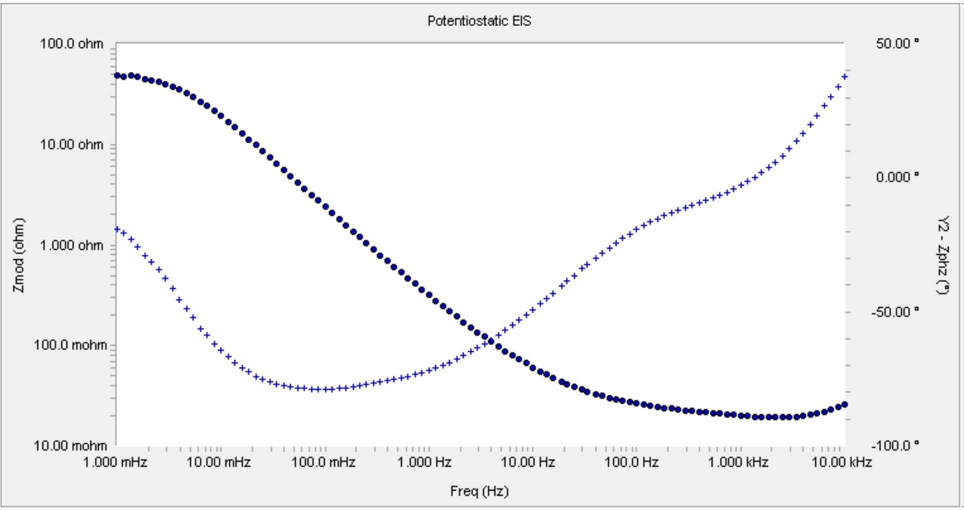


Commercial 18650 Li Ion cell

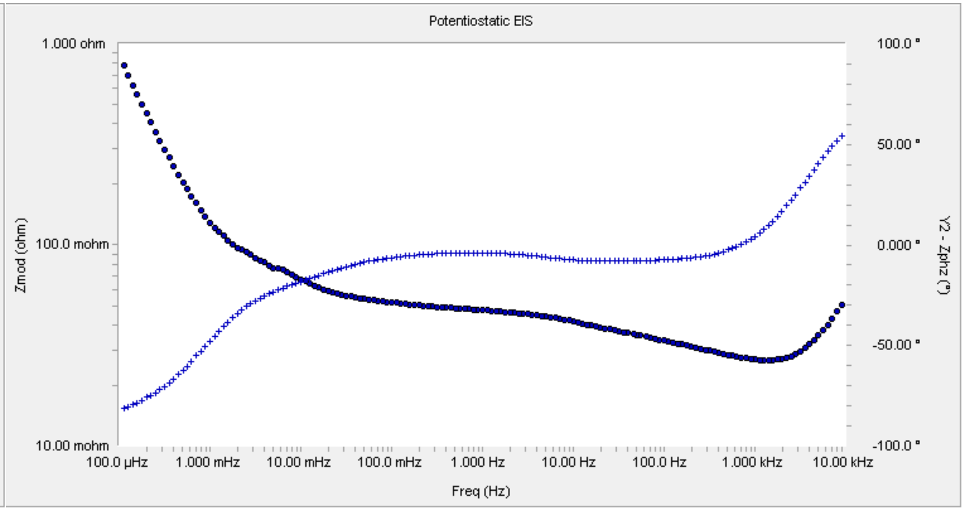


Bode Plot / ESR

Commercial NiCd Cell

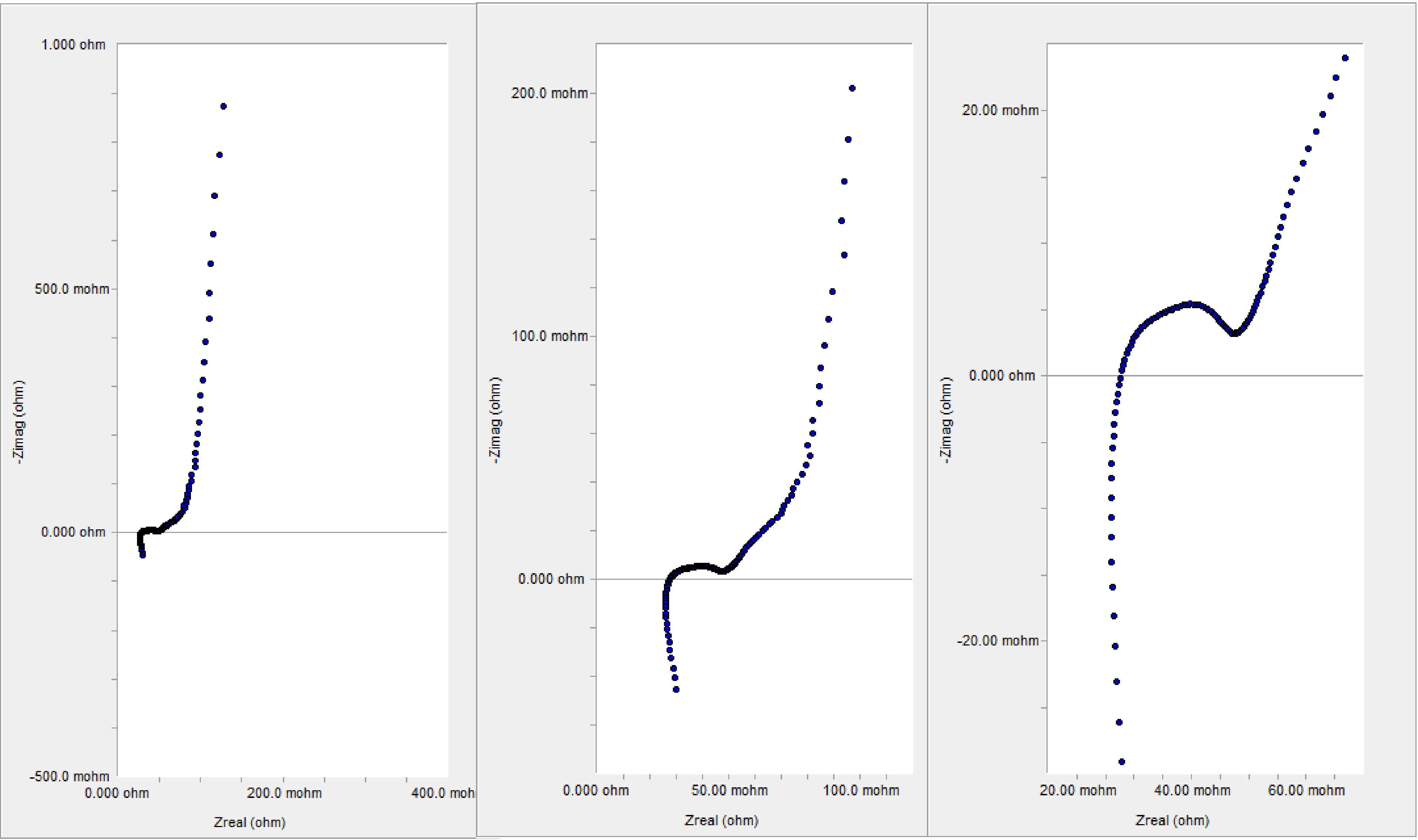


Commercial 18650 Li Ion cell

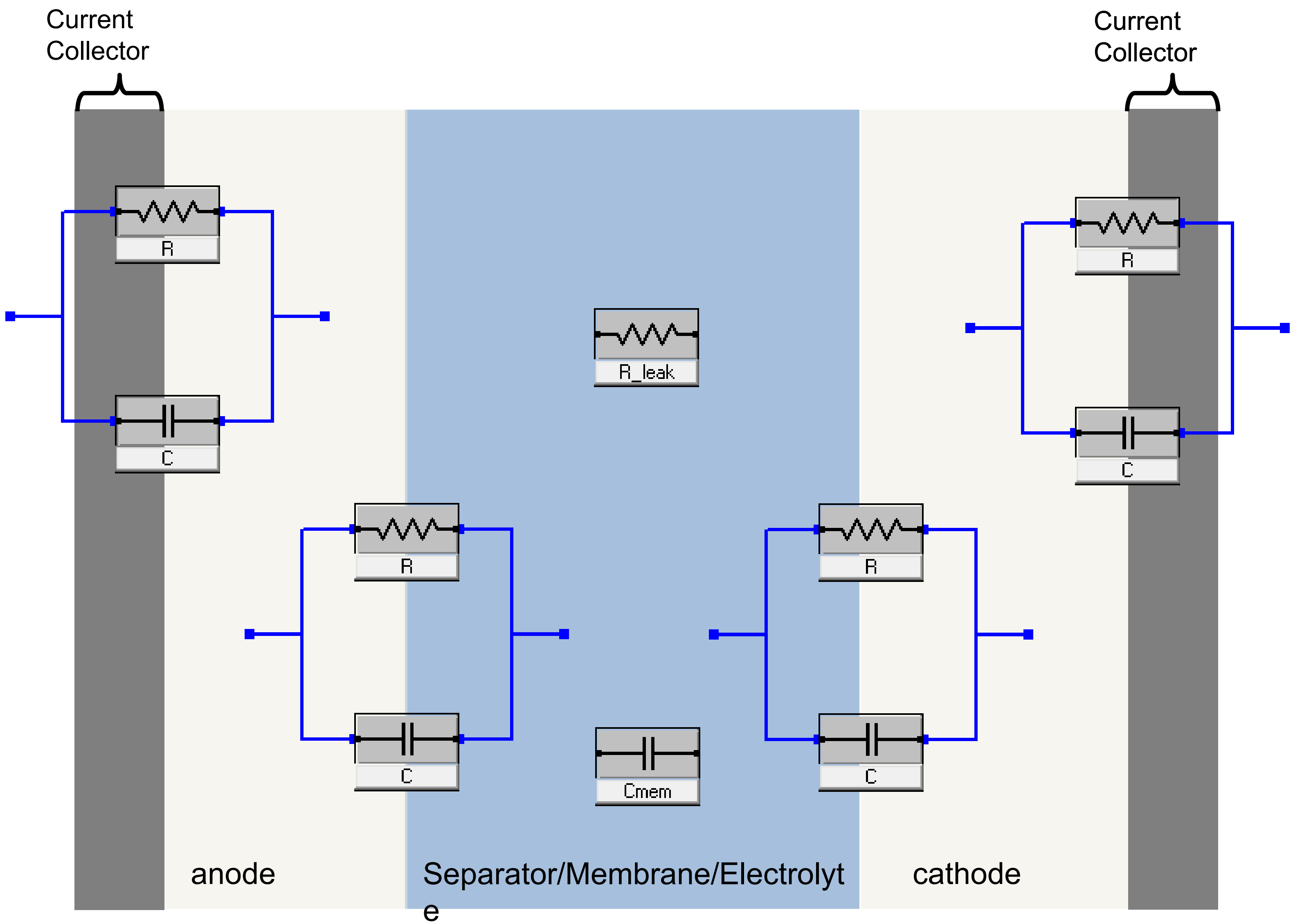


- Harder to read, but generally the lowest value Zmod reaches
- Here is where the magic 1kHz-10kHz range comes from

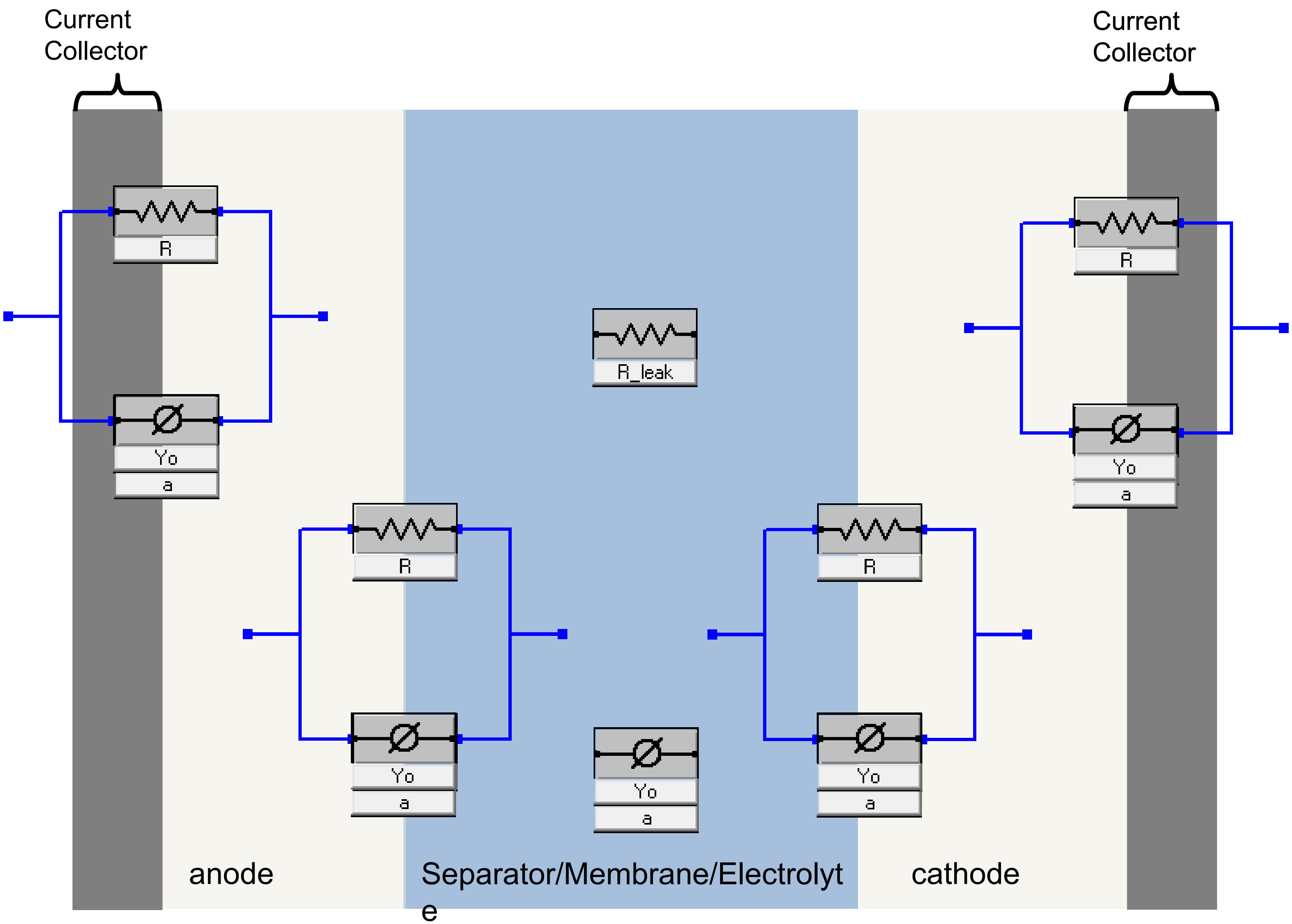
Looking at the whole spectrum of the 18650 LiIon Cell



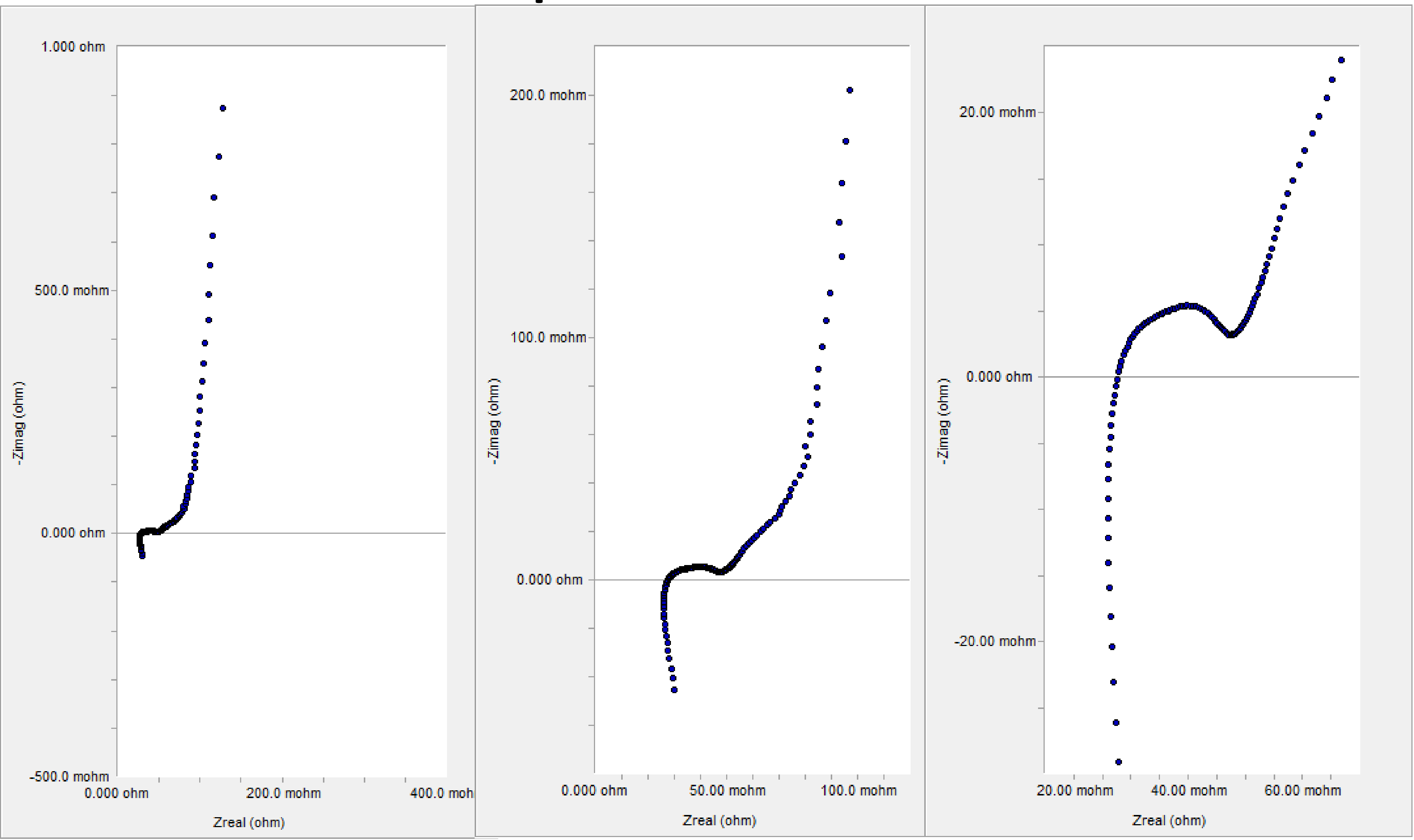
Interfaces Ignoring Porosity



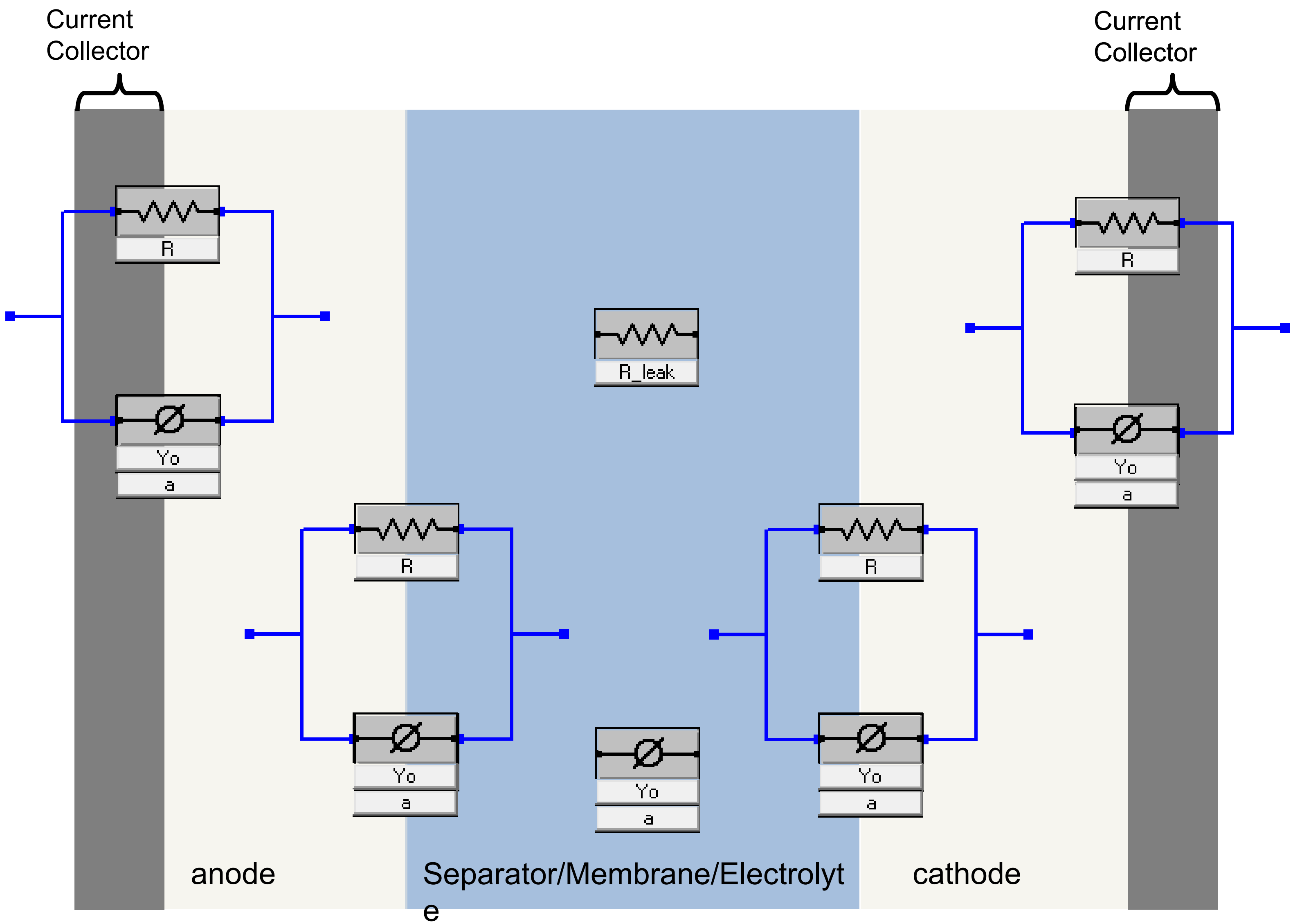
Interfaces Ignoring Porosity



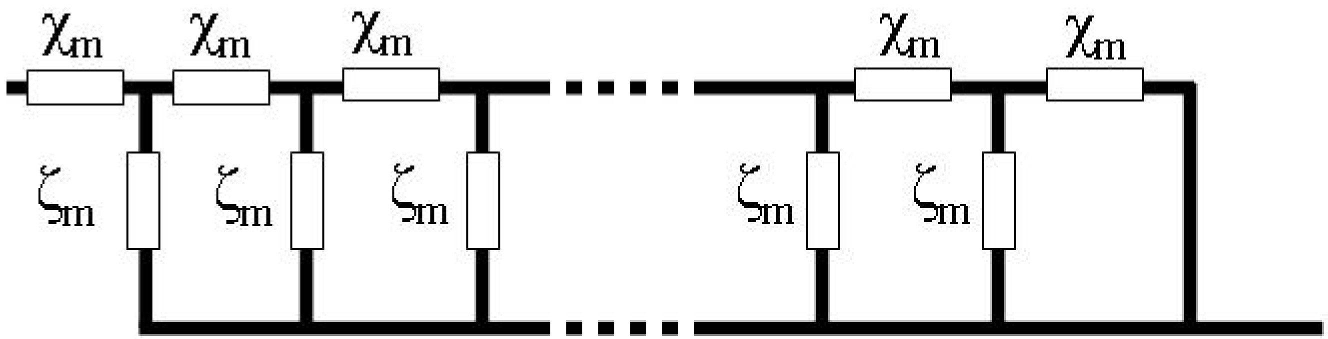
Complete LiIon Cell

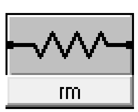


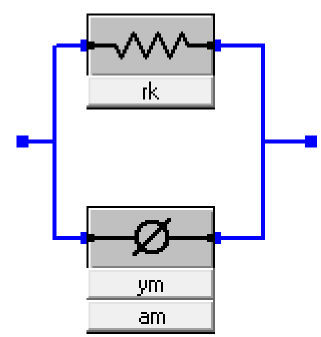
Interfaces Ignoring Porosity

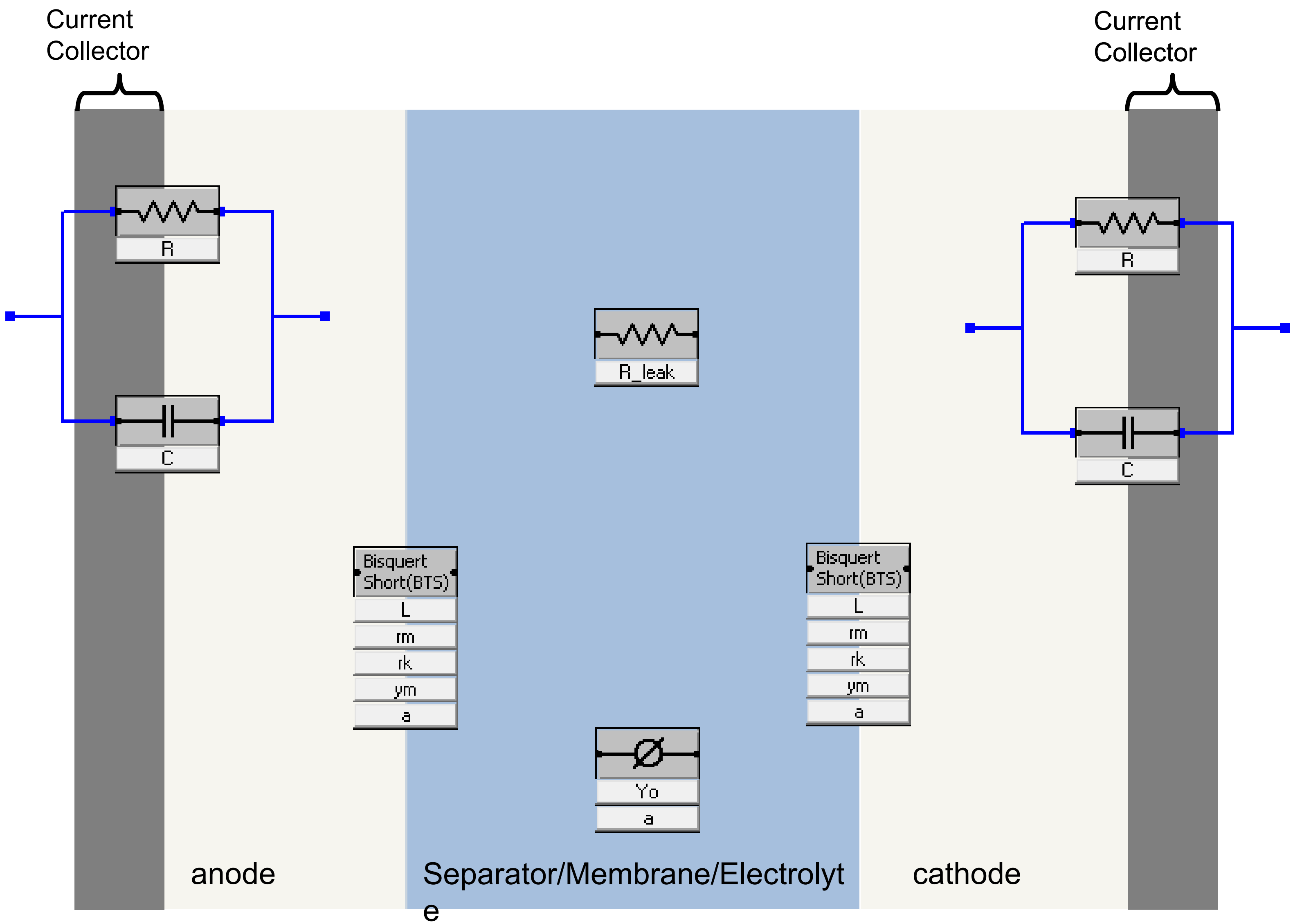


Short Circuit Terminated Bisquert Component (BTS)



$X_m =$ 

$\zeta_m =$ 


Current Collector
Current Collector
R
C
R_leak
R
C
Bisquert Short(BTS)
L
rm
rk
ym
a
Bisquert Short(BTS)
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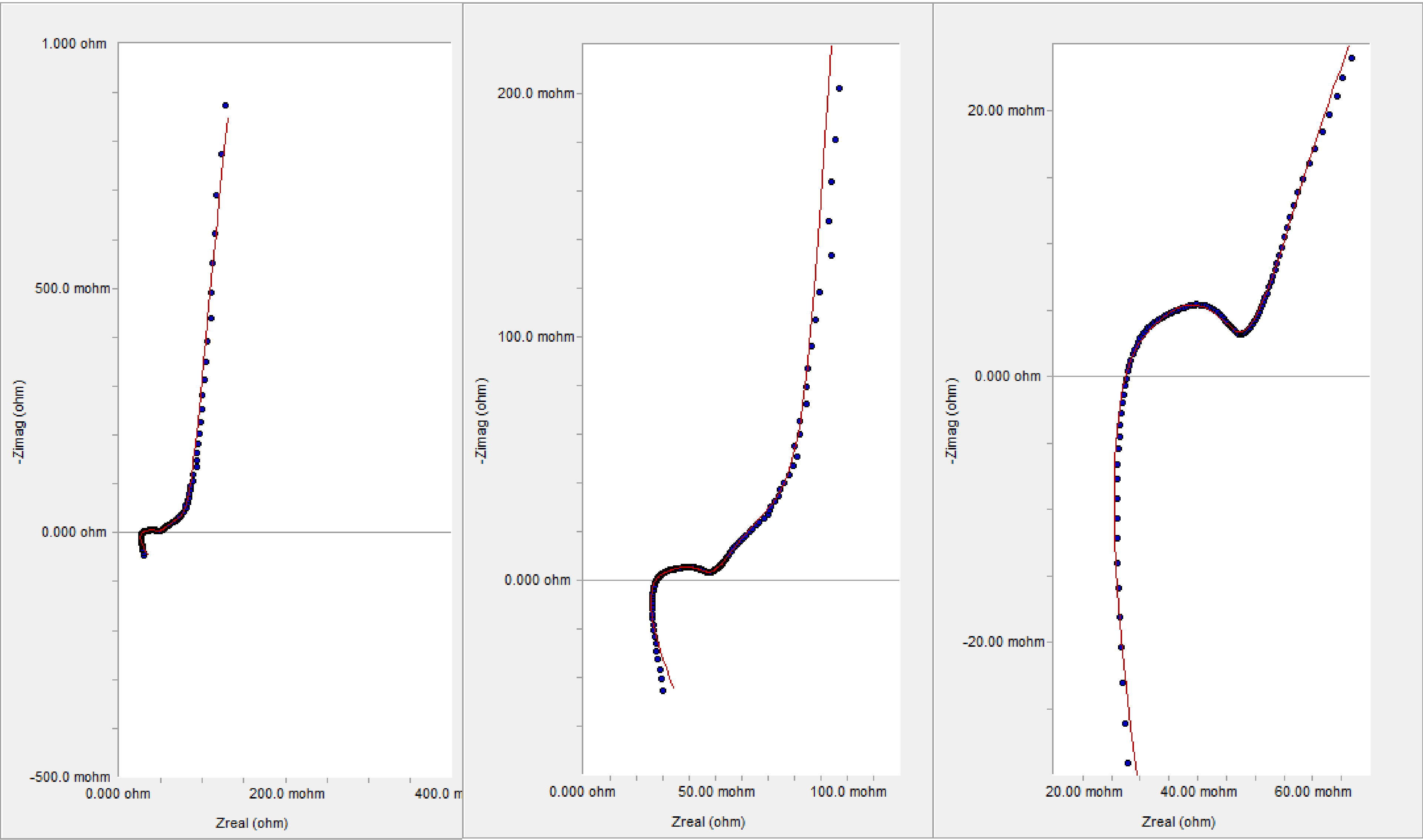
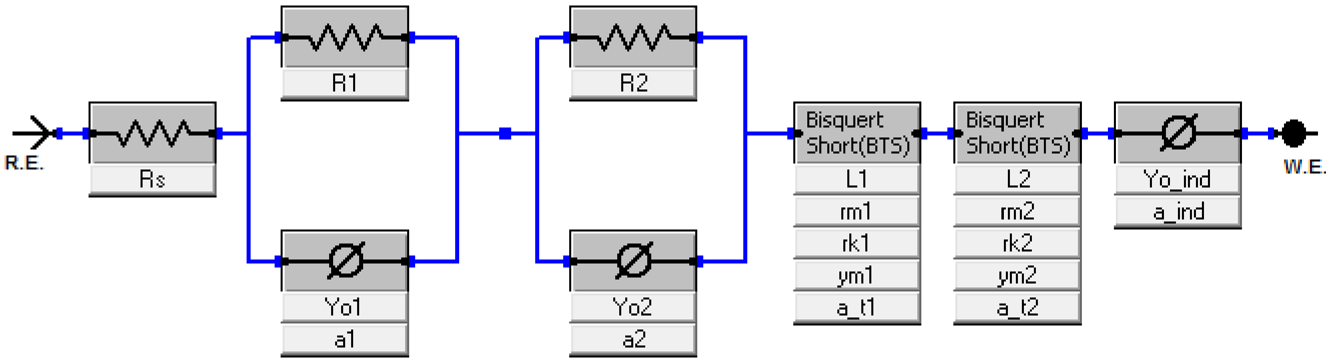
rm
rk
ym
a
Yo
a
anode
Separator/Membrane/Electrolyte
cathode

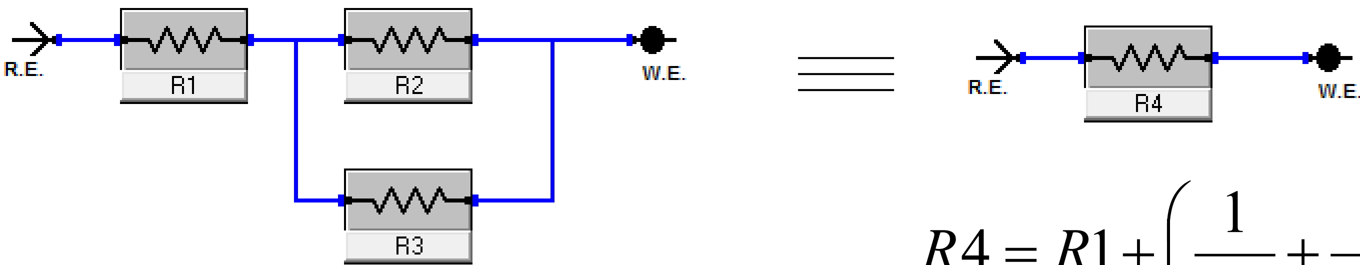


1.000 ohm
500.0 mohm
0.000 ohm
-500.0 mohm
0.000 ohm
200.0 mohm
-Zimag (ohm)
Zreal (ohm)
200.0 mohm
100.0 mohm
0.000 ohm
0.000 ohm
50.00 mohm
100.0 mohm
-Zimag (ohm)
Zreal (ohm)
20.00 mohm
0.000 ohm
-20.00 mohm
20.00 mohm
40.00 mohm
60.00 mohm
-Zimag (ohm)
Zreal (ohm)

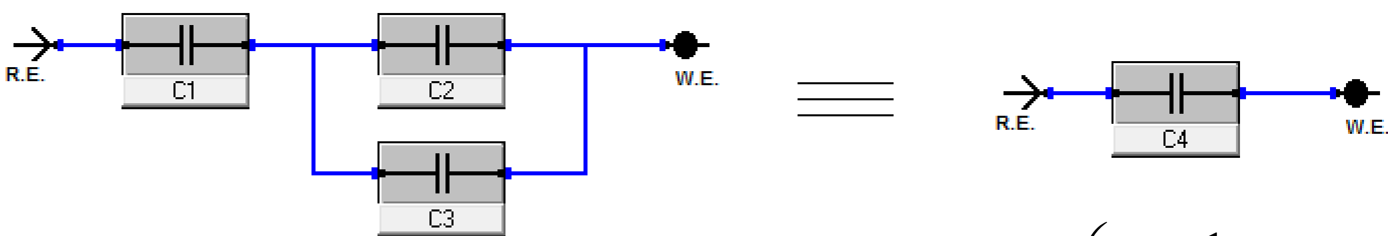
The model used to get the fit



Redundancy of Components



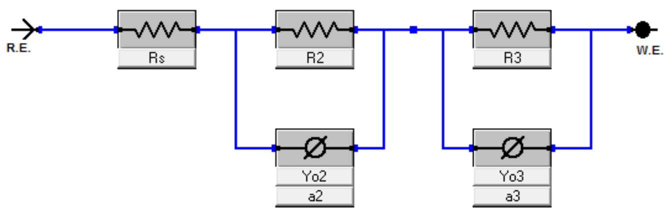
$$R4 = R1 + \left(\frac{1}{R2} + \frac{1}{R3} \right)^{-1}$$



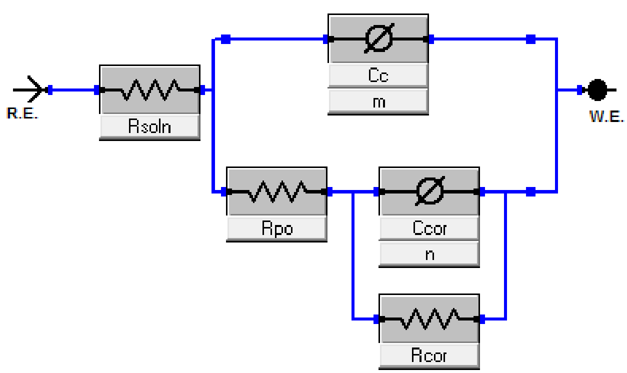
$$C4 = \left(\frac{1}{C2 + C3} + \frac{1}{C1} \right)^{-1}$$

Ambiguity of Models

a)



b)



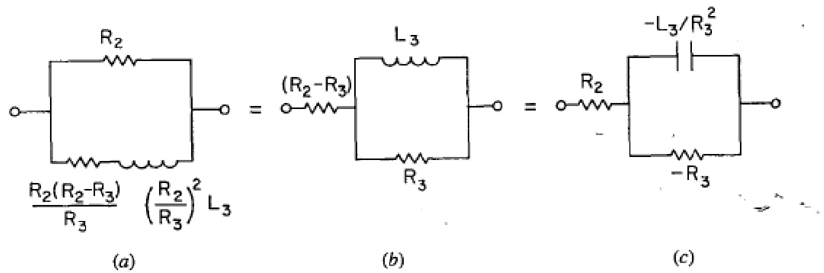


Figure 2.2.3. Three circuits having the same impedance at all frequencies.

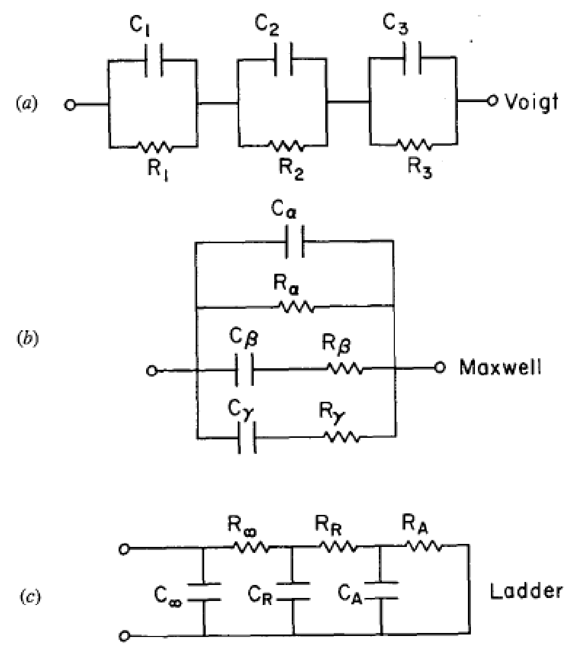
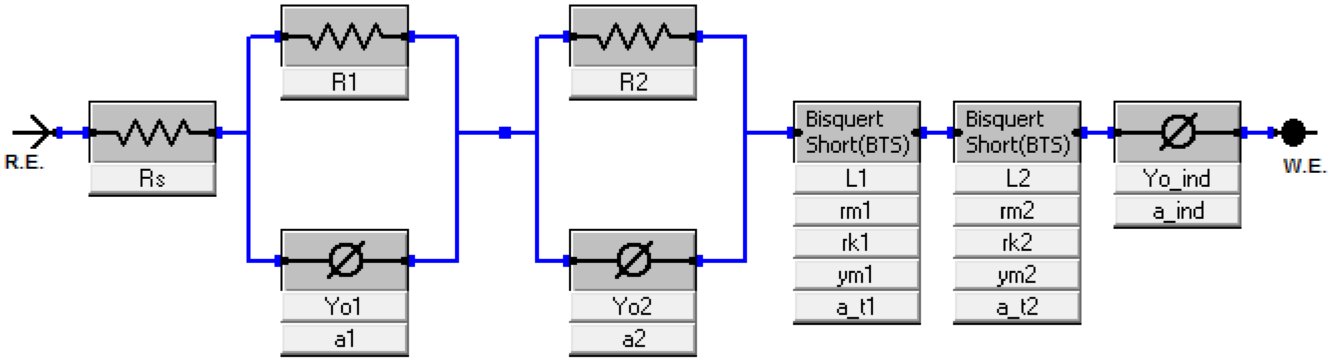
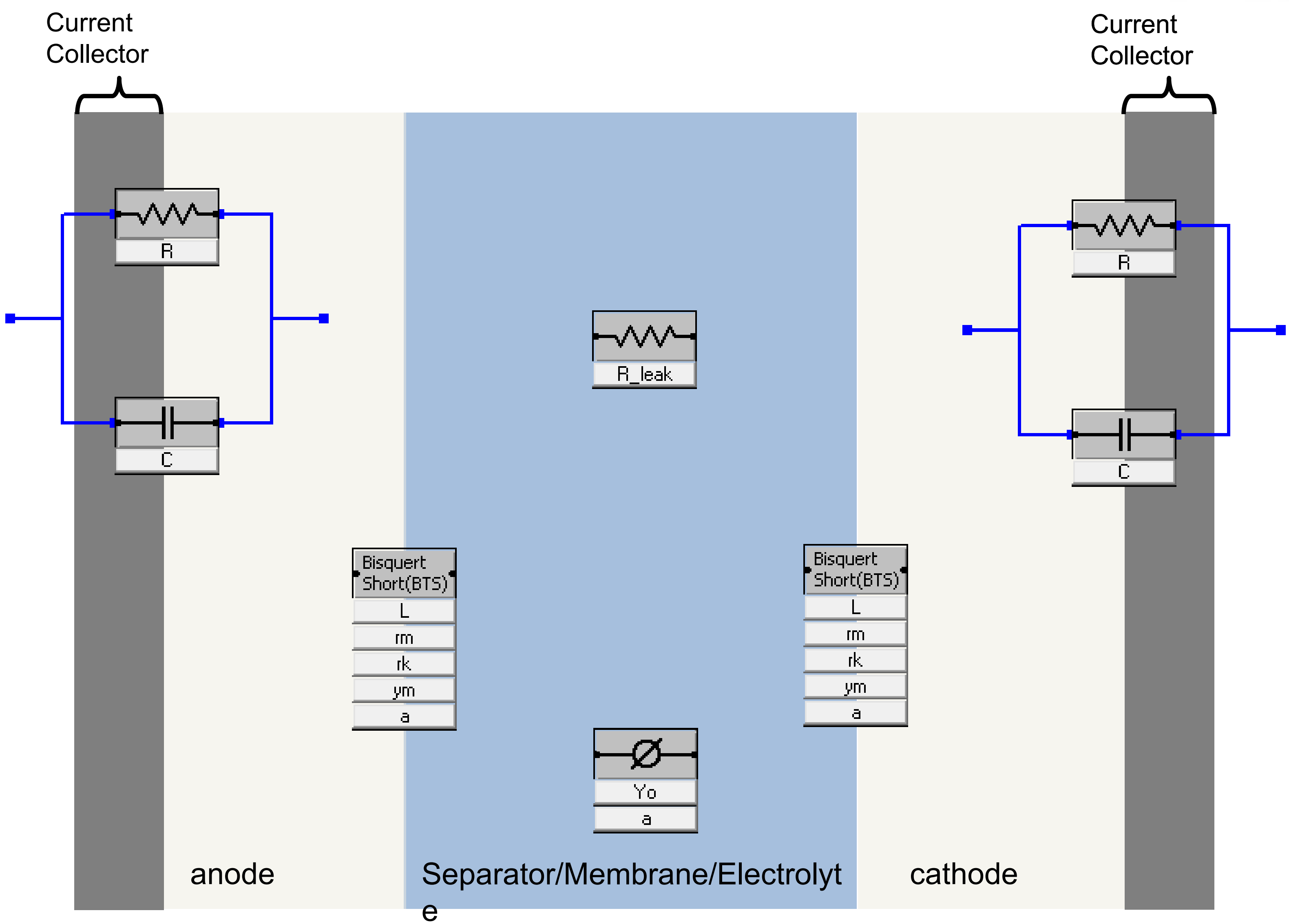


Figure 2.2.4. Three further circuits which can have the same impedance at all frequencies when the parameters of the circuit are properly interrelated.

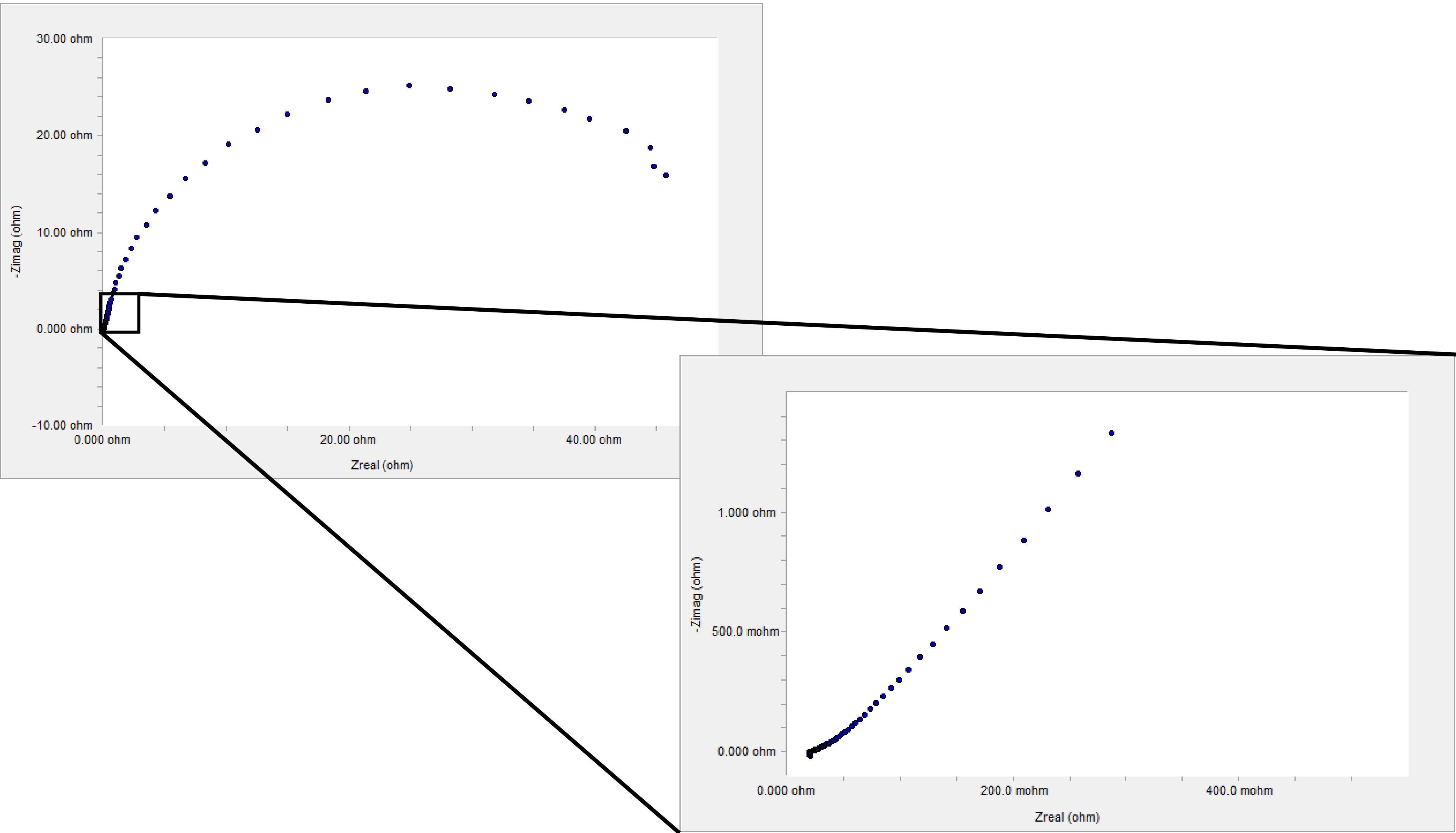
The model



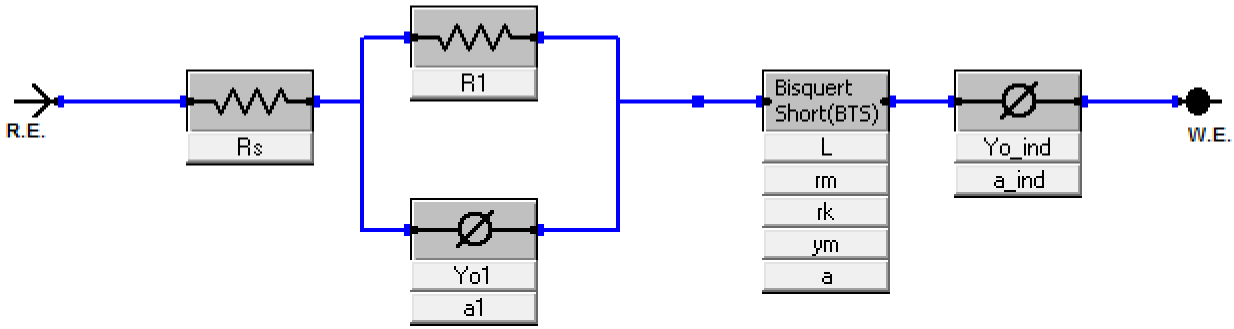
- Trying to assign different parts of this model to actual physical interfaces requires other experiments, scaling checks, etc.
- It is also possible that certain R//CPE combinations are nested.


Current Collector
Current Collector
R
C
R_leak
R
C
Bisquert Short(BTS)
L
rm
rk
ym
a
Bisquert Short(BTS)
L
rm
rk
ym
a
Yo
a
anode
Separator/Membrane/Electrolyte
cathode

The NiCd Cell

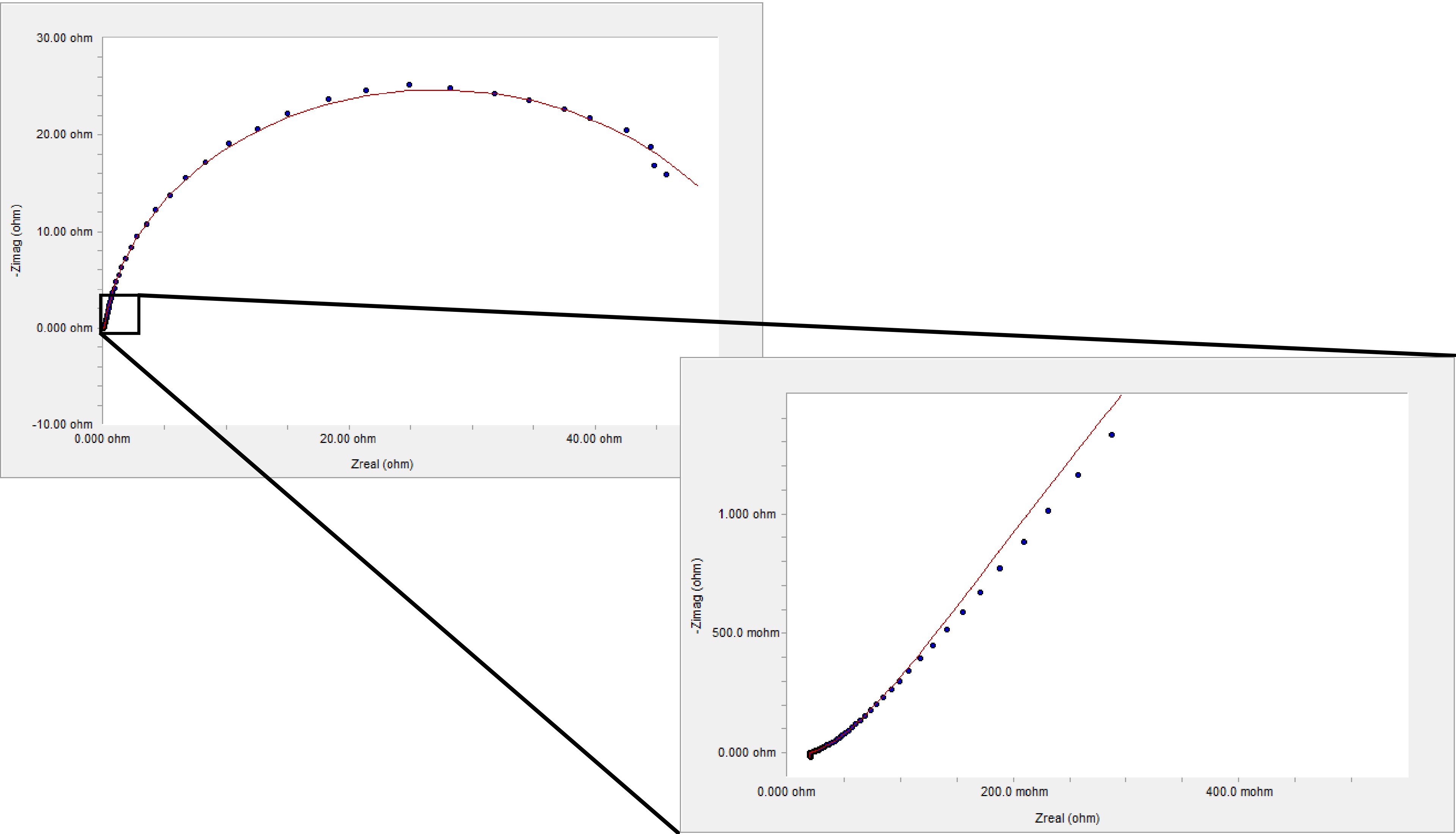


The NiCd Model



- The data doesn't have as much information.
- There are only two time-constants visible

The Complete NiCd Data



EIS Take Home

- EIS is a versatile technique
  - Non-destructive
  - High information content
- Running EIS is easy
- EIS modeling analysis is very powerful
  - Simplest working model is best
  - Complex system analysis is possible
  - User expertise can be helpful

References for EIS

- *Electrochemical Impedance Spectroscopy*, M. Orazem, B Tribollet. ISBN: 978-1118527399
- Electrochemical Impedance and Noise, R. Cottis and S. Turgoose, NACE International, 1999. ISBN 1-57590-093-9.
- Electrochemical Impedance: Analysis and Interpretation, STP 1188, Edited by Scully, Silverman, and Kendig, ASTM, ISBN 0-8031-1861-9.
- *Basics of EIS, Intro to EIS (part 2)*, and other applications notes, Gamry Instruments website, www.gamry.com