

Equivalent Circuits for Battery Related Measurements

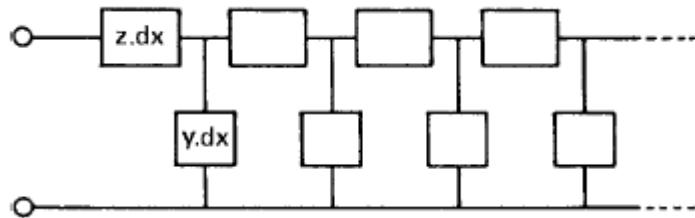
Johan Hjelm [johh@dtu.dk]

Technical University of Denmark

Department of Energy Conversion and Storage

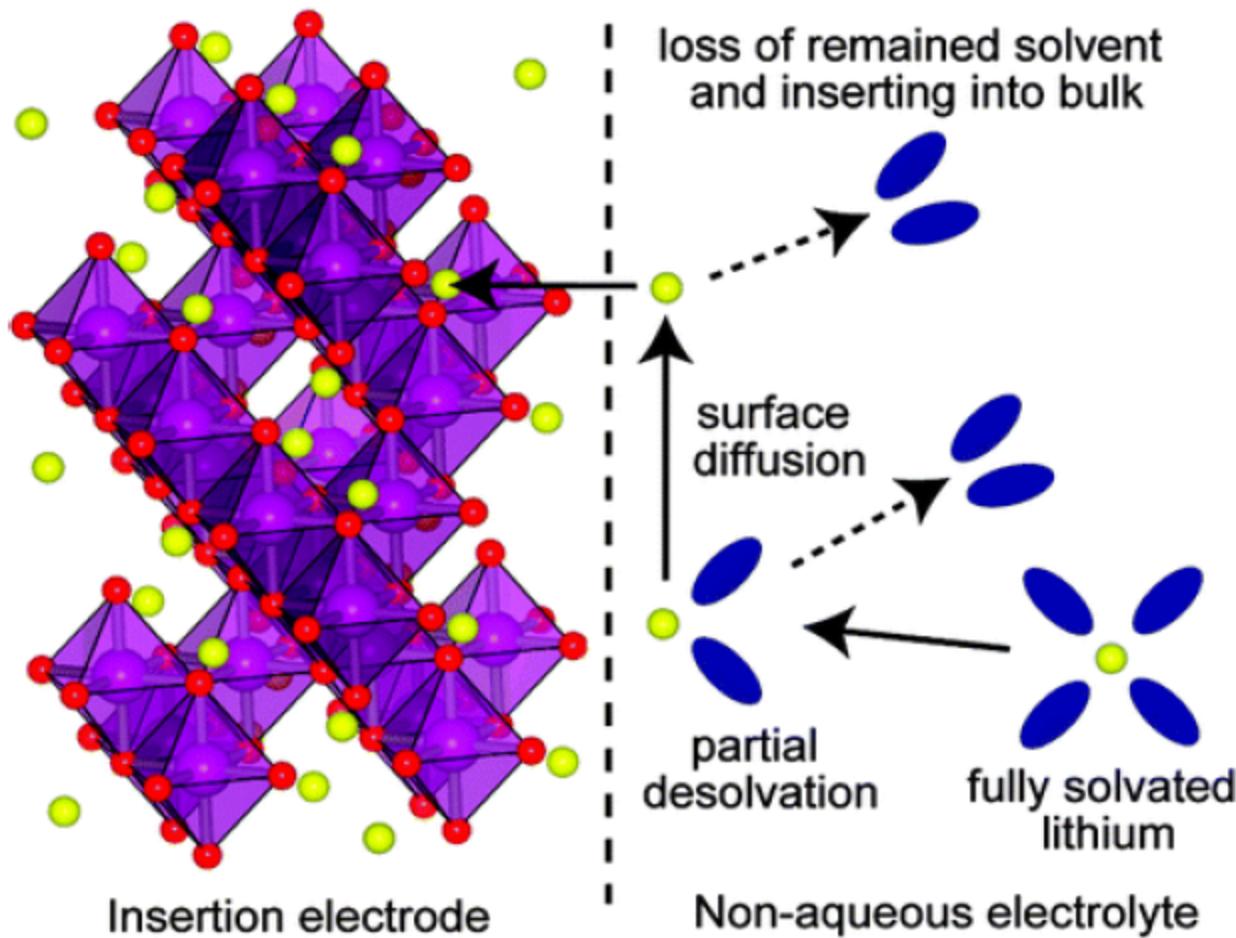
Risø Campus, Roskilde, Denmark

www.energyconversion.dtu.dk



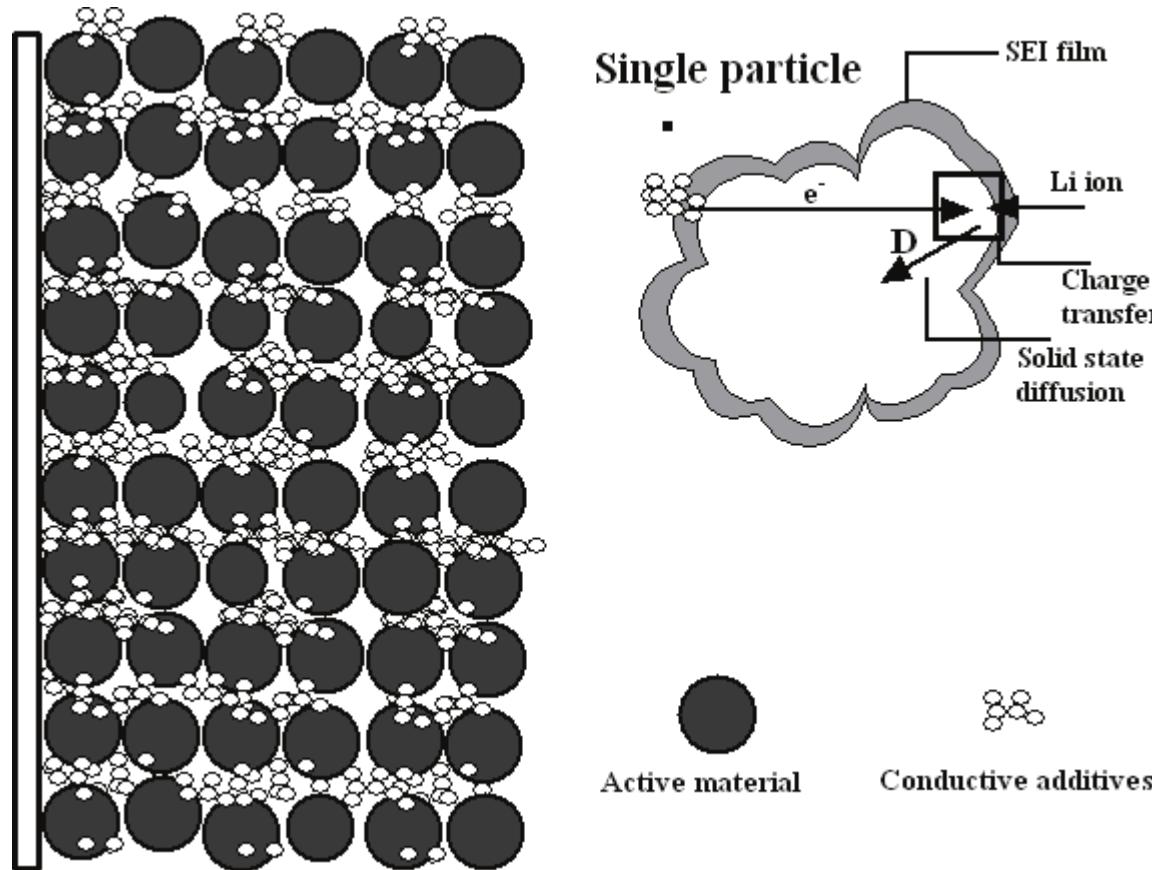
$$\Delta E = 0 \quad \Delta S \geq 0 \quad \int_a^b \mathcal{E} \Theta + \Omega \int_0^\infty \delta e^{i\pi} = \sqrt{17} \sum_{x=1}^{\infty} \frac{1}{x^2} \gg !,$$

Li ion intercalation



Q. C. Zhuang, X. Y. Qiu, S. D. Xu, Y. H. Qiang, and S. G. Sun, (2010)
http://www.intechopen.com/source/pdfs/29293/InTech-Diagnosis_of_electrochemical_impedance_spectroscopy_in_lithium_ion_batteries.pdf.

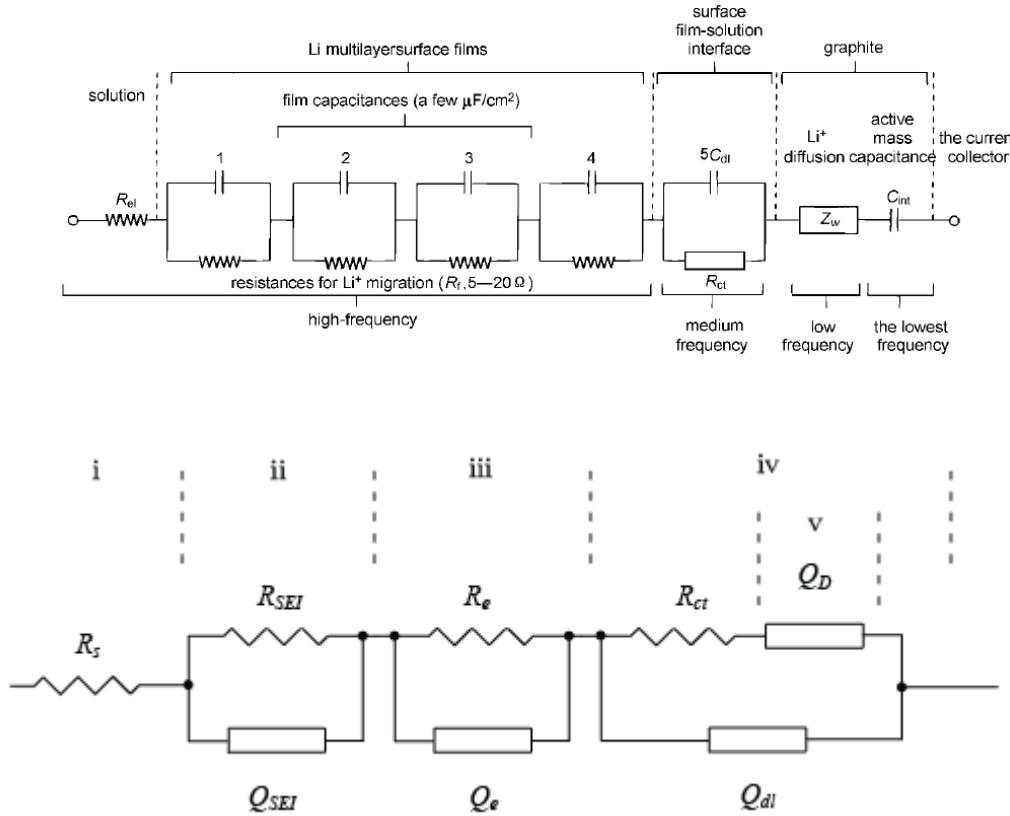
A basic schematic for a Li ion battery



Q. C. Zhuang, X. Y. Qiu, S. D. Xu, Y. H. Qiang, and S. G. Sun, (2010)
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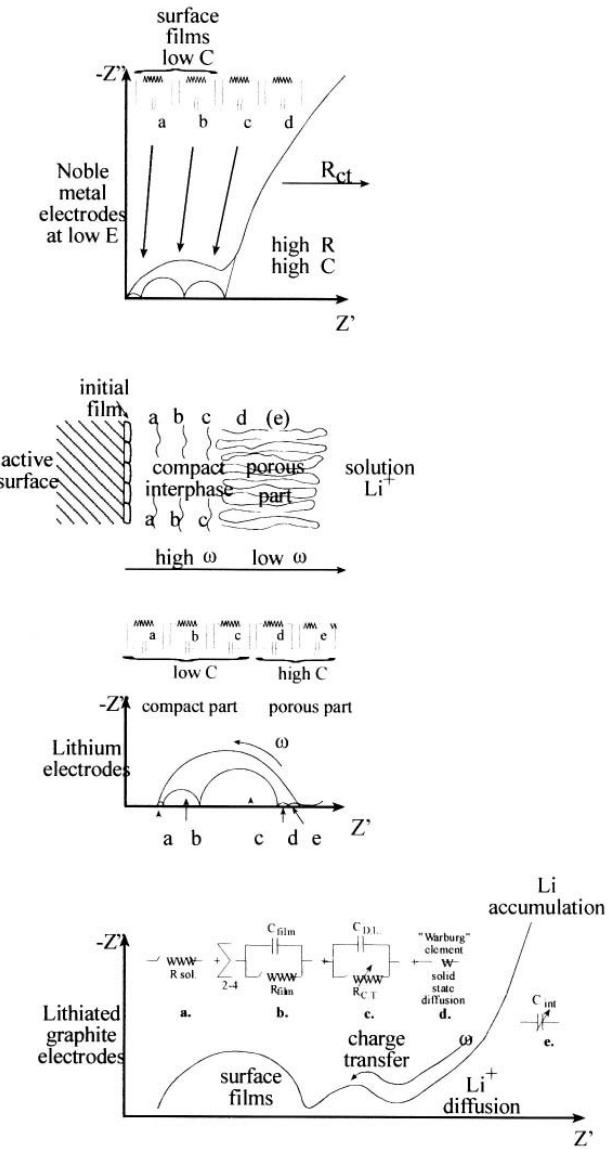
Many different equivalent circuits for batteries...

D. Aurbach, Journal of Power Sources, 89, 206–218 (2000).



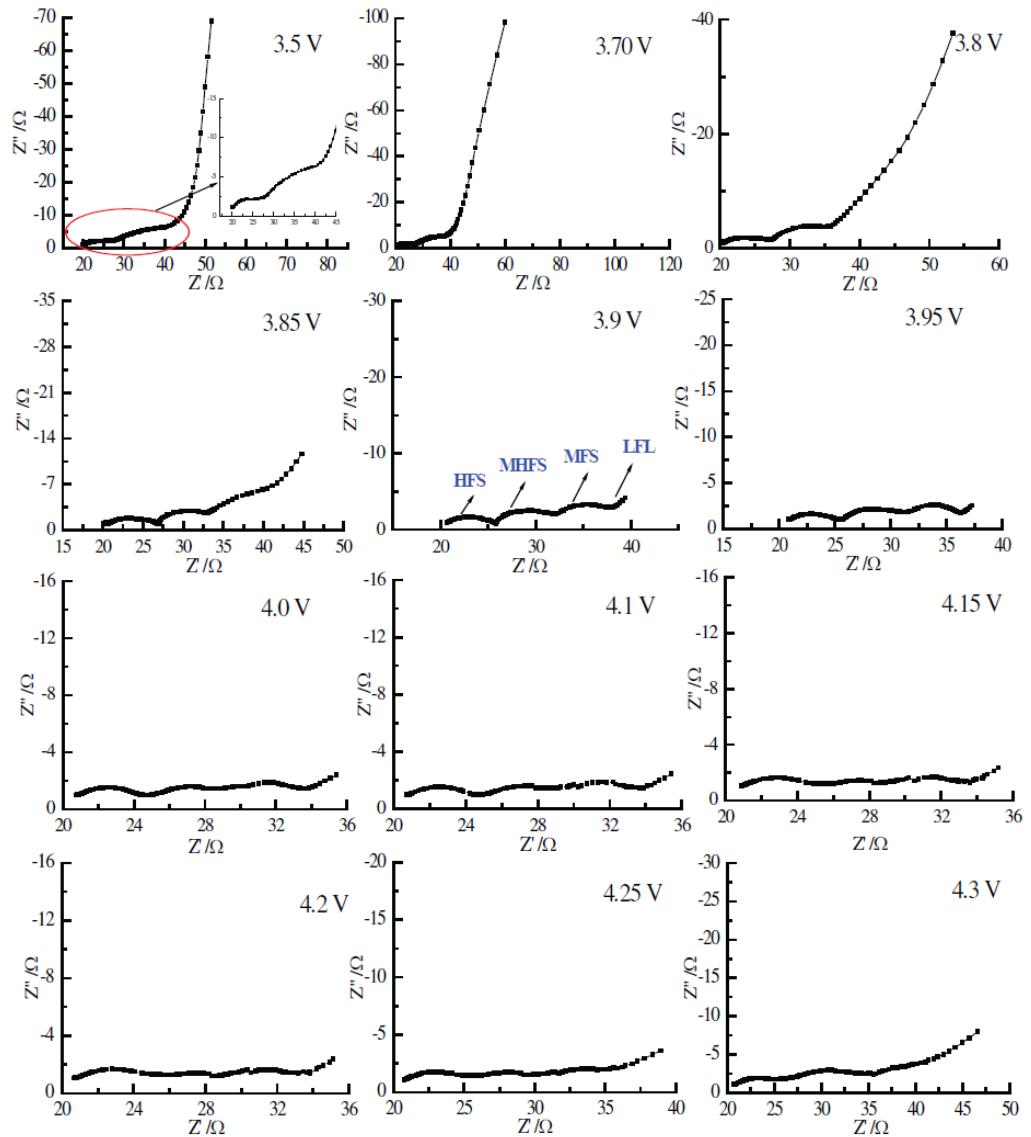
Schalkwijk & Scrosati, 2002 "Advances in Lithium Ion Batteries"

Q. C. Zhuang, X. Y. Qiu, S. D. Xu, Y. H. Qiang, and S. G. Sun, (2010)
http://www.intechopen.com/source/pdfs/29293/InTech-Diagnosis_of_electrochemical_impedance_spectroscopy_in_lithium_ion_batteries.pdf.



Many different impedance spectra...

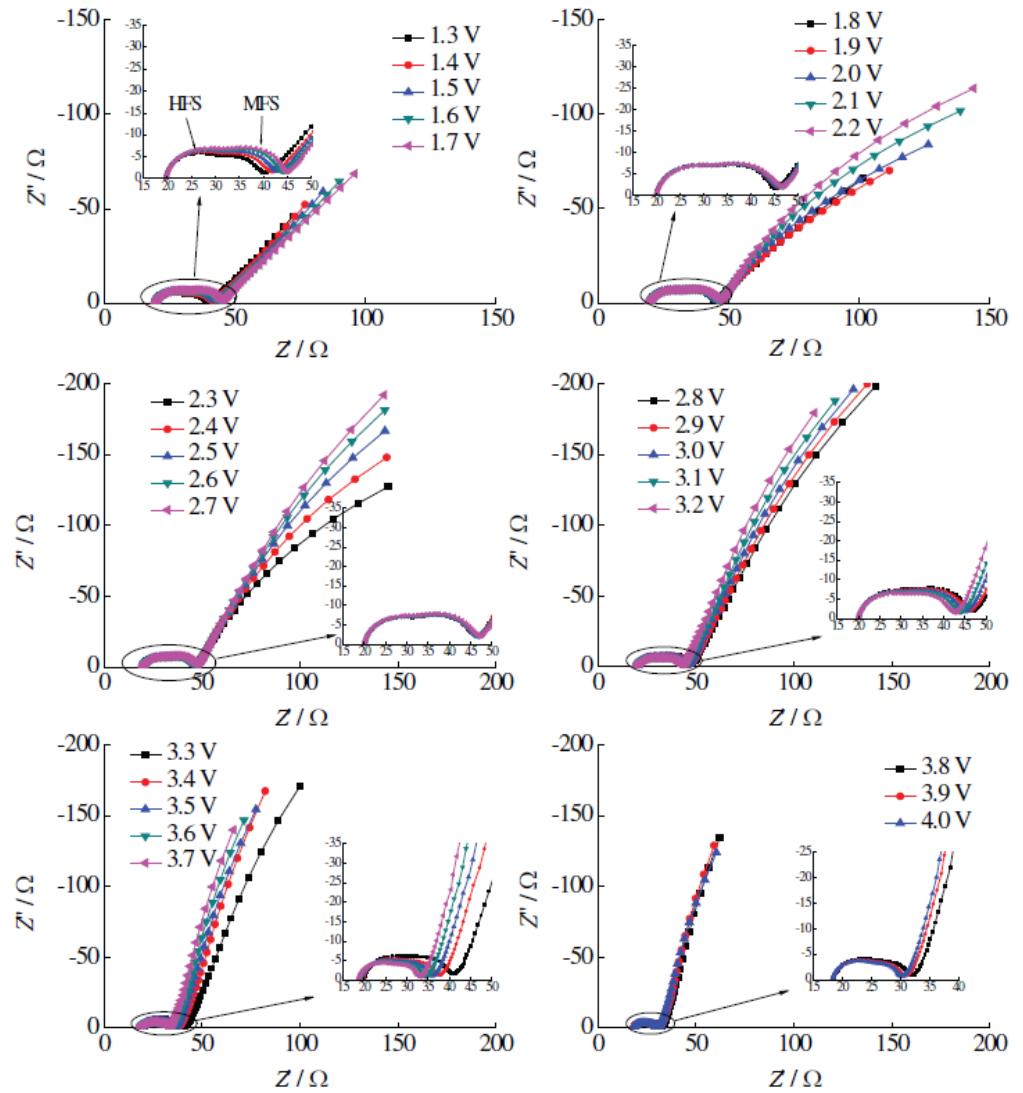
Nyquist plots of the spinel LiMn_2O_4 electrode at various potentials from 3.5 to 4.3 V during the first delithiation.



Q. C. Zhuang, X. Y. Qiu, S. D. Xu, Y. H. Qiang, and S. G. Sun, (2010,) InTech,
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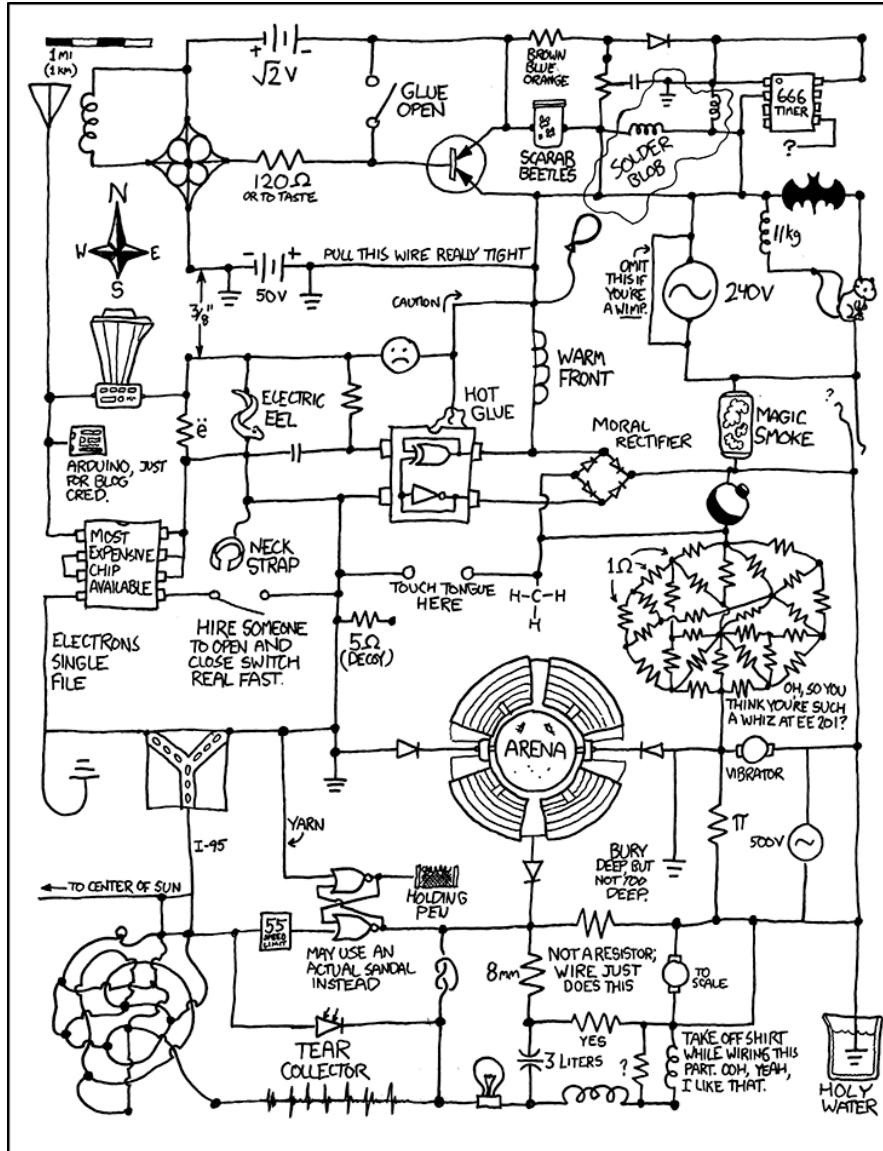
More spectra (now a conversion battery...)

Nyquist plots of a NiF_2/C composite electrode during the first charge process.



Q. C. Zhuang, X. Y. Qiu, S. D. Xu, Y. H. Qiang, and S. G. Sun, (2010,) InTech,
"Diagnosis_of_electrochemical_impedance_spectroscopy_in_lithium_ion_batteries".

A circuit that can account for it all... (?)



<http://xkcd.com/730/>

How to begin...?

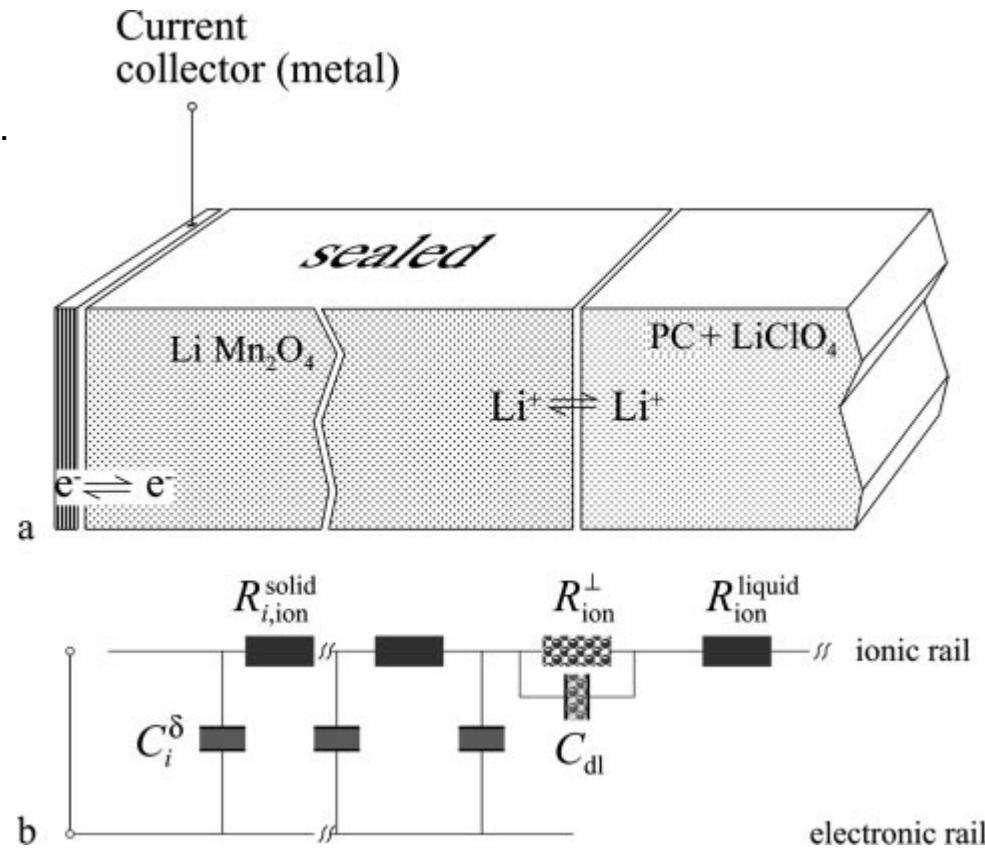
Interfacial and "chemical" (e.g. intercalation) capacitances!

Usually very different in magnitude..

Interfacial capacitance scales with the relevant surface area

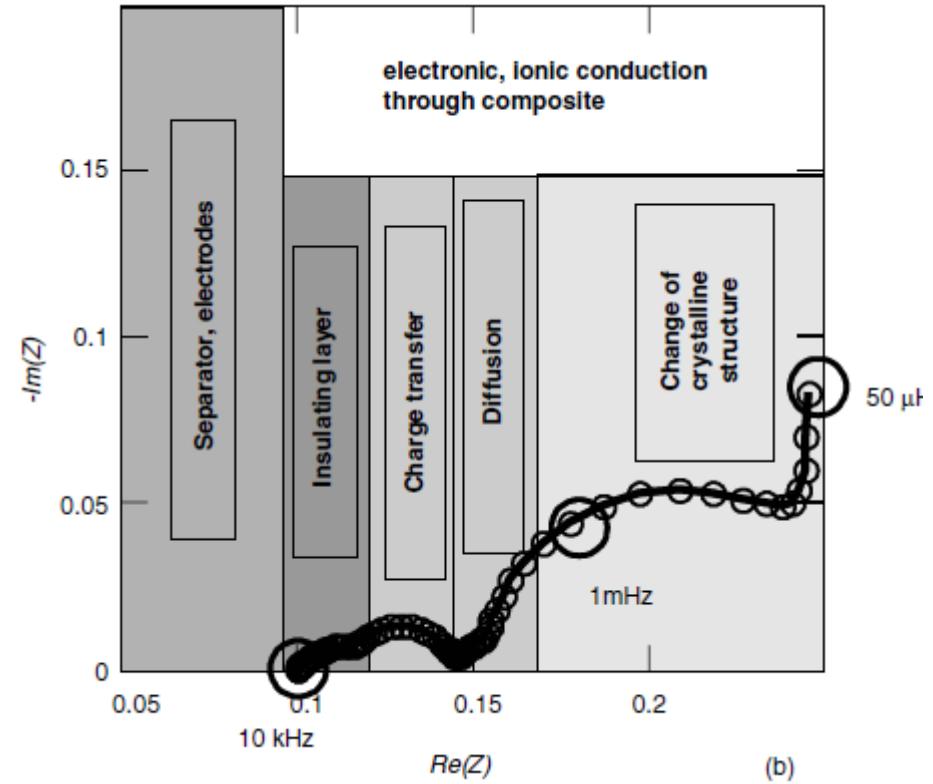
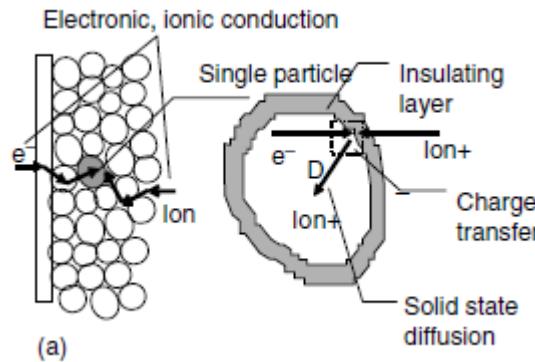
Chemical capacitance scales with volume (thickness)

$$C_{\text{int}} = \frac{Le^2 N}{k_B T} \left[g + \frac{1}{x(1-x)} \right]^{-1}$$



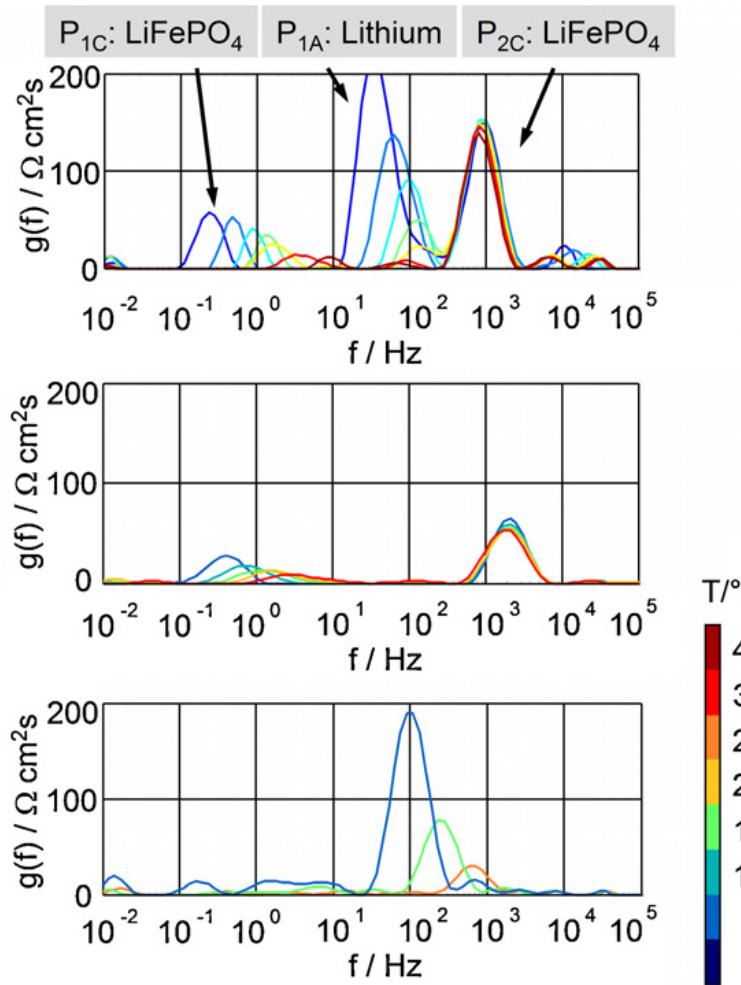
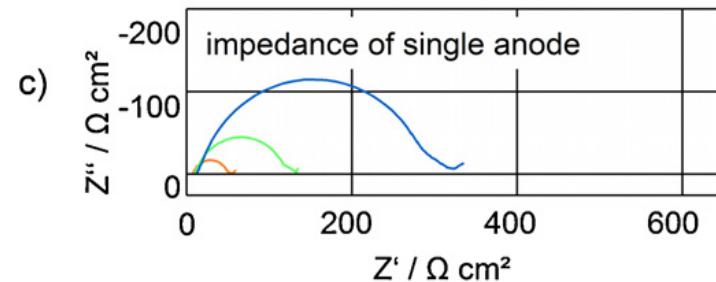
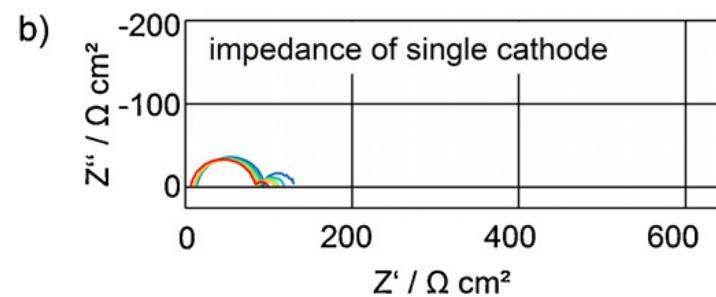
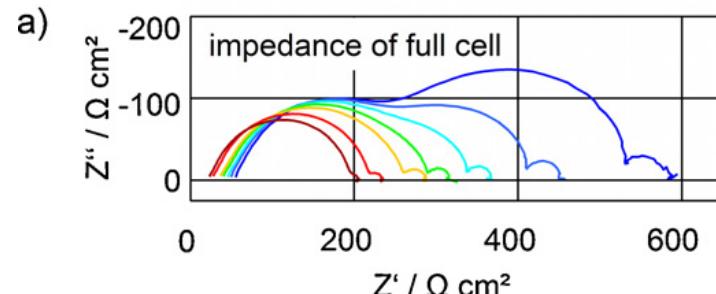
J. Jamnik and J. Maier, Phys. Chem. Chem. Phys., 3, 1668–1678 (2001).

Processes and Timescales in Batteries



Experimental Elucidation of Individual Processes

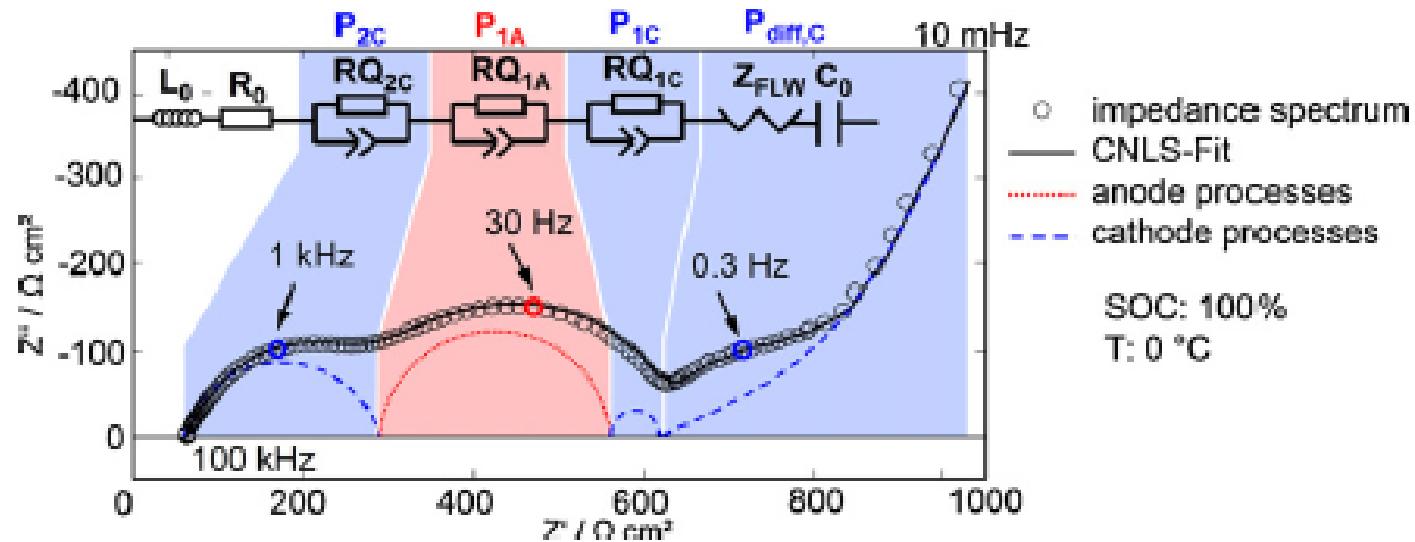
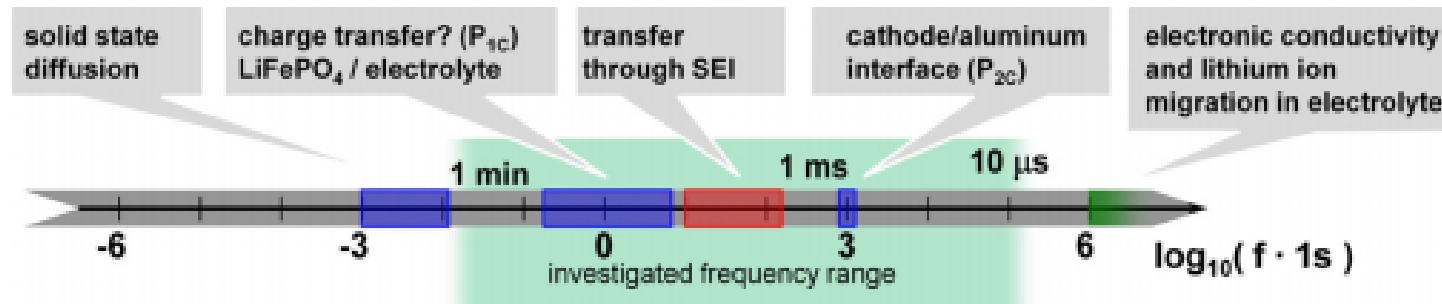
Symmetrical Cells vs Full Cells



Source: J. P. Schmidt et al., Journal of Power Sources, 196, 5342–5348 (2011).

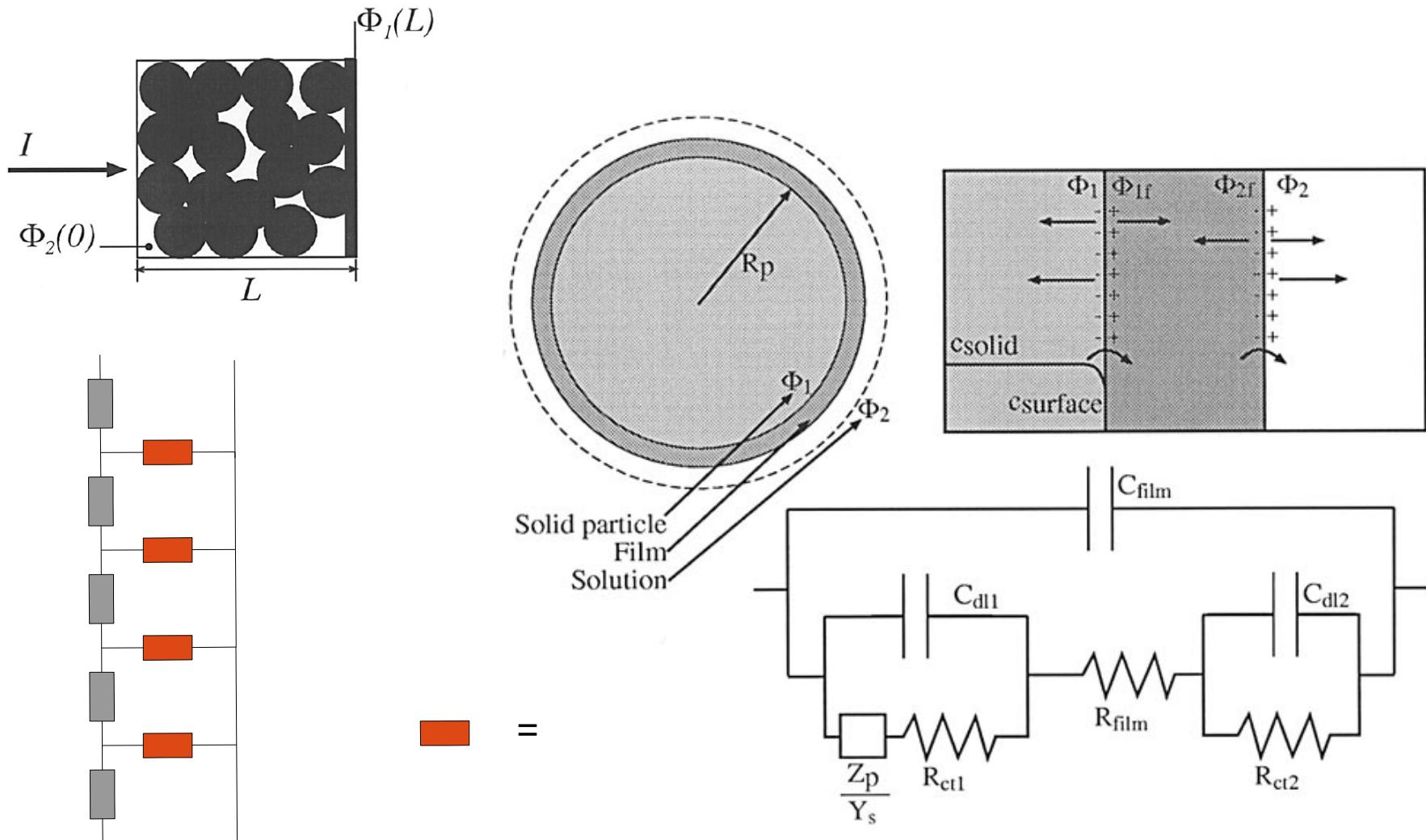
Experimental Elucidation of Individual Processes

Resulting Equivalent Circuit



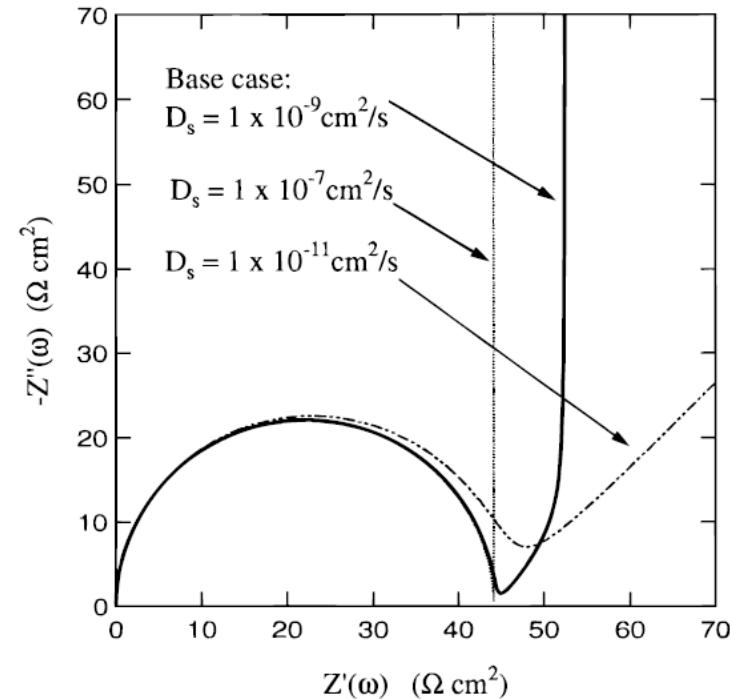
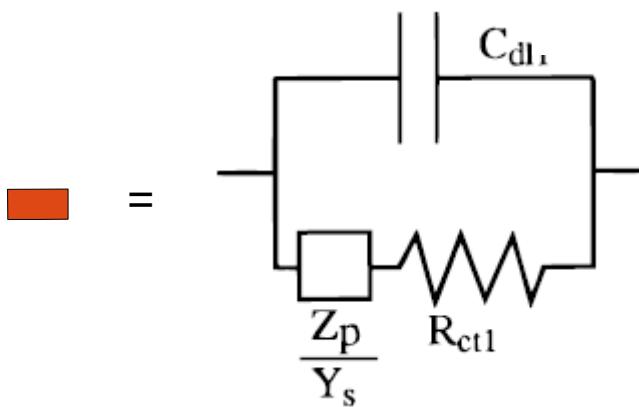
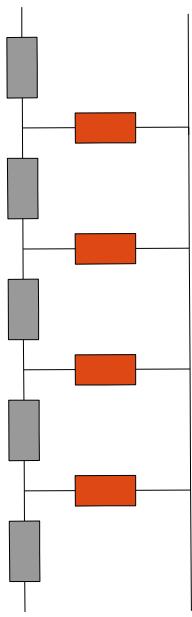
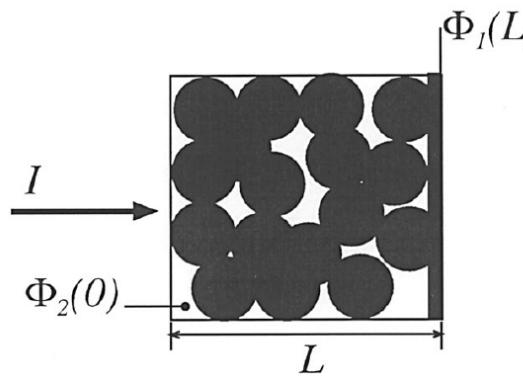
Source: J. P. Schmidt et al., Journal of Power Sources, 196, 5342-5348 (2011).

Impedance of Porous Electrode with Intercalation Particles (Meyers & Newman)



J. P. Meyers, M. Doyle, R. M. Darling, and J. Newman, J. Electrochem. Soc., 147, 2930-2940 (2000).

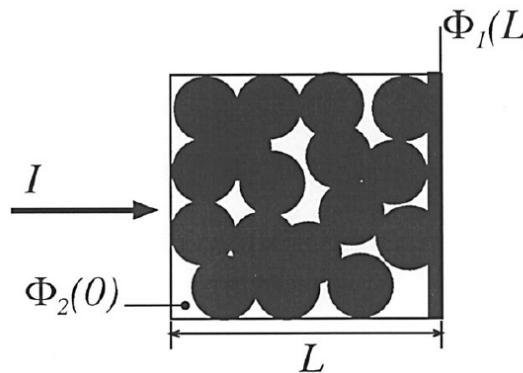
Impedance of Porous Electrode with Intercalation Particles (Meyers & Newman)



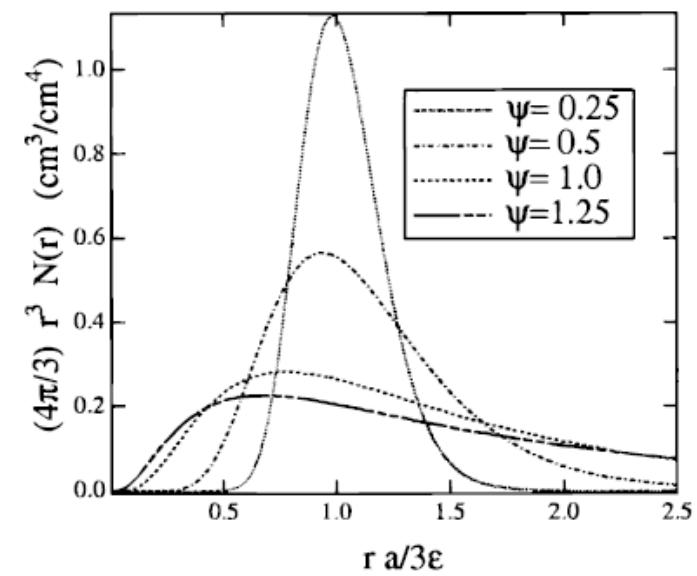
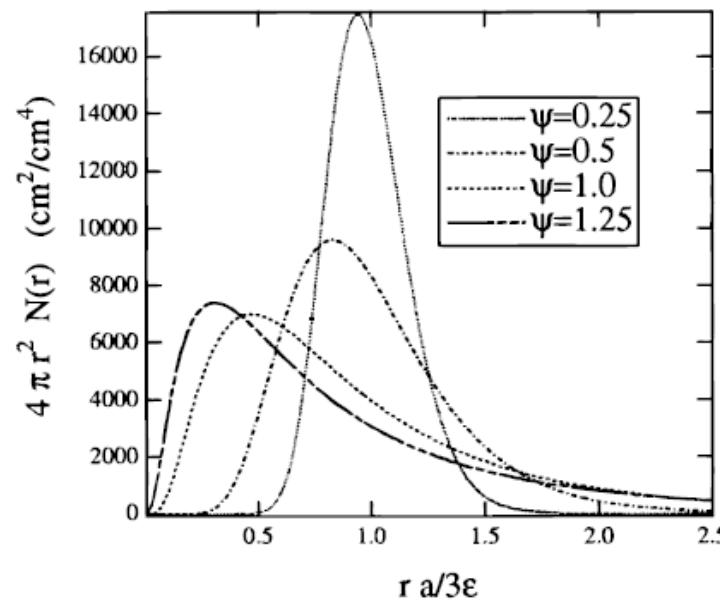
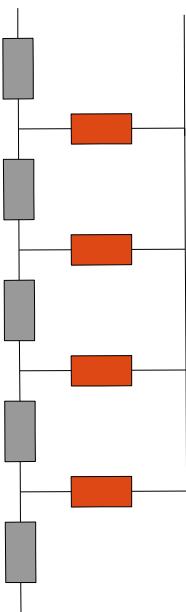
For single particle

J. P. Meyers, M. Doyle, R. M. Darling, and J. Newman, J. Electrochem. Soc., 147, 2930-2940 (2000).

Impedance of Porous Electrode with Intercalation Particles (Meyers & Newman)

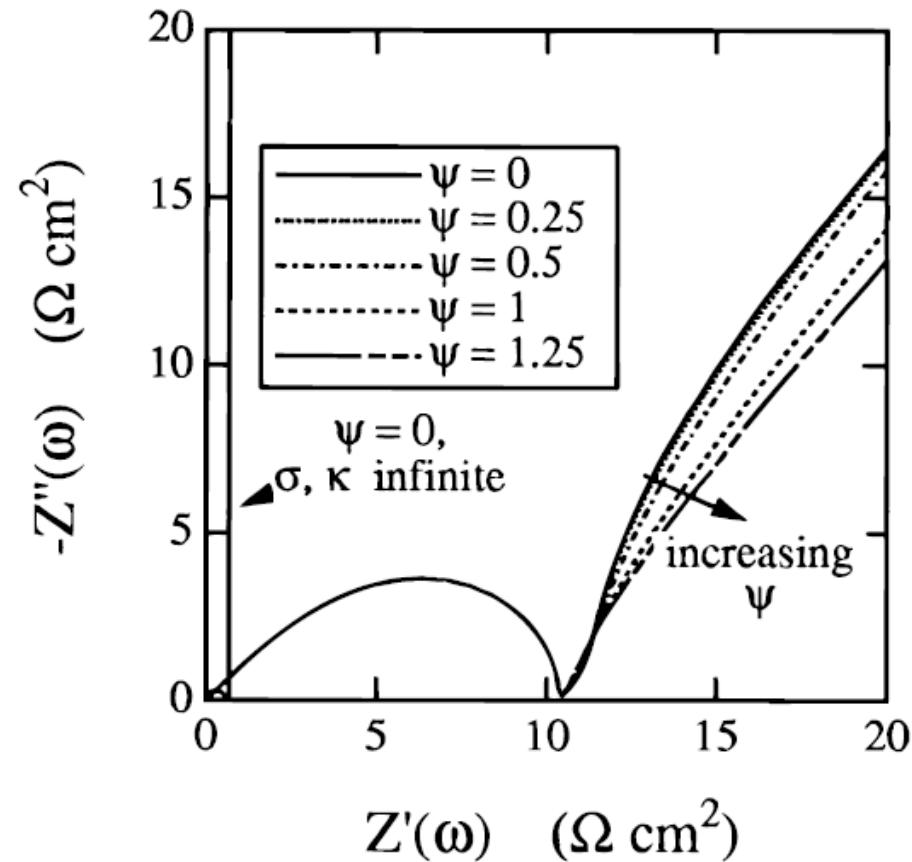
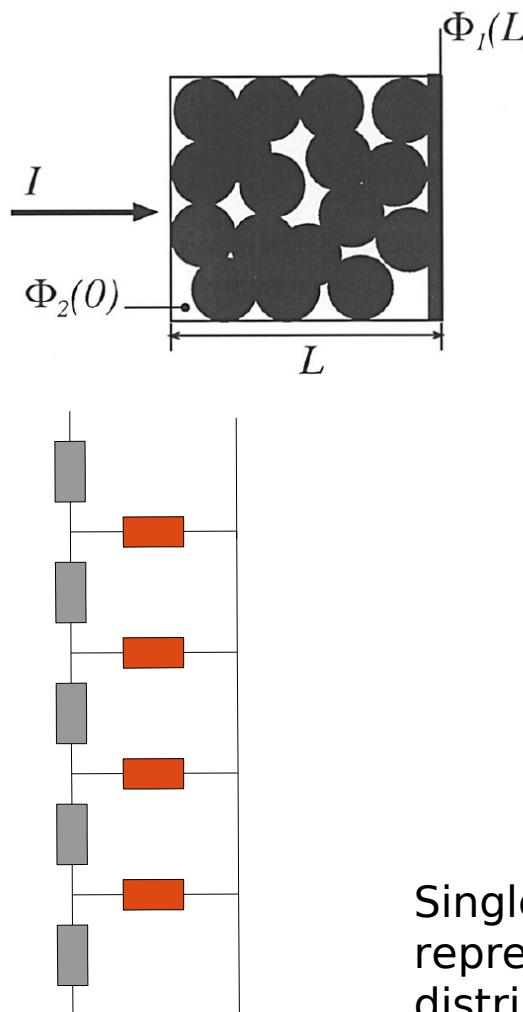


Particle size distributions in electrode. Plots showing Contributions to the total specific particle surface area and particle volume.



J. P. Meyers, M. Doyle, R. M. Darling, and J. Newman, J. Electrochem. Soc., 147, 2930-2940 (2000).

Impedance of Porous Electrode with Intercalation Particles (Meyers & Newman)



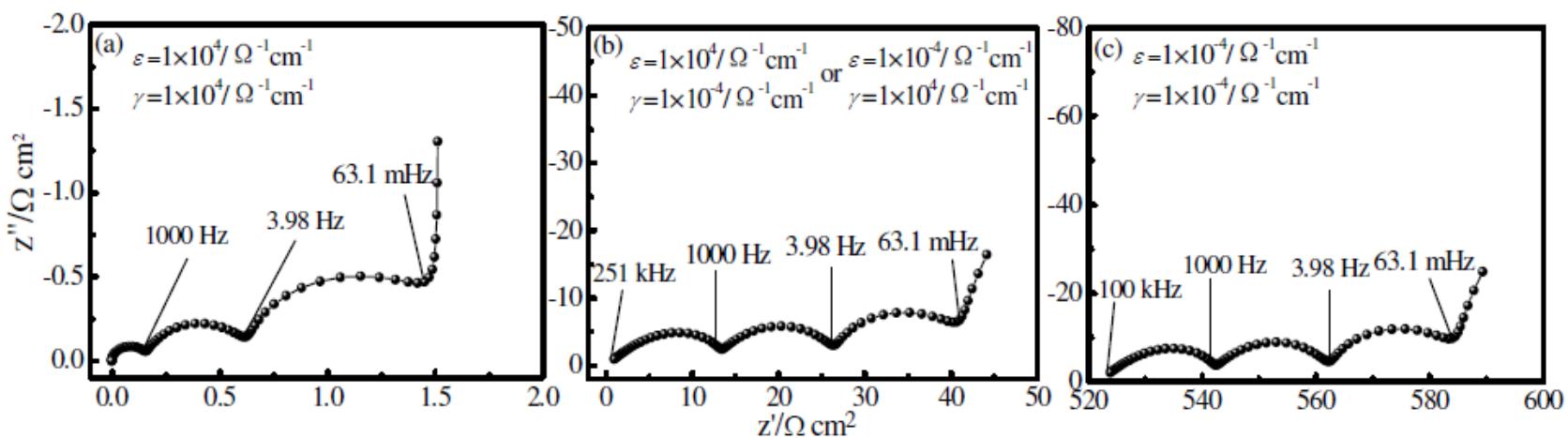
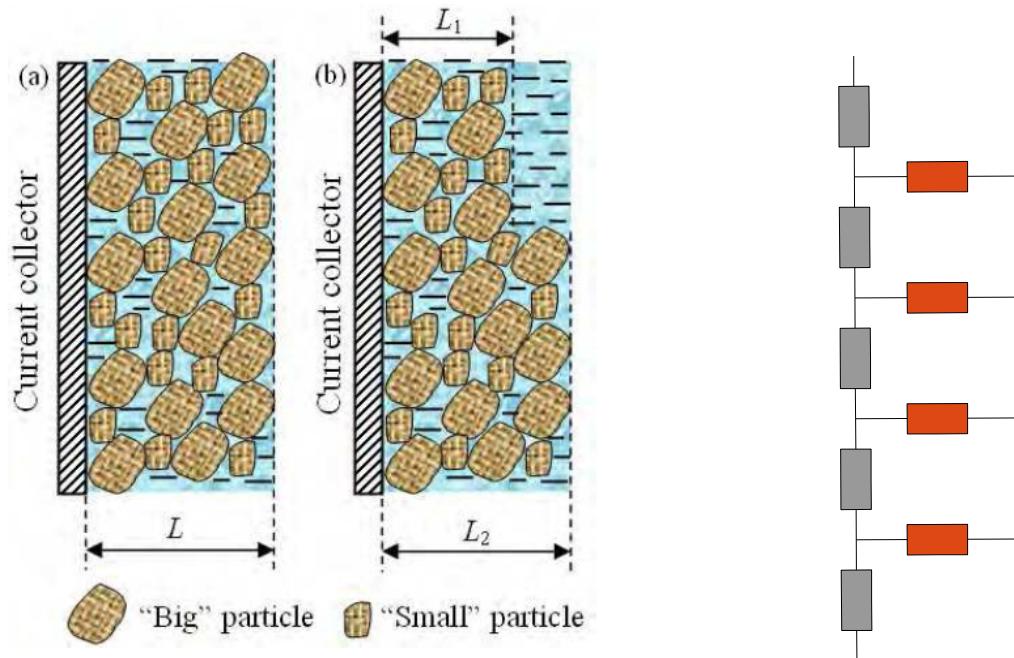
Single particle model incorporated in transmission rail to represent porous electrode. Calculations for various particle size distributions.

J. P. Meyers, M. Doyle, R. M. Darling, and J. Newman, J. Electrochem. Soc., 147, 2930-2940 (2000).

Impedance of Non-homogeneous Porous Electrode with Intercalation Particles (Xu et al)

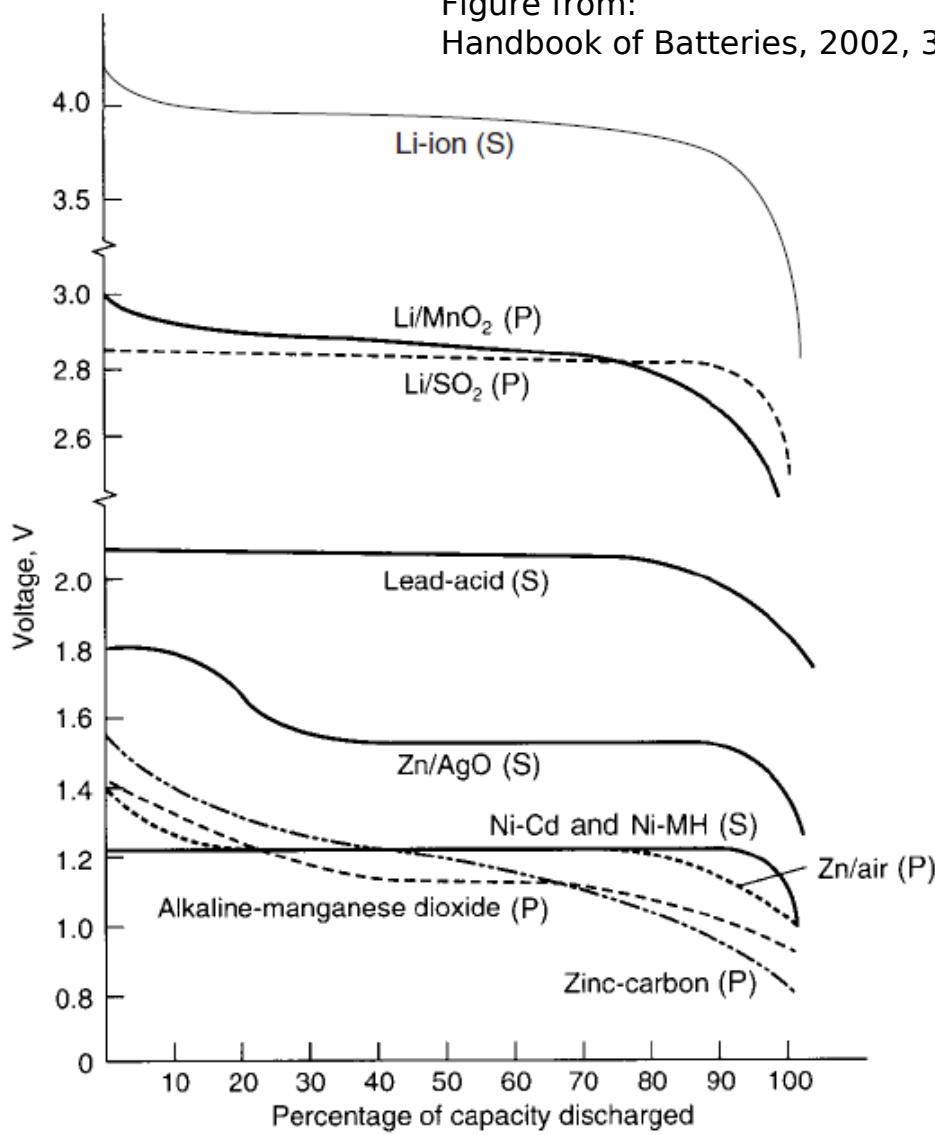
S.-D. Xu et al.,

J. Phys. Chem. C, 115, 9210–9219 (2011).



Charge/Discharge Batteries

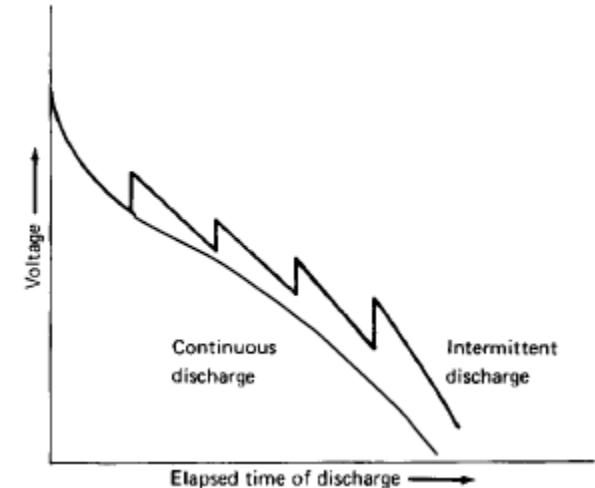
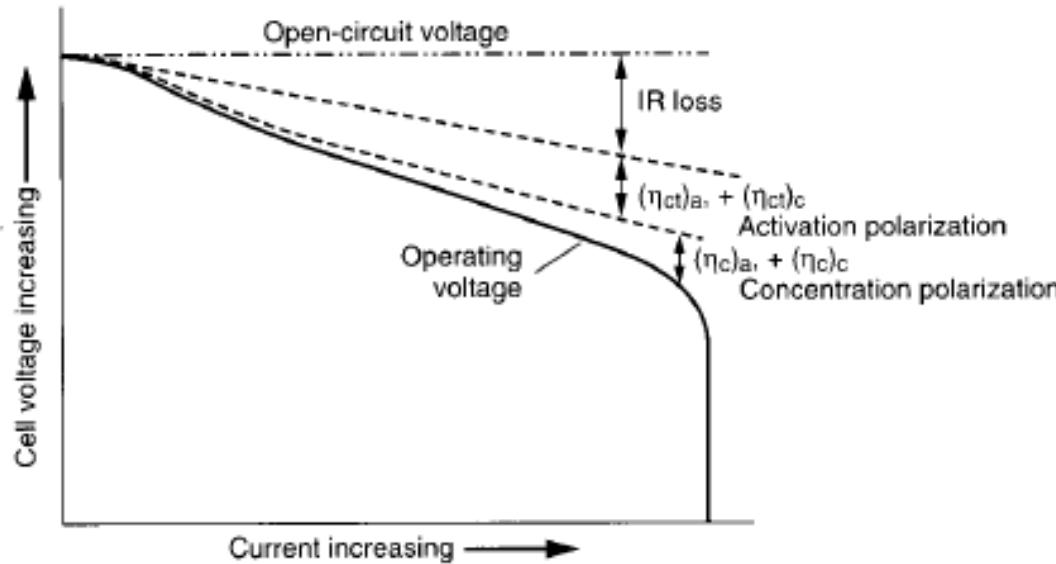
Figure from:
Handbook of Batteries, 2002, 3rd ed., Linden & Reddy



Measuring Impedance of a Battery

I-V relation for a battery

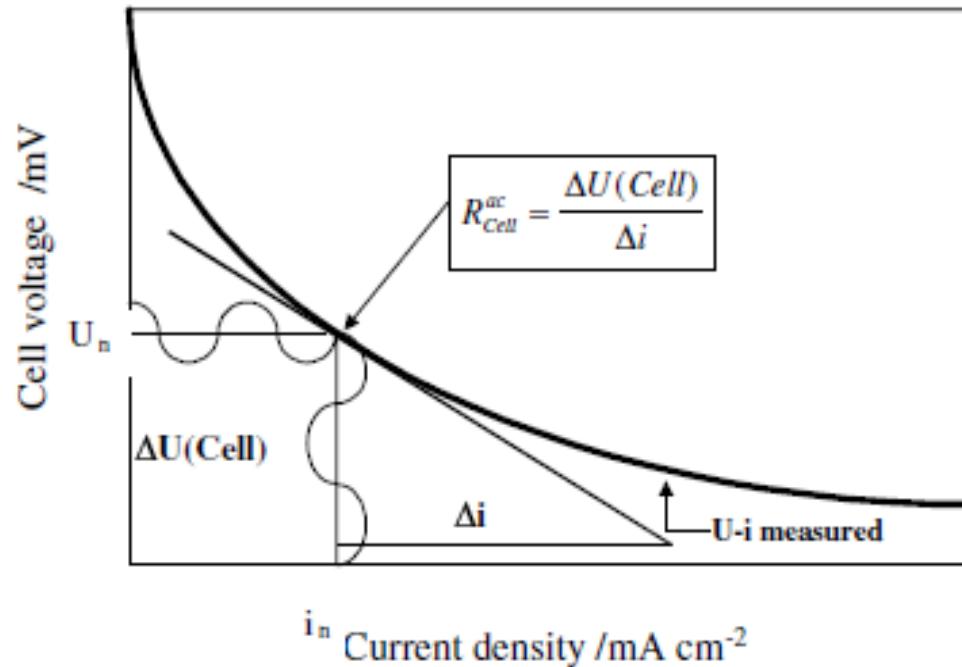
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$$ASR_{diff} = \frac{dU}{dj}$$

Both resistance and capacitance measured using impedance are differential quantities. Integration of the differential capacities should yield the (integral) total battery capacitance...

Measuring Impedance of a Battery



$$ASR_{diff} = \frac{dU}{dj}$$

Both resistance and capacitance measured using impedance are differential quantities. Integration of the differential capacities should yield the (integral) total battery capacitance...

Source: Impedance Spectroscopy, 2nd Edition, Eds. E. Barsoukov & J. Ross Macdonald, John Wiley & Sons, Hoboken, NJ (2005), p.500