Karakterisasi V-I (dc-ac) sel Baterai Li-Ion

Achmad Subhan, S.Si, MT

Metoda Uji Performa sel Baterai

- Cyclic Voltamettry (CV) :
  - Redox and working voltage, cell capacities, impurity materials (reversibility/irr).
- Electrochemical Impedance pectroscopy (EIS).
  - Charge transfer, internal resistance, materials behavior.
- Galvanostatic Charge-Discharge.
  - Plateu voltage (single/multiple), cell capacity, life cycle.

Electrochemical Cell

- Cathode
- Anode
- Electrolyte
- SEI (Solid Electrolyte Interface)

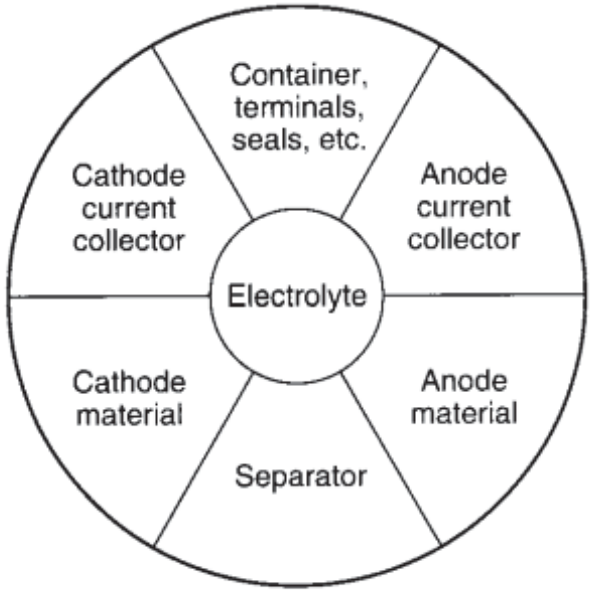


FIGURE 1.3 Components of a cell.

Full & ½ sel :

Profil V-I Baterai Lithium :

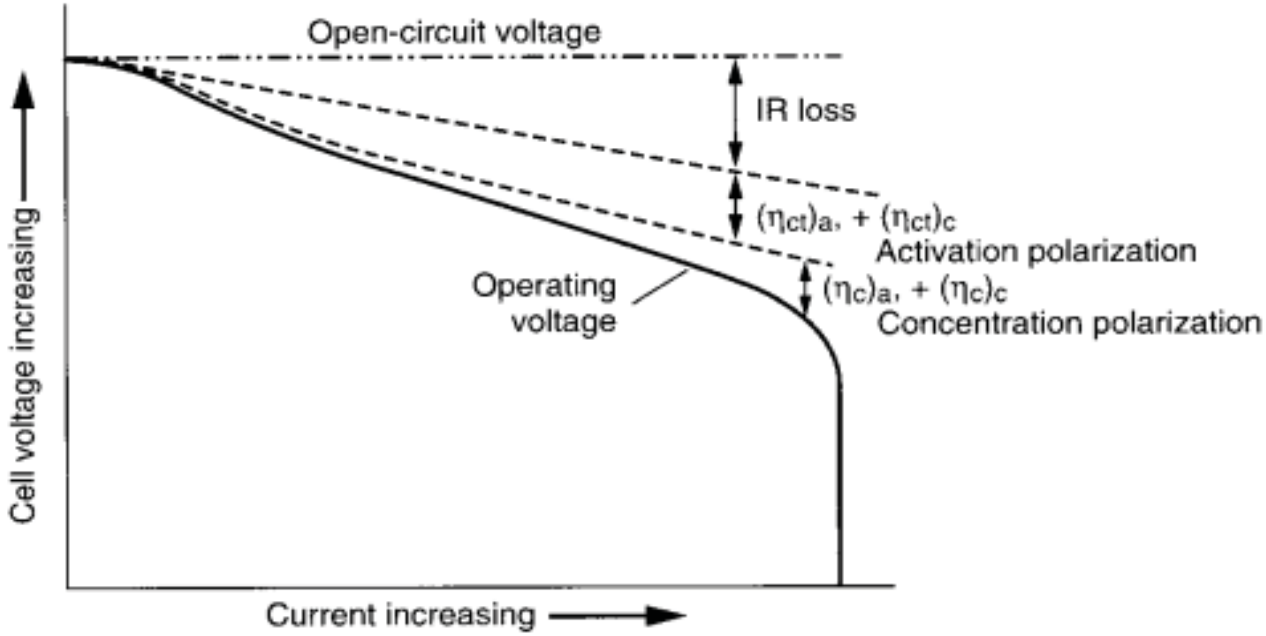


FIGURE 2.1 Cell polarization as a function of operating current.

$$E = E_0 - [(\eta_{ct})_a + (\eta_c)_a] - [(\eta_{ct})_c + (\eta_c)_c] - iR_i = iR \qquad (2.1)$$

where E_0 = electromotive force or open-circuit voltage of cell
$(\eta_{ct})_a$, $(\eta_{ct})_c$ = activation polarization or charge-transfer overvoltage at anode and cathode
$(\eta_c)_a$, $(\eta_c)_c$ = concentration polarization at anode and cathode
i = operating current of cell on load
R_i = internal resistance of cell

Sumber : David Linden, Handbook of Batteries,2.2

Electrodes cell configuration

WBCS3000 setup :

1. Cycler mode
2. Potentiostat mode

2-electrode :

- Working electrode , sense electrode
  - Black & white cable.
- Reference + counter electrode.
  - Green & red.

Metoda 1:CYCLIC VOLTAMMETRY

Voltammetry: metoda elektrokimia aktif , dilakukan dgn mengontrol parameter reaksi elektrokimia dan mengukur arus listrik sebagai fungsi dari perubhan tegangan reaksi kimia. Bentuk signal adalah dc voltage.

.

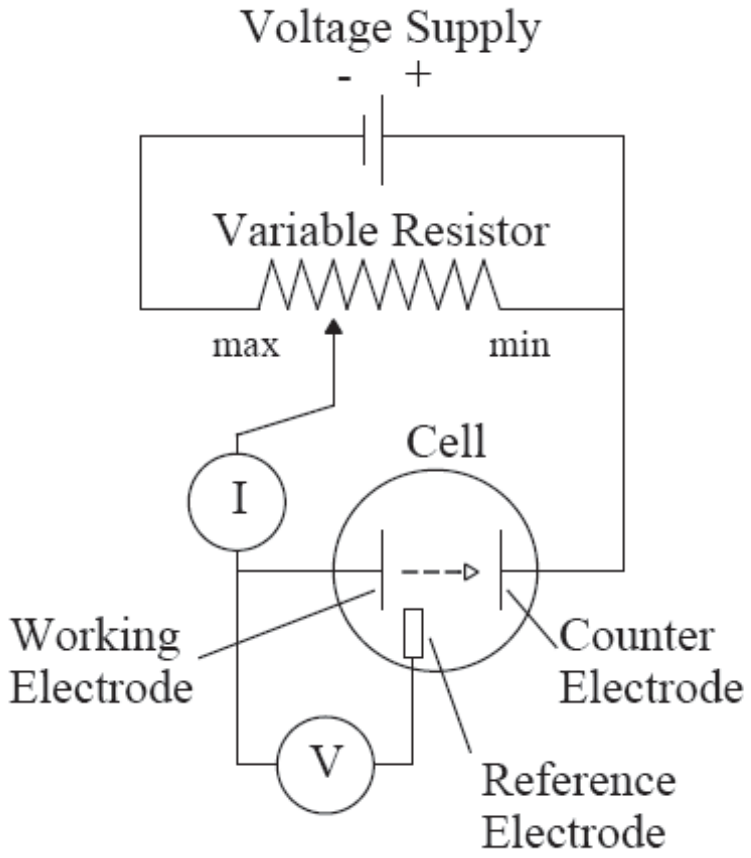
Instrumentation – Three electrodes in solution containing analyte

Working electrode: electrode whose potential is varied with time

Reference electrode: potential remains constant (Ag/AgCl electrode or calomel)

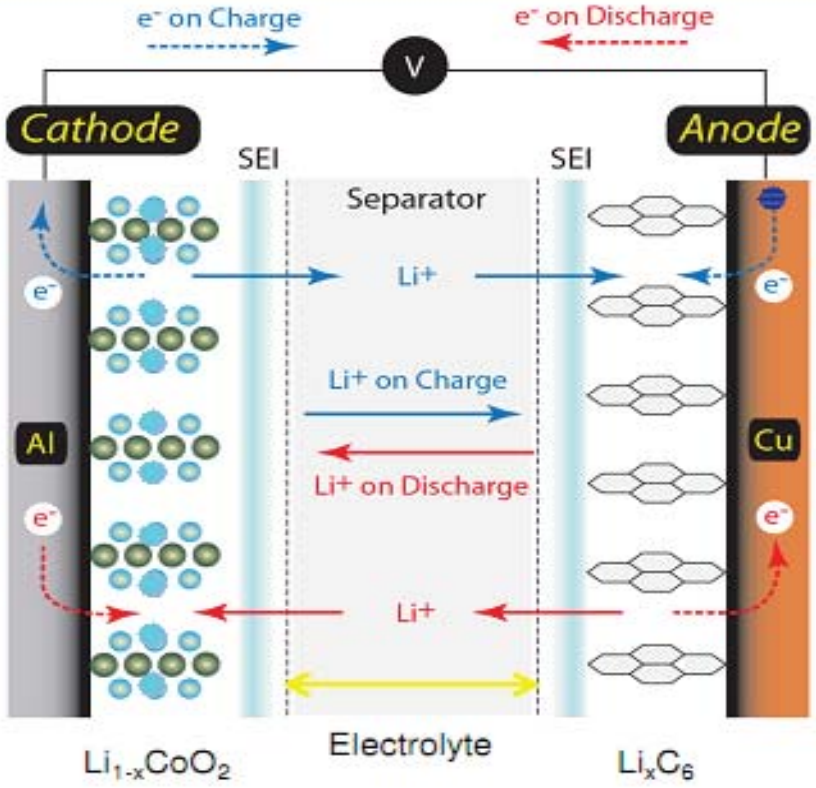
Counter electrode: Hg or Pt that completes circuit, conducts e^- from signal source through solution to the working electrode

Electrolyte: excess of electrolyte (alkali metal) to conduct current



Li Ion Battery

Mechanism and Components of Li-ion Battery



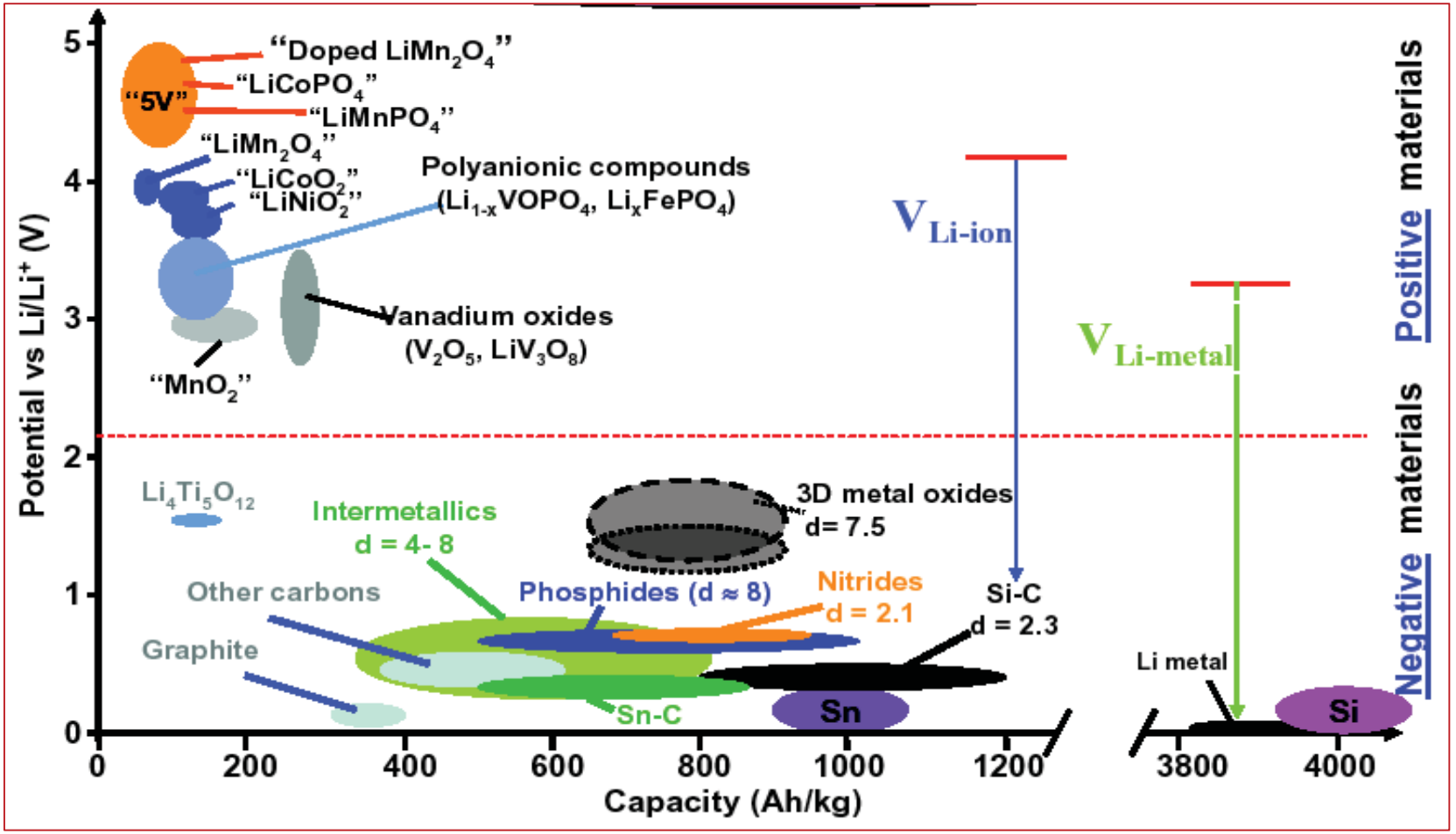
Solid Electrolyte Interface (SEI) is a surface film that generally forms between an electrode and electrolyte. It is an internal resistor that limits power output and generates heat build-up in a standard Li-ion battery.

- Both anode and cathode materials are intercalation compounds
- Anode reaction: $xLi^+ + 6C \rightleftharpoons Li_xC_6$
- Cathode reaction: $LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+$
- Overall reaction: $LiCoO_2 + 6C \rightleftharpoons Li_xC_6 + Li_{1-x}CoO_2$

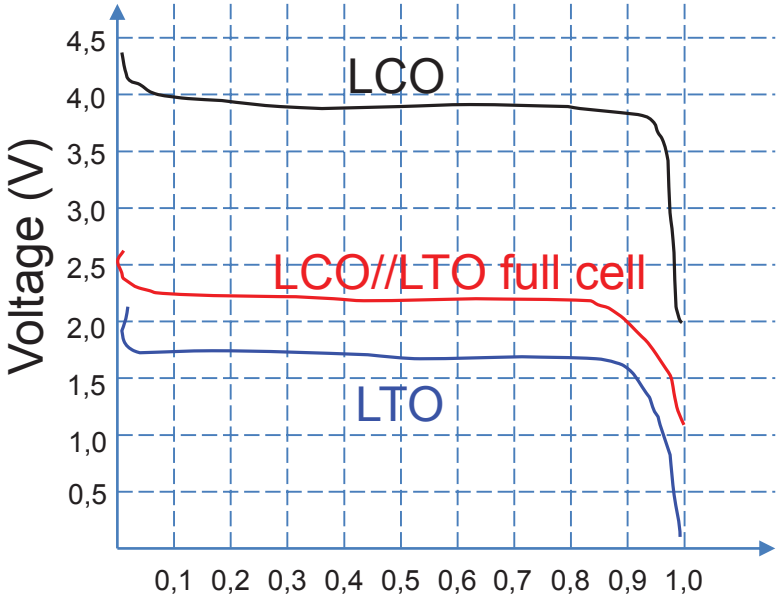
Components	Common Materials
Cathode	Active material: $LiCoO_2$, $LiMnO_4$, $LiFePO_4$ Conducting additives: Acetylene black Binder: PVDF, PTFE Current collector: Al foil
Anode	Active material: graphite, MCMB Conducting additives: Acetylene black Binder: PVDF, PTFE Current collector: Cu foil
Separator	porous polyolefin 
Electrolyte	Solvent: EC, PC, DMC, DEC, DME Solute: $LiClO_4$, $LiPF_6$, $LiBF_4$

Source: Brian J. Landi, Potential Environmental Benefits of Nanotechnology: Fostering Safe Innovation-Led Growth, July 17th, 2009

Working voltage design



Working voltage of full-cell LIB



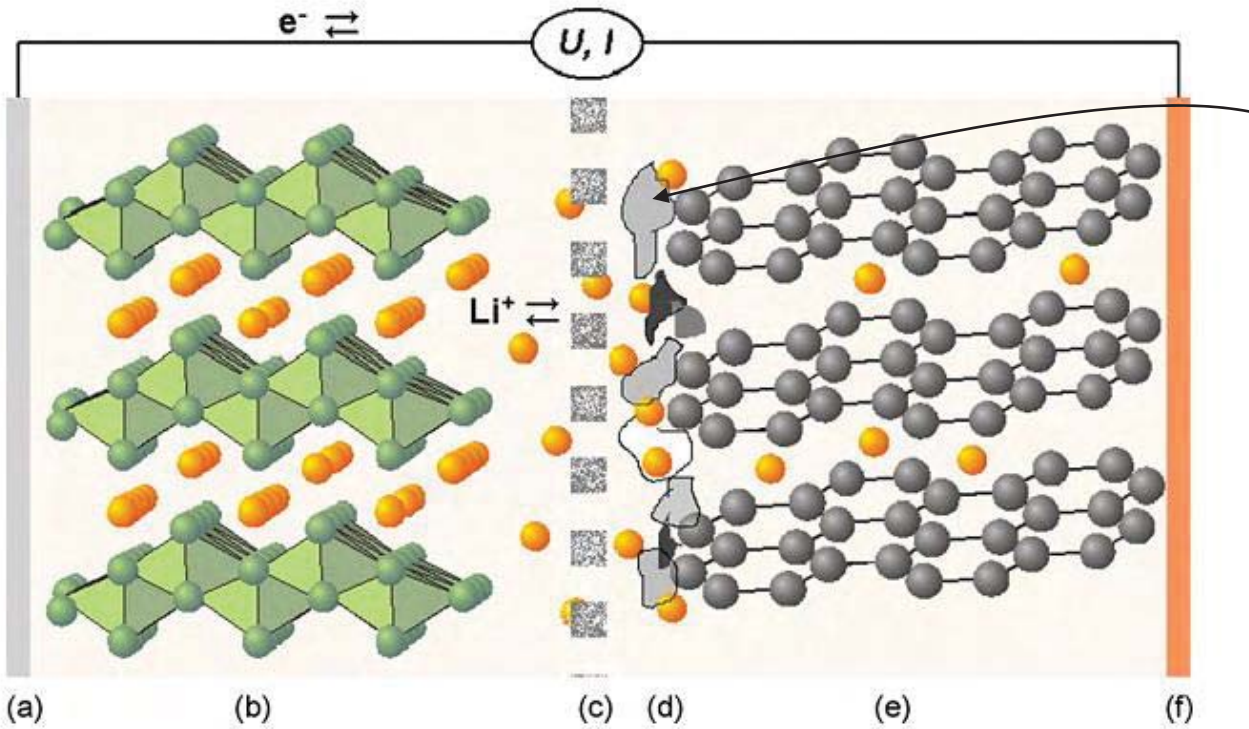
Normalized capacity

LTO is good for specialty battery, such as for stationary storage or smart grid battery.

P85D = 85kWh → 7104 cells (NCA//Graphite)

If we use LCO//LTO battery, we need more than 14000 cells to power this car.

SEI



(a) aluminum current collector; (b) oxide active material; (c) porous separator soaked with liquid electrolyte (d) inhomogeneous SEI layer; (e) graphite active material and (f) copper current collector.

near lithium potential

No end of charge *)

Antisipasi: **)

- Memperluas kontak permukaan → teknologi nano
- Meningkatkan kapasitas jumlah Li-ion yg berinterkalasi → pemilihan/ sintesa material yg tepat.
- Menaikkan konduktifitas komponen → doping, coating carbon.
- Material redox higher equilibrium potential.

*) P Verma et al, A review of the features and analyses of the solid electrolyte interphase in Li-ion Batteries, Electrochimica Acta, 55 (2010)

**) Ting-Feng Yi et al, Recent development and application of LTO as anode material of lithium ion battery, Physics and Chemistry of Solids, 71 (2010)

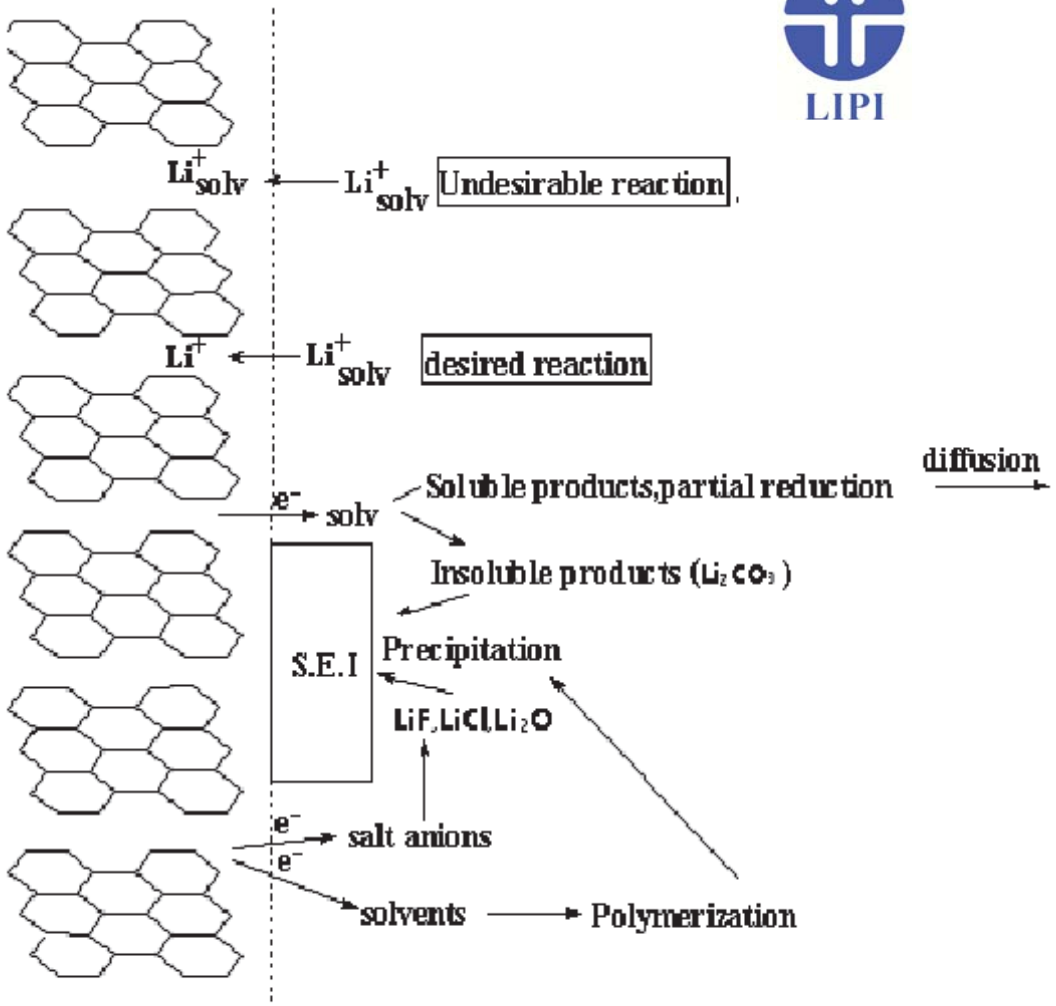


Figure 2 Schematic presentation of the SEI formation on carbon. Reproduced from [7] by permission of the Materials Research Society.

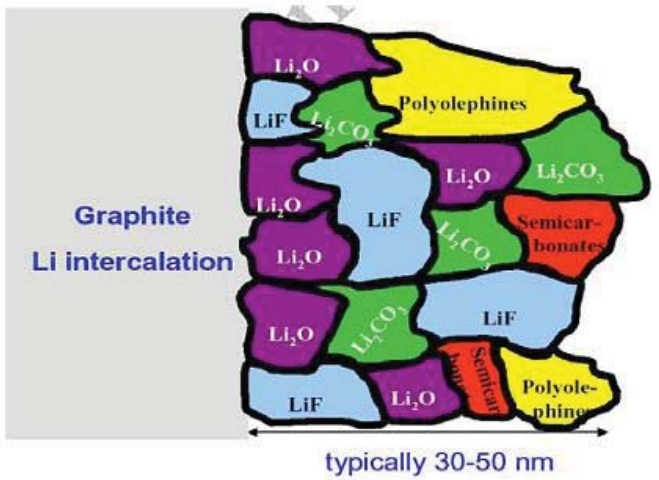
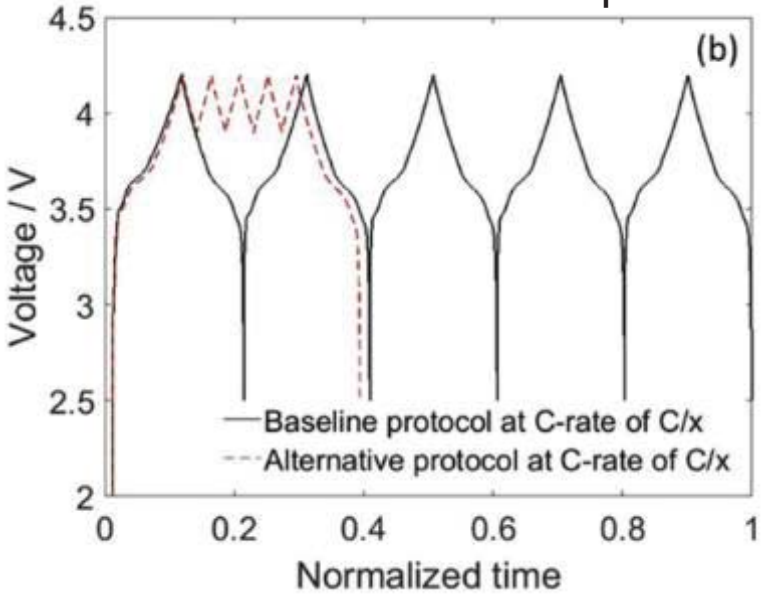


Figure 7. A proposed model of the electrode near a complex SEI. Even the SEI has intra-component interfaces.

Formation step

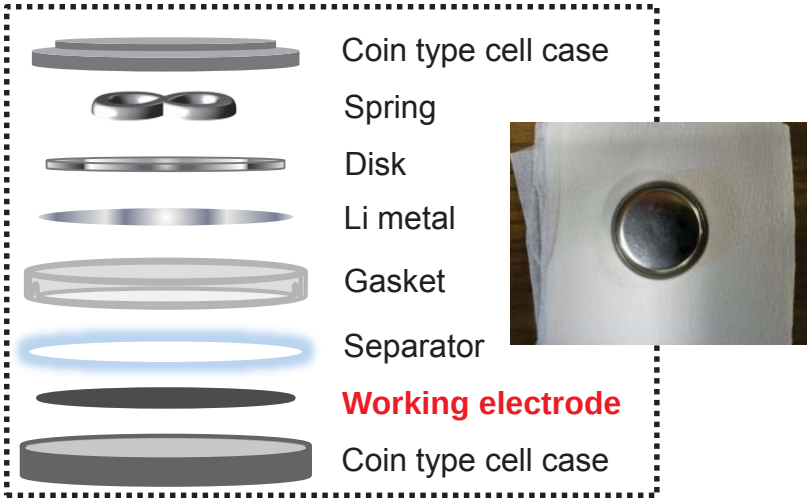


*) Lithium handbook SEI p-15; libob report of xxx workshop.pdf, p-32.

Instrumentation

- Hioki 3522-50 = autolab
- YOKOGAWA 7651 Programmable DC source
- DMM Scanner, Fluke Multimeter.
- WBCS 3000 8 channel.
- Pico ADC20 data logger.
- UPS

- Anode: graphite, Si, $Li_4Ti_5O_{12}$
- Cathode: $LiCoO_2$, $LiFePO_4$, $LiNi_xMn_yCo_zO_2$, $LiNi_xCo_yAl_zO_2$
- Electrolyte : $LiPF_6$
- Ethylene carbonate (EC)
- Dimethyl carbonate (DMC)
- Ethyl methyl carbonate (EMC)



B.) Teori voltametriTheory of Voltammetry

1.) Excitation Source: tegangan diset pada instrumen (working electrode)

- concentration of Reduced and Oxidized Species at electrode based on Nernst Equation:

$aA + bB \leftrightarrows cC + dD$

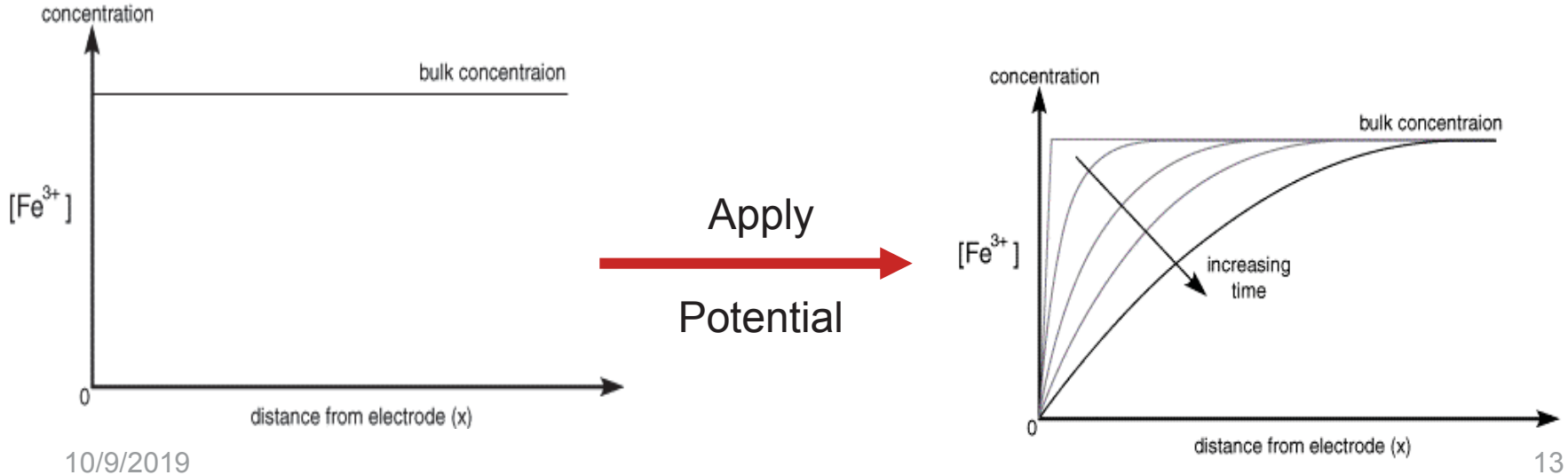
$$\Delta G^0 = -nFE^0$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{reactants}]}$$

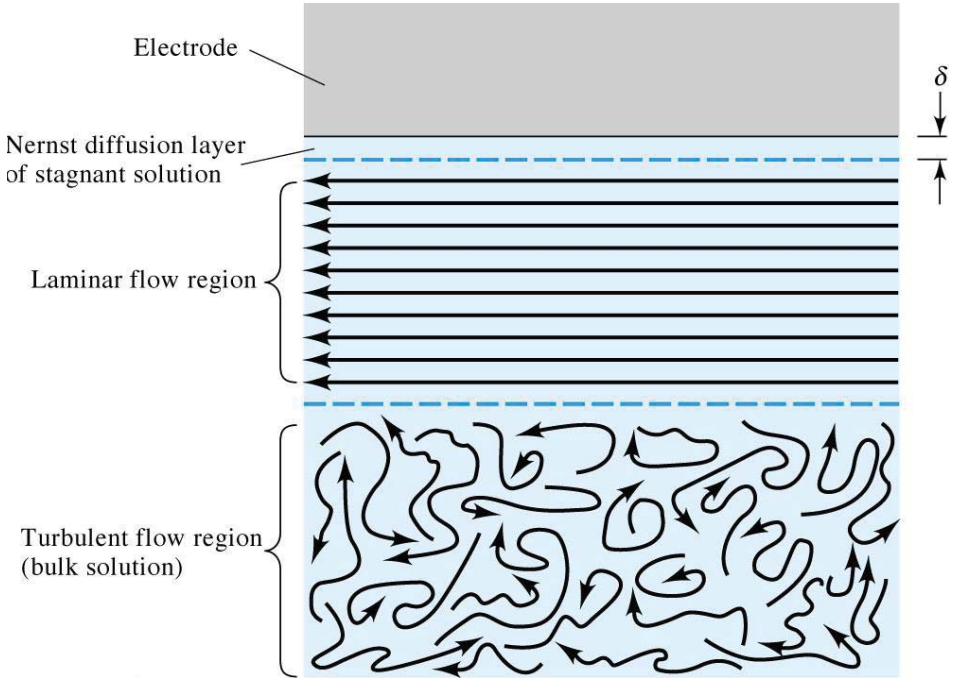
- reaction at the surface of the electrode

$$E_{electrode} = E^0 - \frac{0.0592}{n} \log \frac{(a_R)}{(a_o)}$$

$$Fe^{3+}(s) + e^-(m) \xrightarrow{k_{red}} Fe^{2+}(s)$$



Current is just measure of rate at which species can be brought to electrode surface



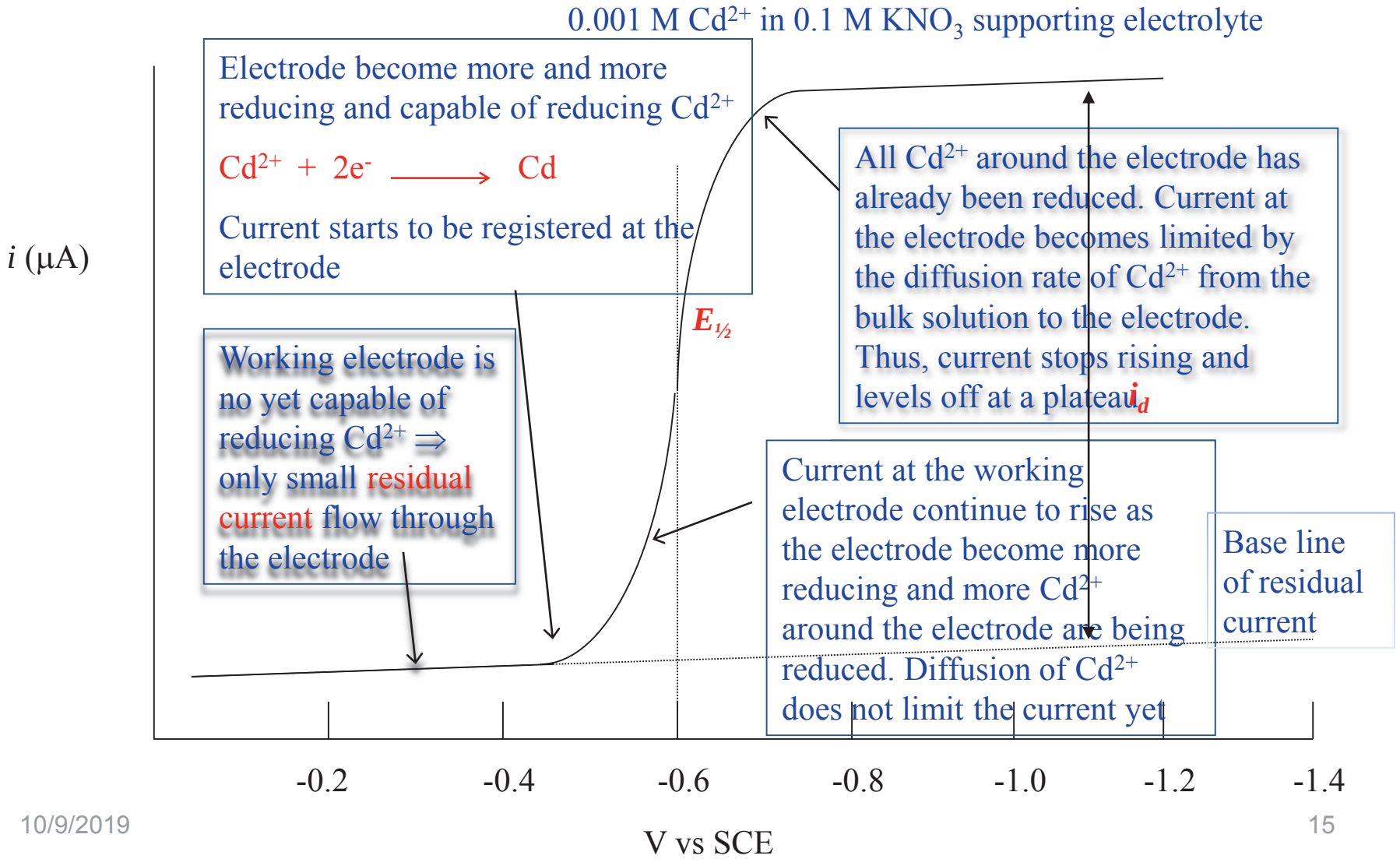
Three transport mechanisms:

(i) *migration* – movement of ions through solution by electrostatic attraction to charged electrode

(ii) *convection* – mechanical motion of the solution as a result of stirring or flow

(iii) *diffusion* – motion of a species caused by a concentration gradient

Potential applied on the working electrode is usually swept over (i.e. scan) a pre-defined range of applied potential

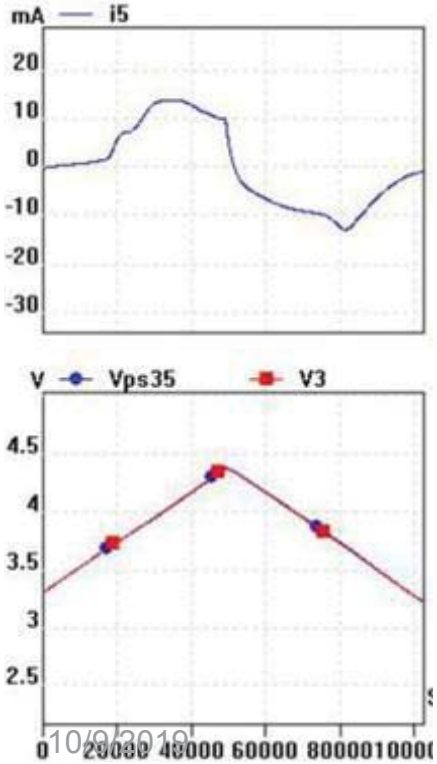


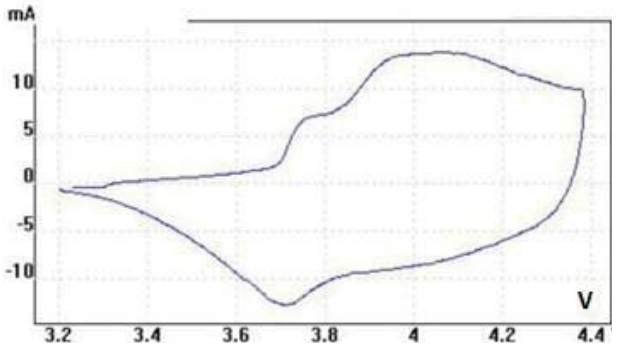
e) Cyclic Voltammetry (reversible redox)

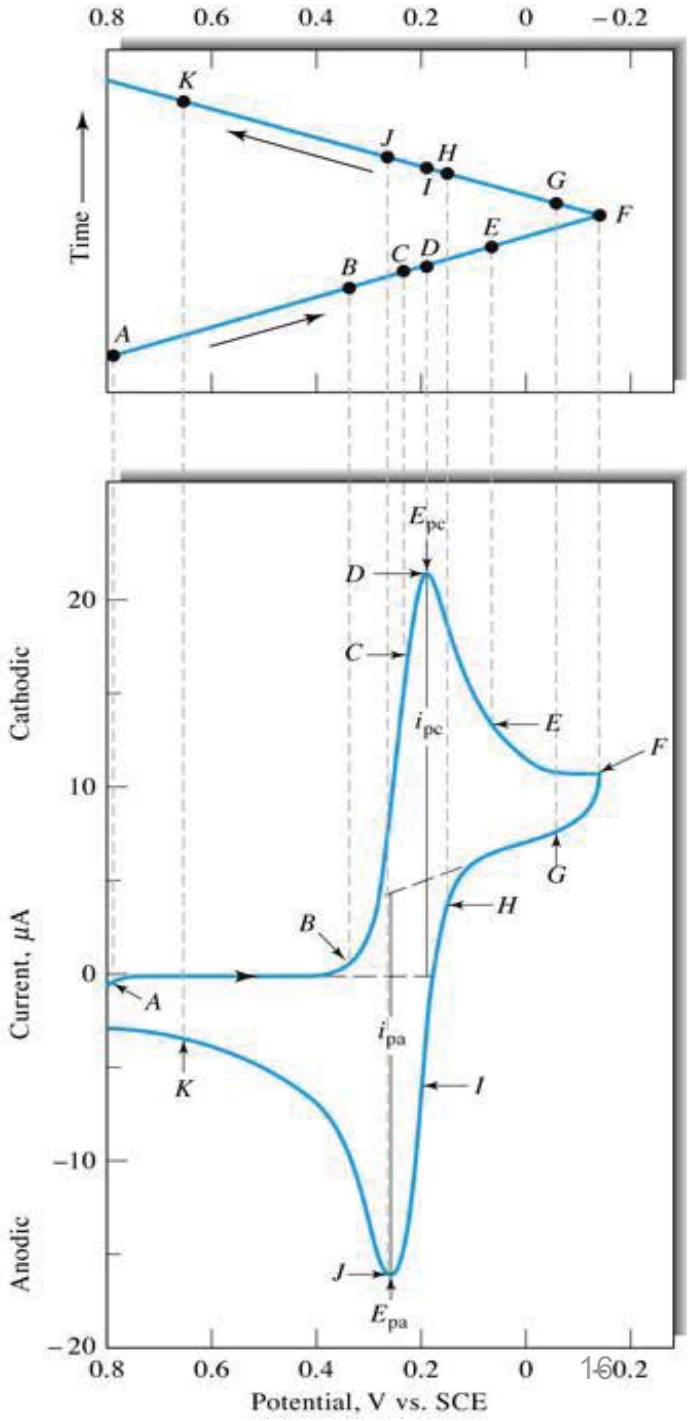
1) Method used to look at mechanisms of redox reactions in solution.

2) Looks at *i* vs. *E* response of small, stationary electrode in unstirred solution using triangular waveform for excitation

Cyclic voltammogram

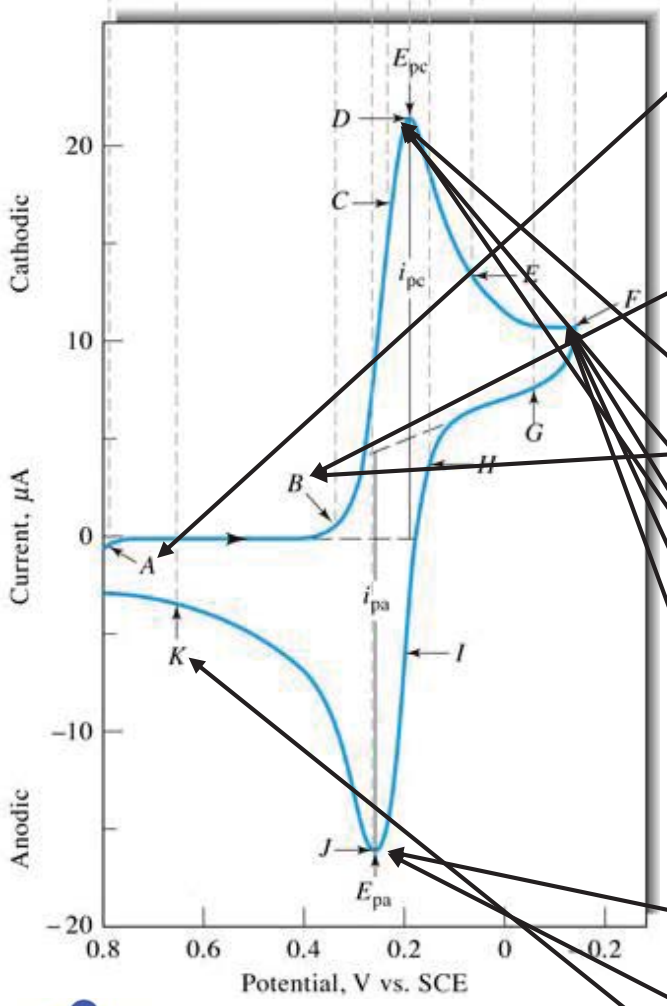






Working Electrode is Pt & Reference electrode is SCE

6 mM $K_3Fe(CN)_6$ & 1 M KNO_3



A. Initial negative current due to oxidation of H_2O to give O_2

No current between A & B (+0.7 to +0.4V) no reducible or oxidizable species present in this potential range

B. At 0.4V, current begins because of the following reduction at the cathode:

$$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$$

B.-D. Rapid increase in current as the surface concentration of $Fe(CN)_6^{3-}$ decreases

D. Cathodic peak potential (E_{pc}) and peak current (i_{pc})

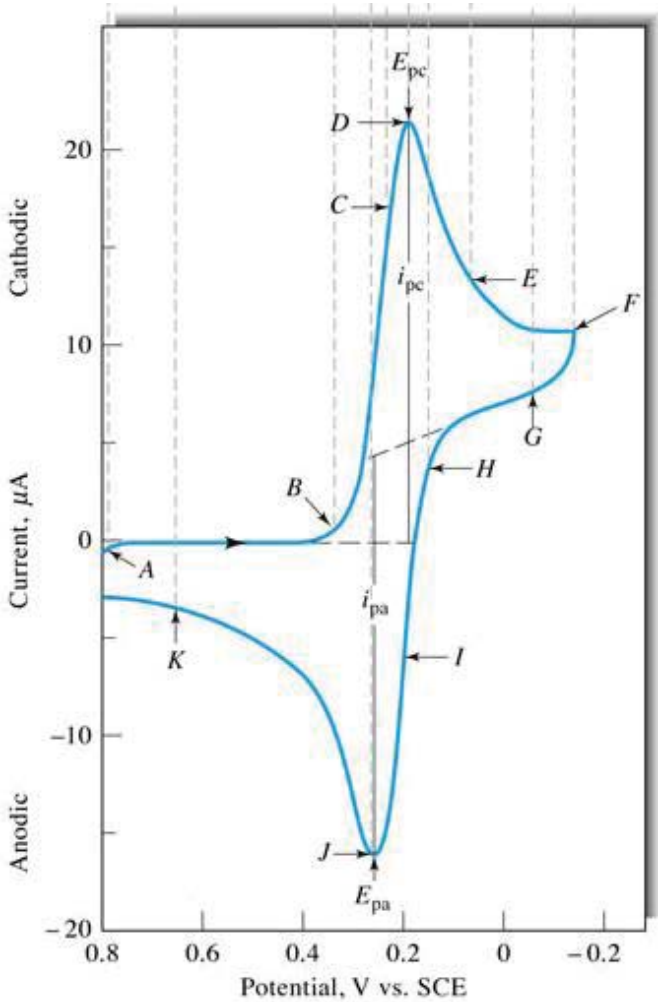
D.-F. Current decays rapidly as the diffusion layer is extended further from electrode surface

F. Scan direction switched (-0.15V), potential still negative enough to cause reduction of $Fe(CN)_6^{3-}$

F.-J. Eventually reduction of $Fe(CN)_6^{3-}$ no longer occurs and anodic current results from the reoxidation of $Fe(CN)_6^{4-}$

J. Anodic peak potential (E_{pa}) and peak current (i_{pa})

K. Anodic current decreases as the accumulated $Fe(CN)_6^{4-}$ is used up at the anodic reaction



Important Quantitative Information

- i_{pc} i_{pa}
- $\Delta E_p = (E_{pa} - E_{pc}) = 0.0592/n$,
  where n = number of electrons in reaction
- E^0 = midpoint of $E_{pa} \rightarrow E_{pc}$
- $i_p = 2.686 \times 10^5 n^{3/2} A c D^{1/2} v^{1/2}$

  - *A*: electrode area
  - *c*: concentration
  - v: scan rate
  - *D*: diffusion coefficient

$$D = 0.5\left(\frac{RT}{AF^2\sigma_w C}\right)^2$$

[Cm^2/s]

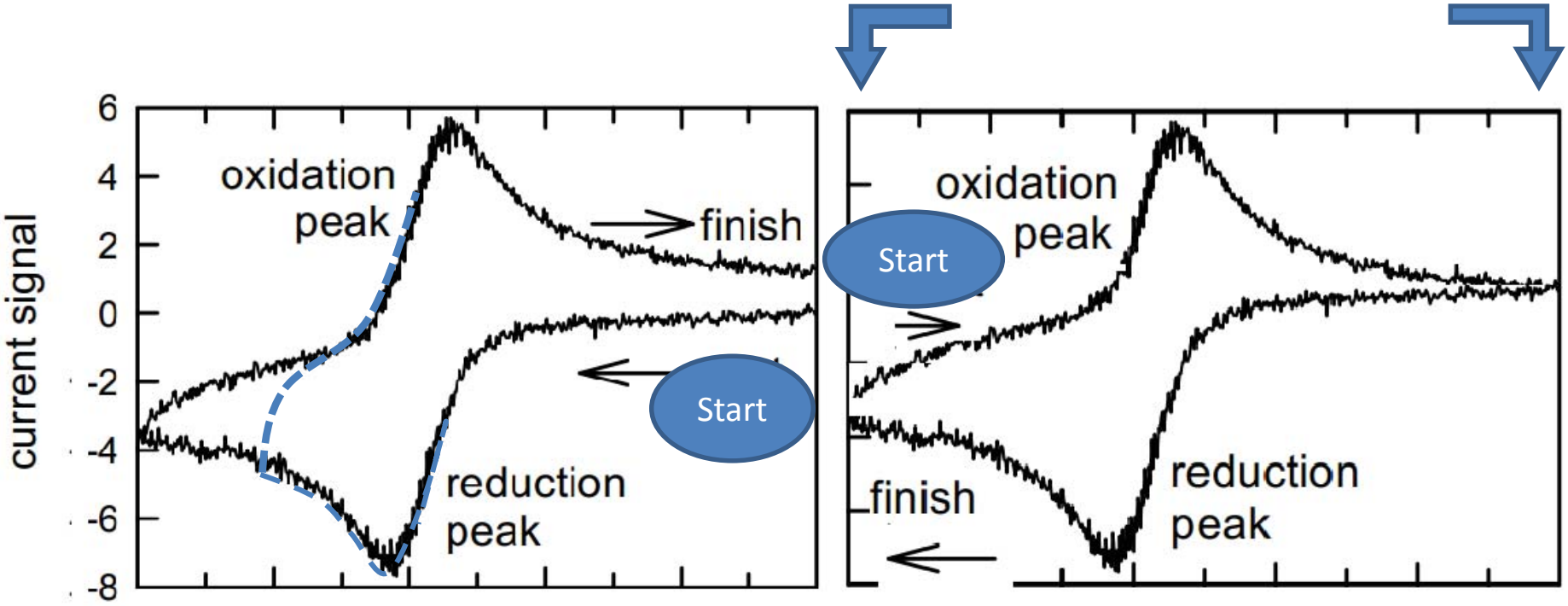
Thus,

- can calculate standard potential for half-reaction
- number of electrons involved in half-reaction
- diffusion coefficients
- if reaction is reversible

*) Bingbing, niobium doped lithium titanate, electrochim acta 55, 2010

study case:

Scan rate, V_{low}, V_{high}



$Li_4Ti_5O_{12} + 3Li^+ + 3e \leftrightarrow Li_7Ti_5O_{12}$, E= 1.5V

Half Cell for anode measurement

$LiFePO_4 \leftrightarrow Li^+ + e^- + FePO_4$

Half cell for cathode

Reduction : Ti^{4+} -> Ti^{3+}

Oxidation : Fe^{2+} -> Fe^{3+}

4.) CV- reversible/ irreversible

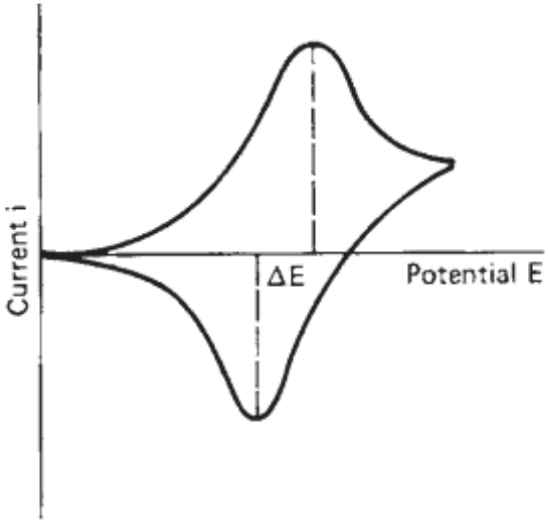


FIGURE 2.20 Cyclic voltammogram of a reversible diffusion-controlled process.

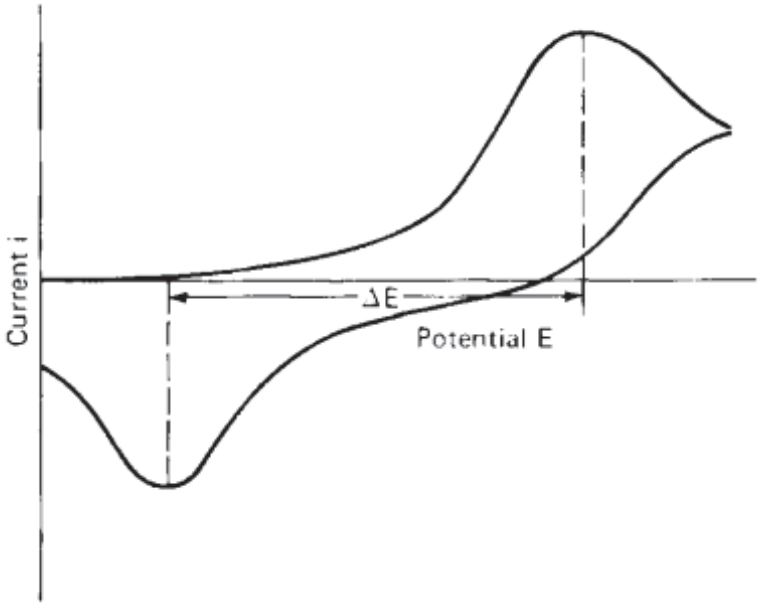


FIGURE 2.22 Cyclic voltammogram of a quasi-reversible process.

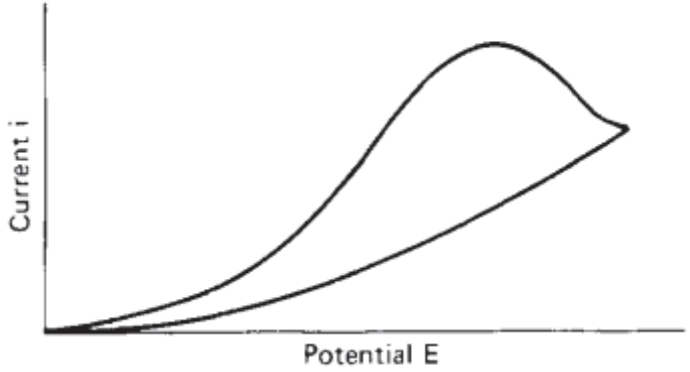
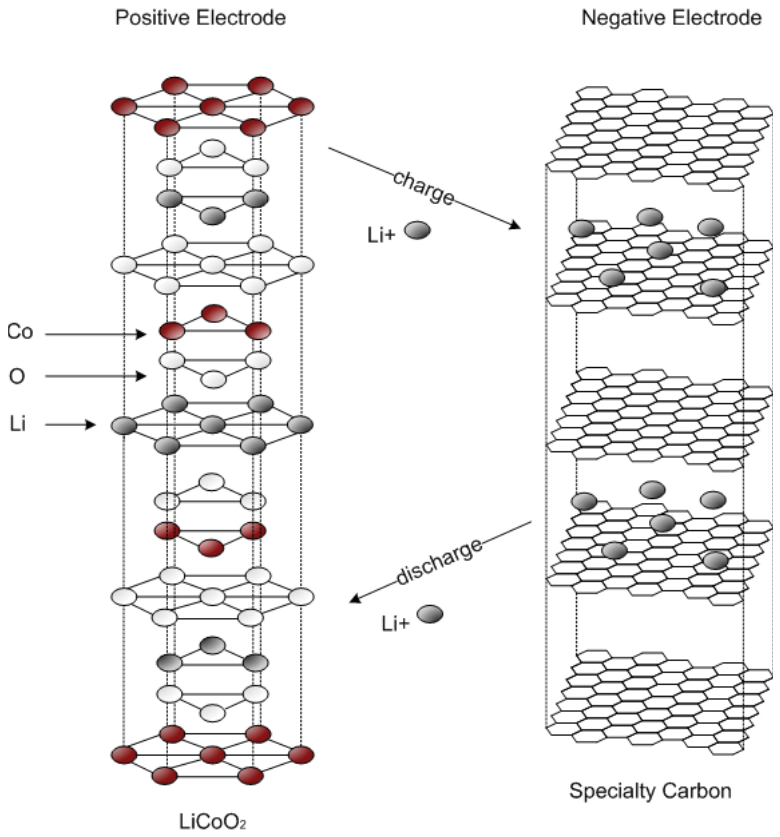


FIGURE 2.23 Cyclic voltammogram of an irreversible process.

Sumber : David Linden, Handbook of Batteries,2.2

Reactions at electrode surfaces

- Charging
  - Li ions deintercalate (move out) from cathode, intercalte (move in) into anode
  - At the cathode: $\mathbf{LiCoO_2 - Li^+ - e^- \leftrightarrow Li_{0.5}CoO_2}$
  - At the anode: $\mathbf{6C + Li^+ + e^- \leftrightarrow LiC_6}$
- Discharging
  - Li ions intercalete (move in into) cathode, diintercalte (move out from anode)
  - Overall reaction on a Li-ion cell: $\mathbf{C + LiCoO_2 \leftrightarrow LiC_6 + Li_{0.5}CoO_2}$



CELL SETUP

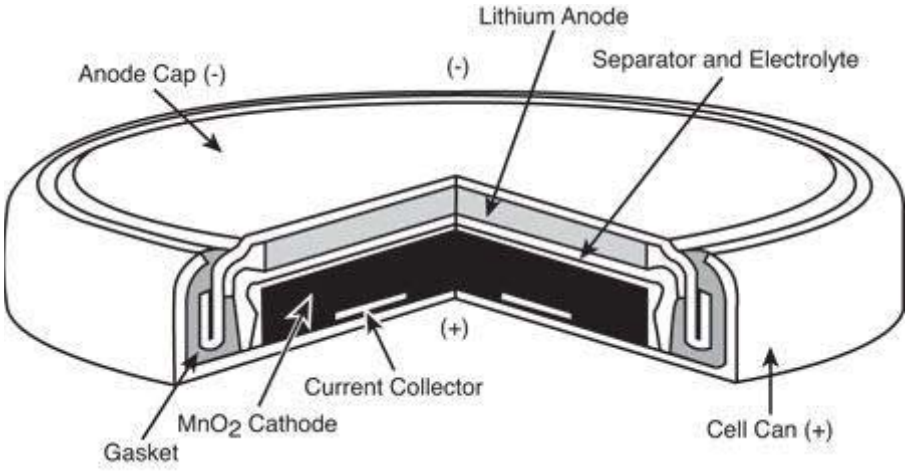
-half cell setup

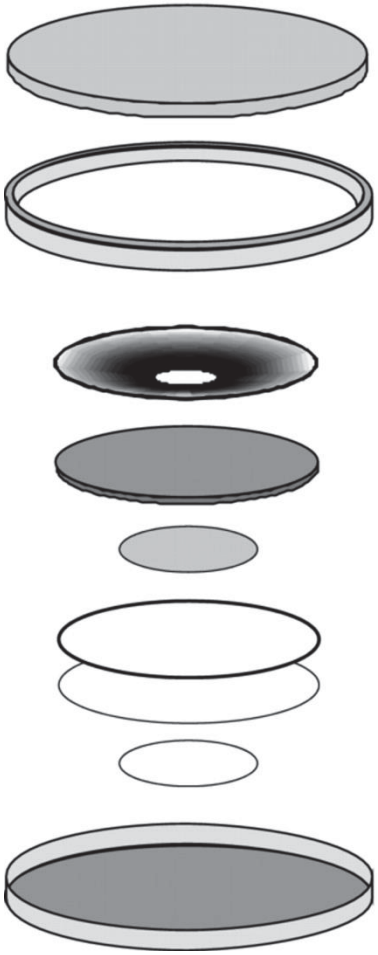
- three electrodes configuration
-working electrode; electrode to be tested (WE)
-reference electrode; Li(RE)
-counter electrode; Li (CE)

-FULL CELL SETUP

-Two electrodes configuration
-working electrode; electrode to be tested
-reference and Counter electrode; both connected to counter electrode terminals

Coin Cell Assembly (Two electrodes assembly)





Cap (Ni-coated)

Gasket

Cone Spring (Ni-coated)

Spacer (Ni-coated)

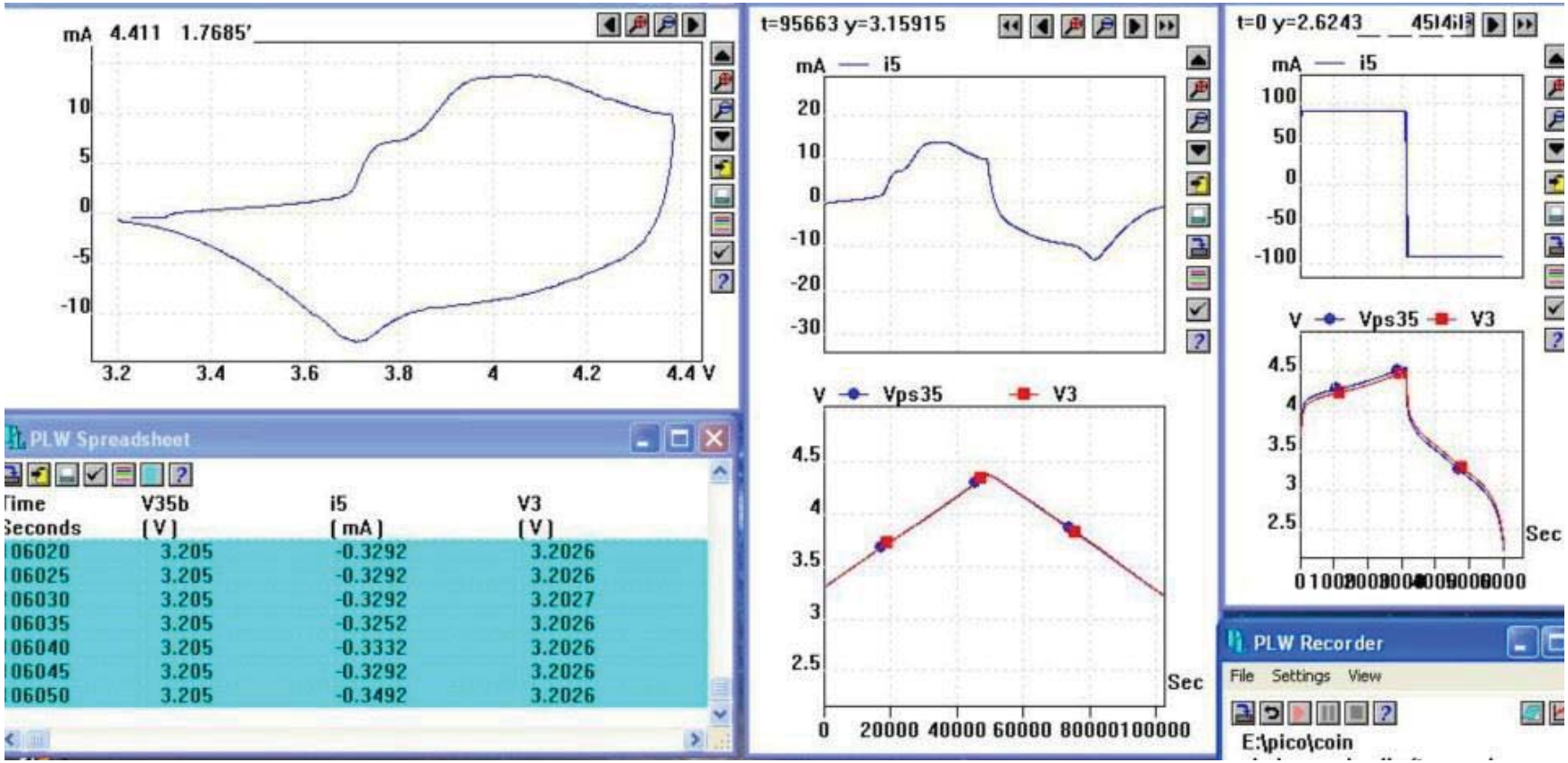
$Ni(OH)_2$ Electrode

Non-woven Separator
Microporous Separator

ZnO Electrode

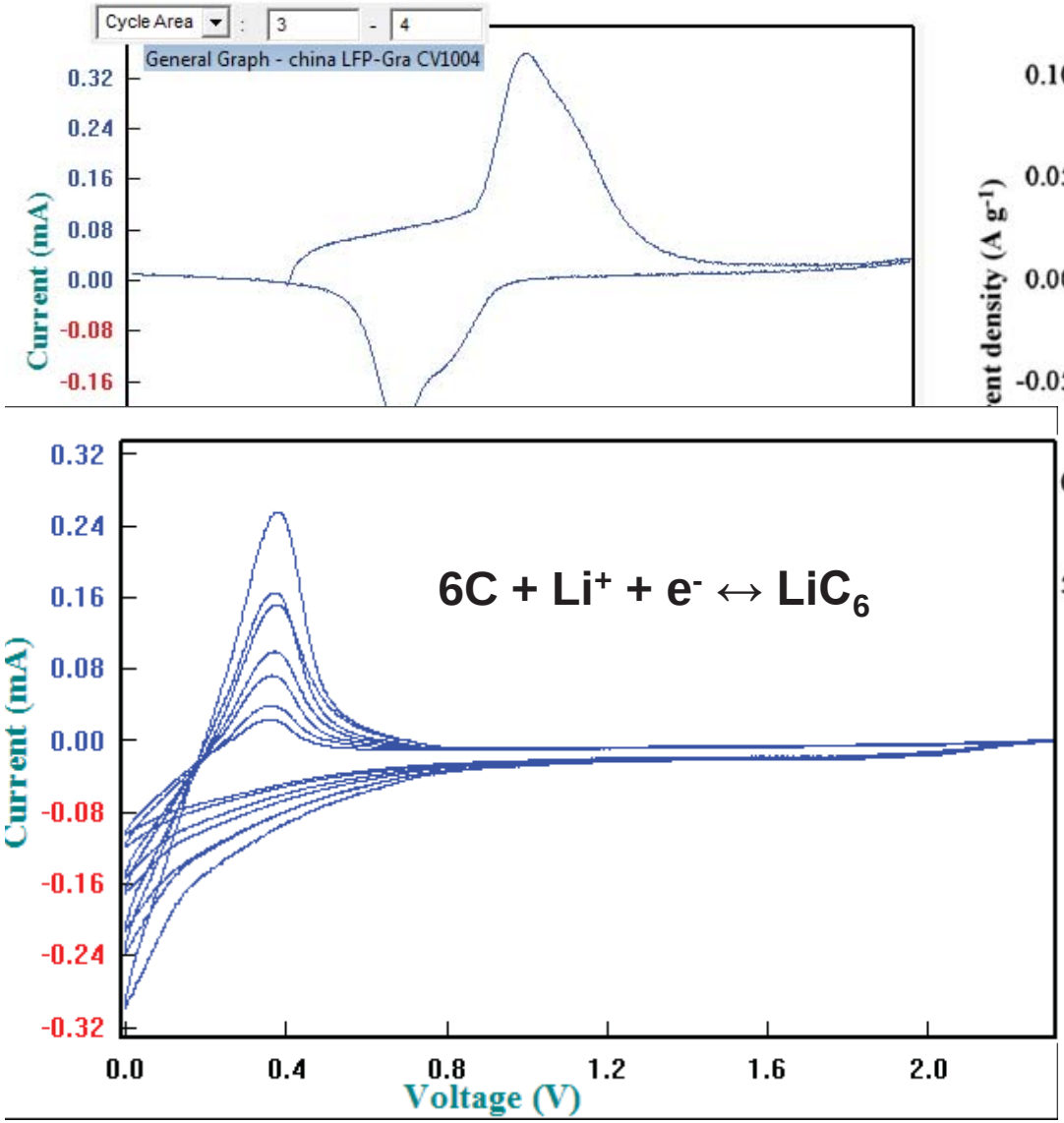
Can (Sn-coated)

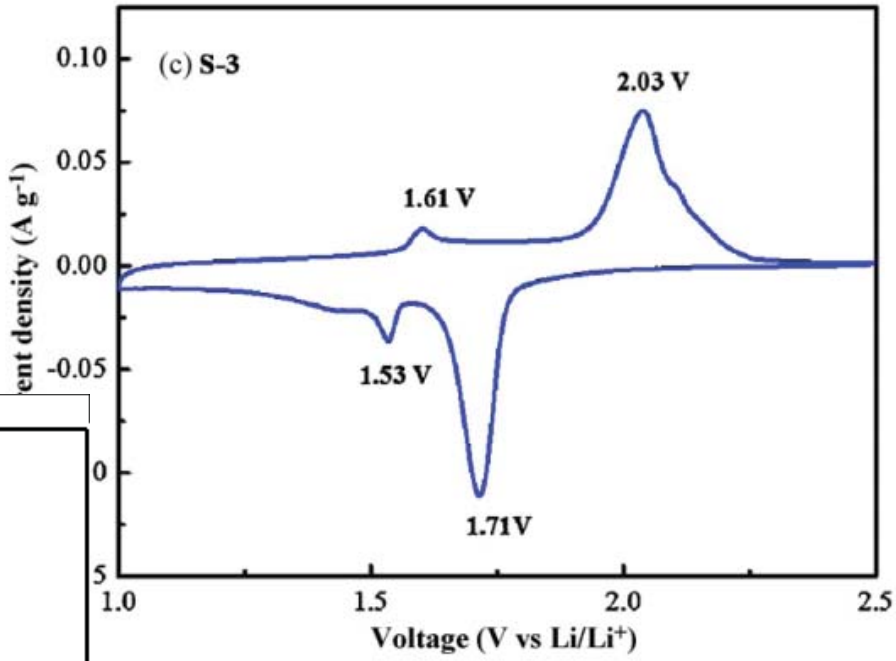
CV using yokogawa 7651



Example :

- Single phase
- double phase

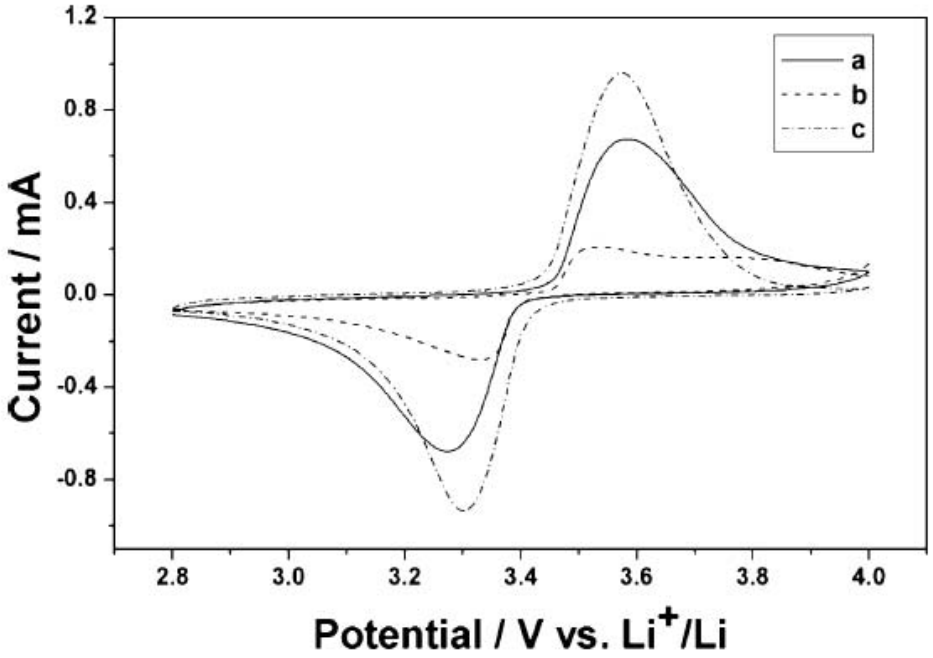




$$Li_4Ti_5O_{12} + xLi^+ + xe^- \leftrightarrow Li_{4+x}Ti_5O_{12} \quad (1)$$

$$TiO_2 + xLi^+ + xe^- \leftrightarrow Li_xTiO_2 \quad (2)$$

Rahman, Basic molten salt process-Li4Ti5O12-TiO2 , wollongong, power sources 195, 2010.



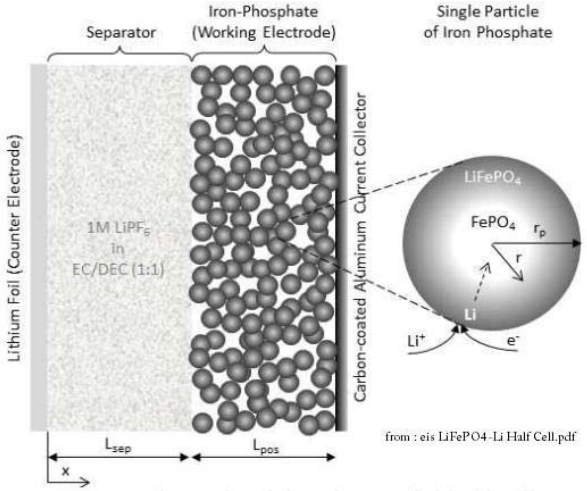
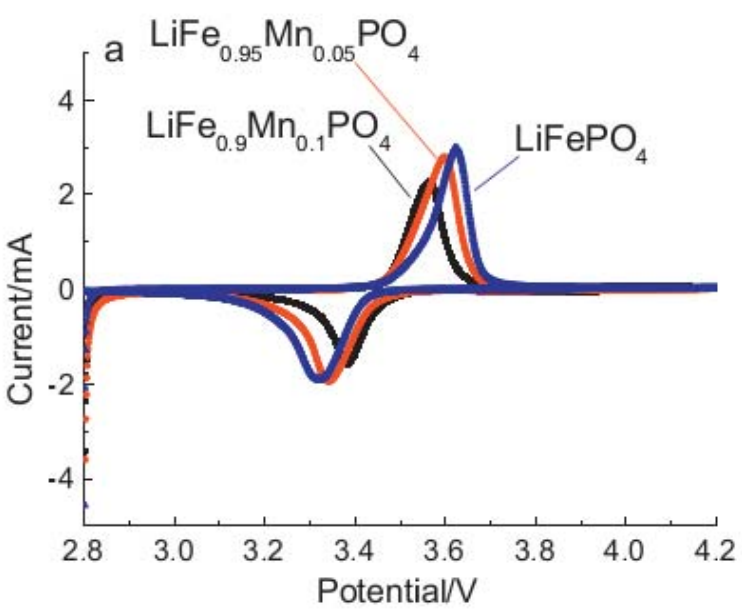
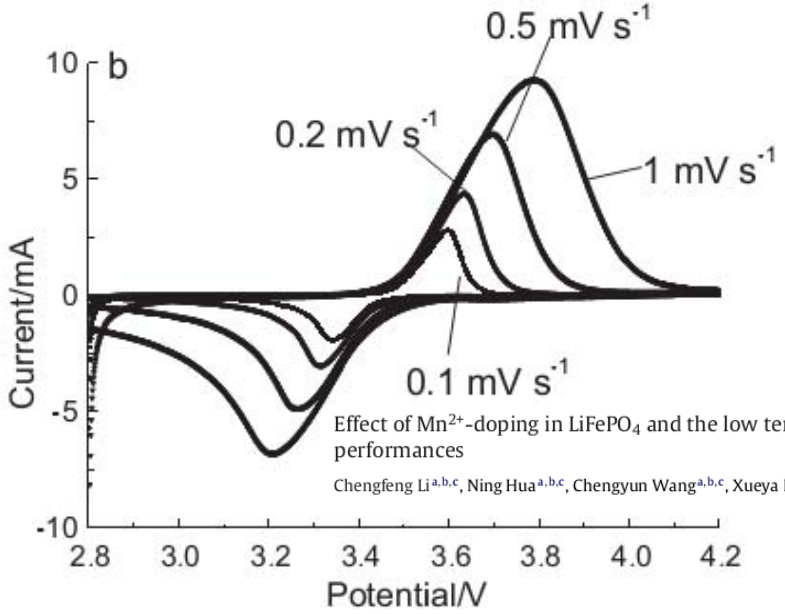


Figure 1. Schematic of the $LiFePO_4$/Li half-cell working electrode

(1) $Li^+ + e^- + FePO_4 \leftrightarrow LiFePO_4$

counter electrode (lithium foil)





Effect of Mn^{2+}-doping in $LiFePO_4$ and the low temperature electrochemical performances

Chengfeng Li[a,b,c], Ning Hua[a,b,c], Chengyun Wang[a,b,c], Xueya Kang[a,c,*],

Fig. 2. (a) CV curves of the composites at 0.1 mV s^{-1}. (b) CV profiles of $LiFe_{0.95}Mn_{0.05}PO_4$ at different sweeping rate.

Ionics
https://doi.org/10.1007/s11581-018-2633-0

ORIGINAL PAPER

Effects of activated carbon treatment on $Li_4Ti_5O_{12}$ anode material synthesis for lithium-ion batteries

Achmad Subhan[1] · Ferensa Oemry[1] · Siti Nailul Khusna[2] · Erna Hastuti[2]

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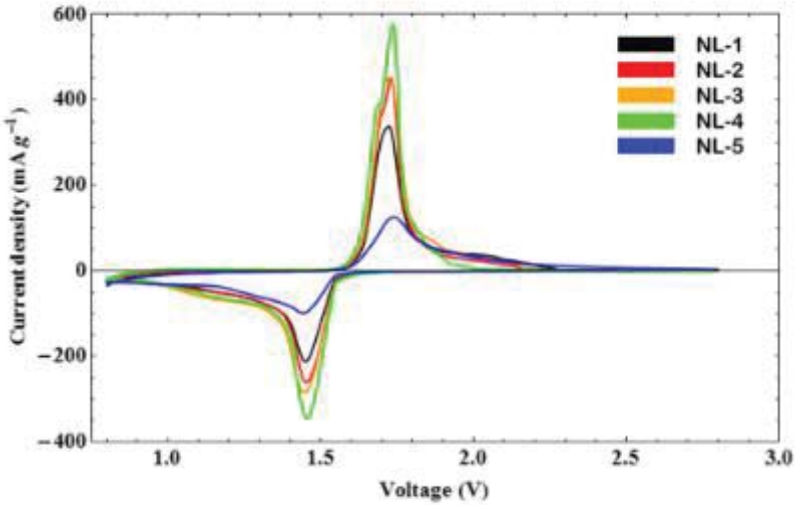
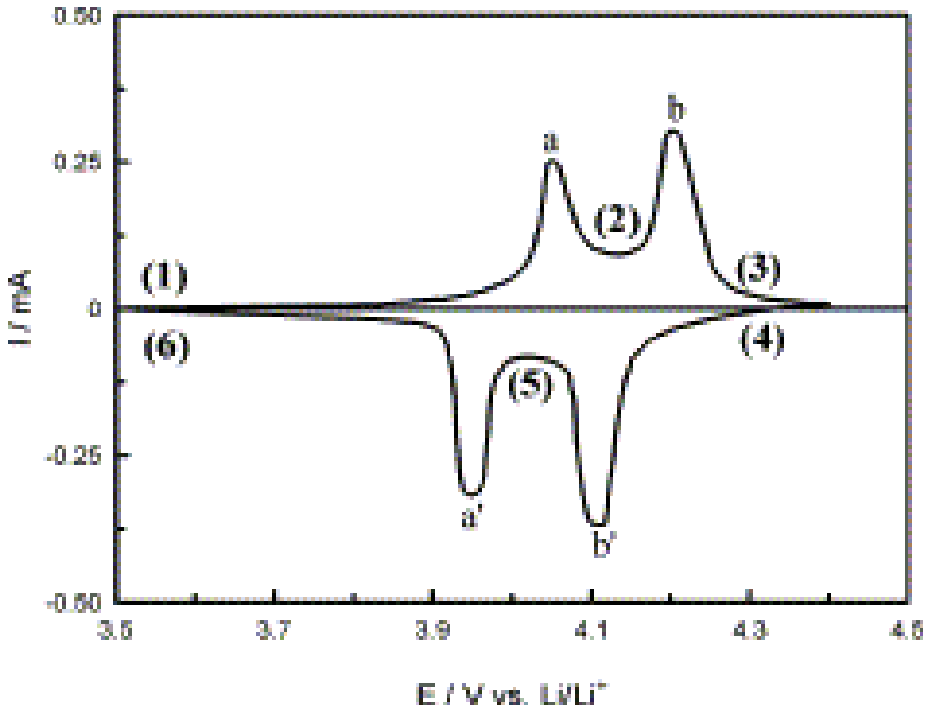


Fig. 7 CV curves of samples NL-1, NL-2, NL-3, NL-4, and NL-5 at scan rate 0.12 mV/s

Table 3 Charge and discharge capacities calculated from CV curves data

wt% AC	Charge capacity (mAh g^{-1})	Discharge capacity (mAh g^{-1})
NL-1 (0)	125.75	134.93
NL-2 (3)	134.84	143.97
NL-3 (6)	154.54	166.75
NL-4 (10)	156.27	168.35
NL-5 (15)	103.50	96



Typical cyclic voltammetric characterization of the $LiMn_2O_4$ electrode in conventional nonaqueous medium of lithium batteries (1 M $LiClO_4$+PC). The CV shows two redox couples designated as the first (a, a') and the second (b, b') pairs of peaks. The points (regions) indicated on the curve correspond to different states of $Li_{1-x}Mn_2O_4$ spinel formed as the

result of progress in the intercalation/deintercalation processes.

$$LiMn_2O_4\ (1) \rightarrow Li_{0.5}Mn_2O_4\ (2) + 0.5Li^+ + 0.5e^- \qquad (1)$$

(the reaction accomplished at the first anodic peak)

$$Li_{0.5}Mn_2O_4\ (2) \rightarrow Mn_2O_4\ (3) + 0.5Li^+ + 0.5e^- \qquad (2)$$

(the reaction accomplished at the second anodic peak)

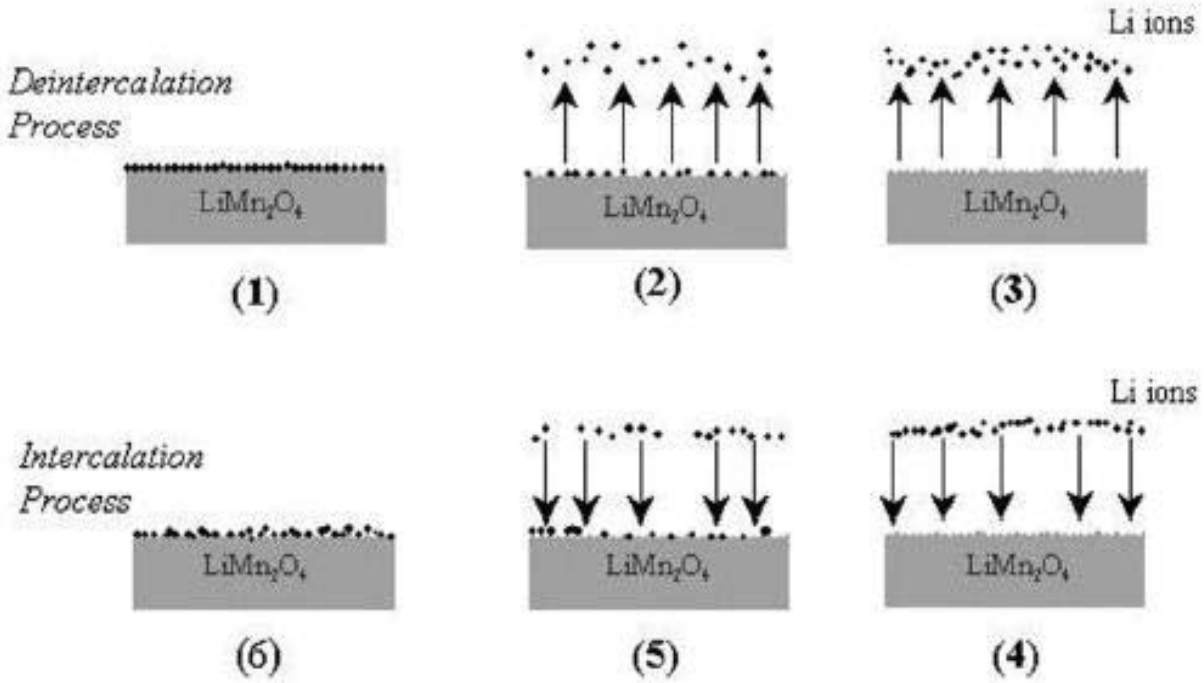
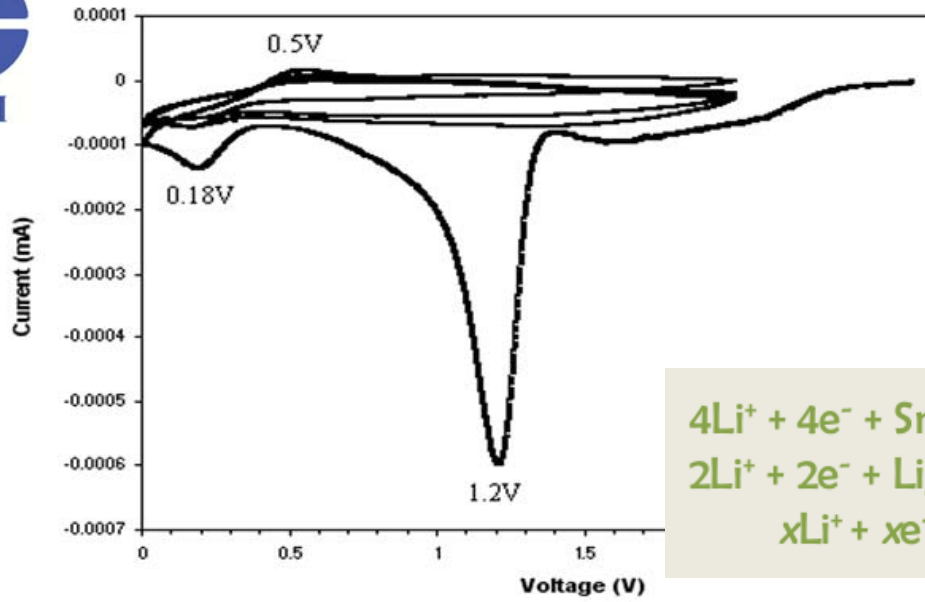


Fig. 6. Simple model of Li ion intercalation/deintercalation into/from $LiMn_2O_4$ spinel during a complete charge/discharge cycle. The black circles indicate Li ions and the white items on the electrode surface denote vacated places (places available for ideal intercalation of Li ions). The numbers noted in bold correspond to different states of the $LiMn_2O_4$ spinel during the intercalation/deintercalation processes as noted in Fig. 2.

Mesoporous tin phosphate calcined at 400°C.



1.19V
decomposition of the mesoporous SnP_2O_7
formation metallic Sn
0.7V
irreversible lithium phosphate phase
0.18V and 0.58V
reversible Li^+ insertion and extraction process

$$4Li^+ + 4e^- + SnP_2O_7 \Rightarrow Li_4P_2O_7 + Sn \quad [a]$$
$$2Li^+ + 2e^- + Li_4P_2O_7 \Rightarrow Li_6P_2O_7 \quad [b]$$
$$xLi^+ + xe^- + Sn \Leftrightarrow Li_xSn \quad (0 \le x \le 4.4) \quad [c]$$

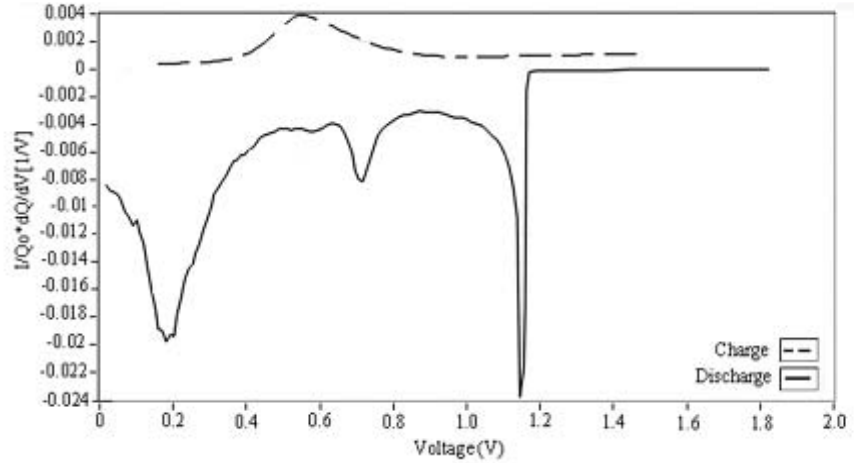


Fig. A: Differential capacity plot from initial charge discharge curve of mesoporous SnP_2O_7

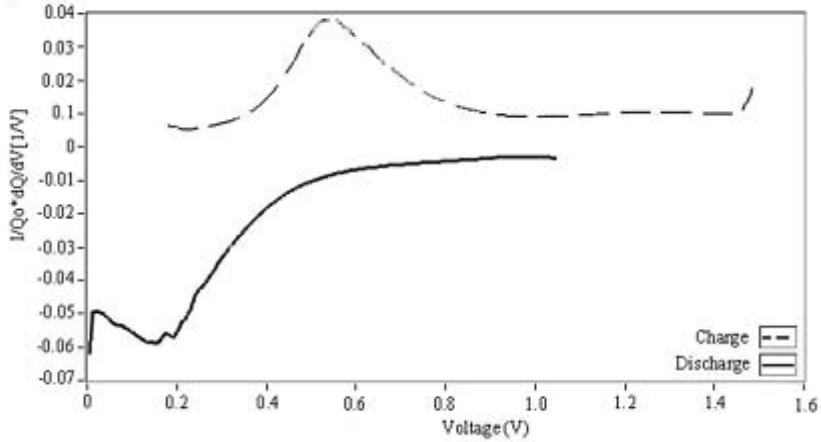
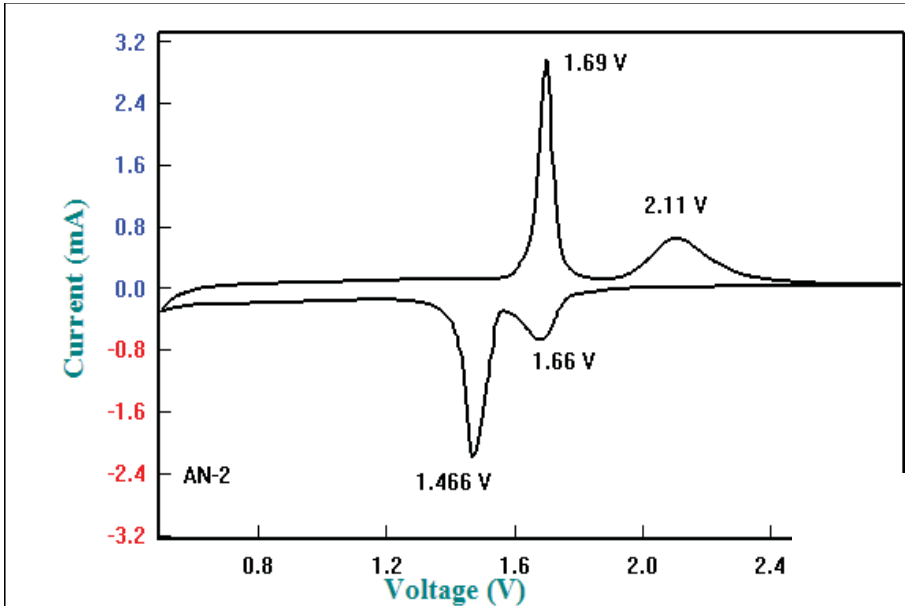
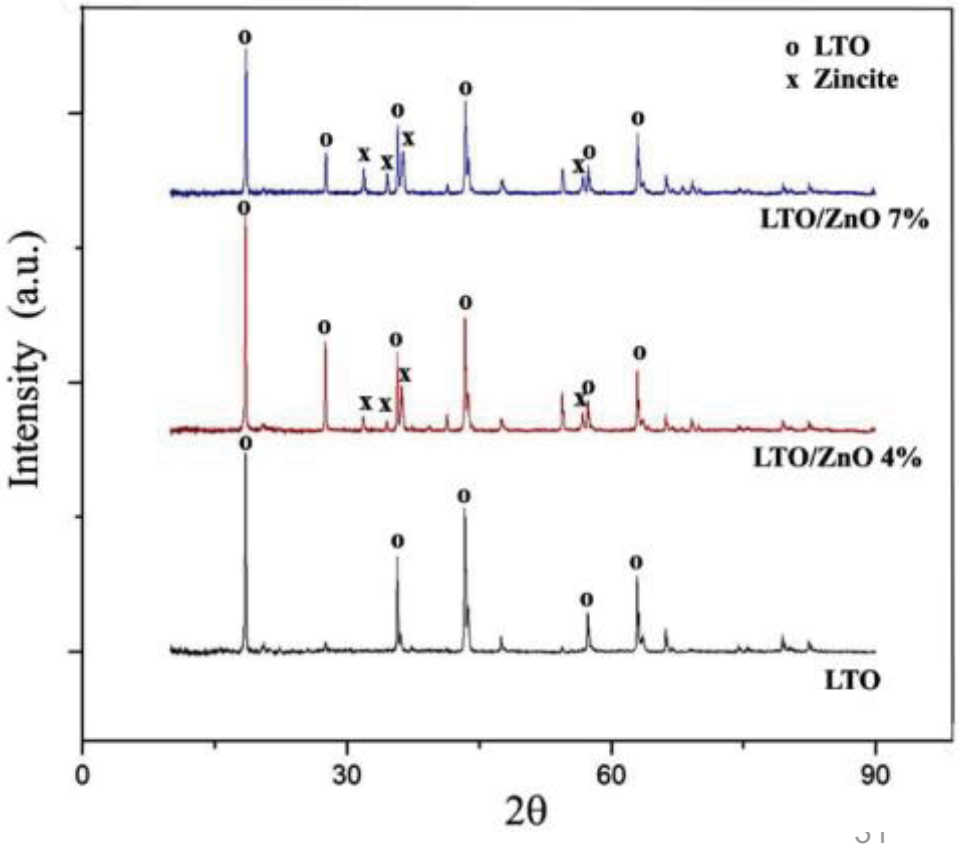


Fig. B: Differential capacity plot from second charge discharge curve of mesoporous SnP_2O_7


3.2
2.4
1.6
0.8
0.0
-0.8
-1.6
-2.4
-3.2
Current (mA)
1.69 V
2.11 V
1.66 V
1.466 V
AN-2
0.8
1.2
1.6
2.0
2.4
Voltage (V)


o LTO
x Zincite
LTO/ZnO 7%
LTO/ZnO 4%
LTO
Intensity (a.u.)
0
30
60
90
2θ

interpretation CV :?

- Identification of intercalation/diintercalation process, reversibility.
- Capacity calculation of the electrode
  - C=Q/V
- Working voltage. Phase confirmation to xrd crystal structures.
- Etc.

2. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY EIS

Introduction.

Impedance Spectroscopy is also called AC Impedance or just Impedance Spectroscopy. The usefulness of impedance spectroscopy lies in the ability to distinguish the dielectric and electric properties of individual contributions of components under investigation.

Impedance spectroscopy is a non-destructive technique and so can provide time dependent information about the properties but also about ongoing processes such as corrosion or the discharge of batteries and e.g. the electrochemical reactions in fuel cells, batteries or any other electrochemical process.

http://www.gamry.com/App_Notes/EIS_Primer/EIS_Primer.htm

Some the advantages and disadvantages of the technique :

Advantages.

1. Useful on high resistance materials such as paints and coatings.
2. Time dependent data is available
3. Non- destructive.
4. Quantitative data available.
5. Use service environments.

Disadvantages.

1. Expensive --→ easy damage.
2. Complex data analysis for quantification. -→ need software and expert.

Basic theory :

- Resistance : DC signal
- Ohms Law $R = \frac{E}{I}$
- For a resistor, R, it follows Ohm's Law at all current and voltage levels
- The resistance value is independent of frequency
- AC current and voltage signals through a resistor are in phase with each other

Basic theory :

- Impedance (X) : AC signal
- Impedance applies to AC voltage and current
- Like resistance impedance is a measure of the ability of a circuit to resist the flow of electrical current
- The excitation potential or AC voltage can be expressed as a function of time

$$\omega = 2\pi f$$

$E_t = E_0 \sin(\omega t)$

E_t = potential at time t
E_0 = the amplitude of the voltage
ω = the radial frequency

$I_t = I_0 \sin(\omega t + \phi)$

I_t = response current
I_0 = the amplitude of the current
ϕ = the phase shift

Input signal → Cell battery → output signal

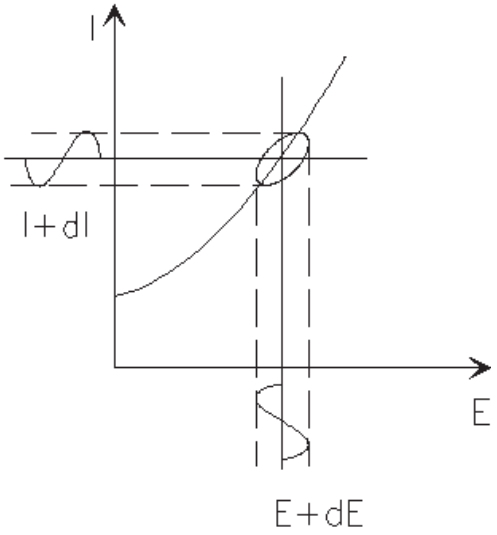
Impedance calculation :

- Similar to Ohm's law

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$

- The important point to remember is that when an AC voltage is applied to a pure capacitor the resulting AC current is shifted in phase by 90^o
- There is no phase shift for a pure resistor

Complex writing



$$Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$

Using Eulers relationship $\exp(i\phi) = \cos\phi + i\sin\phi$

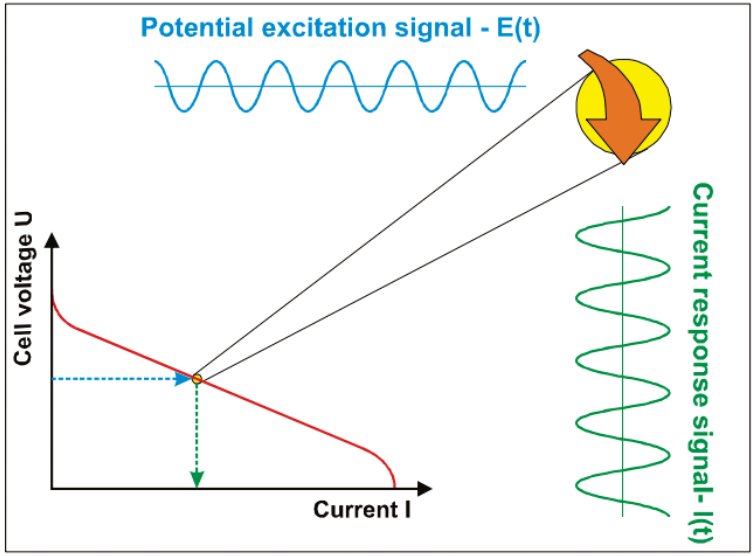
it is possible to express the impedance as a complex function. The potential is described as $E(t) = E_0 \exp(j\omega t)$

and the current response as $I(t) = I_0 \exp(i\omega t - i\phi)$

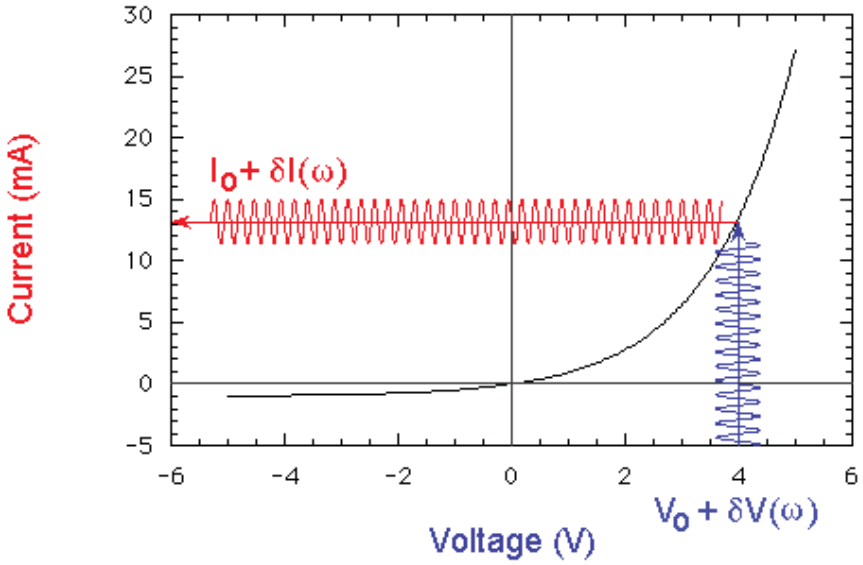
The impedance is then represented as a complex number,

$$Z = \frac{E}{I} = Z_0 \exp(i\phi) = Z_0(\cos\phi + i\sin\phi)$$

Electrochemical Impedance Spectroscopy:



Measure $Z(\omega,V_{bias})$



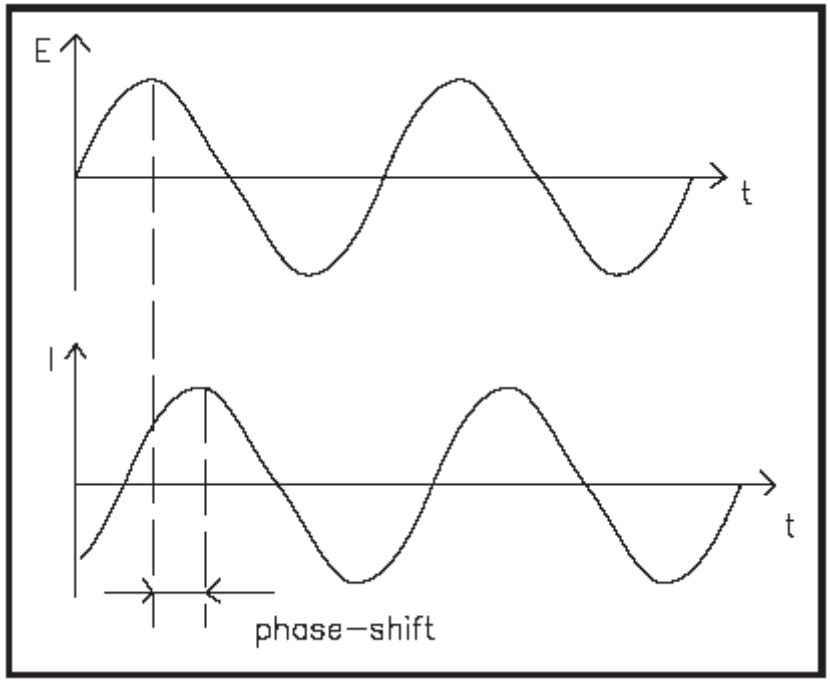
The result will be $Z(\omega,V_o) = \delta V(\omega) / \delta I(\omega)$

Phase shift

Current phase shift due to impedance. Through a capacitor this phase shift is 90^{o}

Applied Voltage

Resulting Current



LIPI

Simple EIS

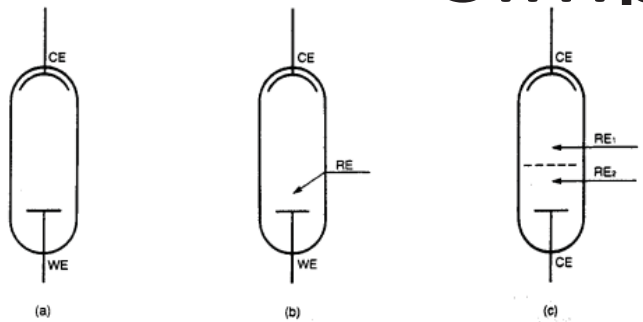


Fig 2.1 Scheme of experimental electrochemical cells:

(a) 2-electrode cell
(b) 3-electrode cell
(c) 4-electrode cell

WE Working electrode
CE Counter electrode
RE reference electrode

Technical Report Number 004/83

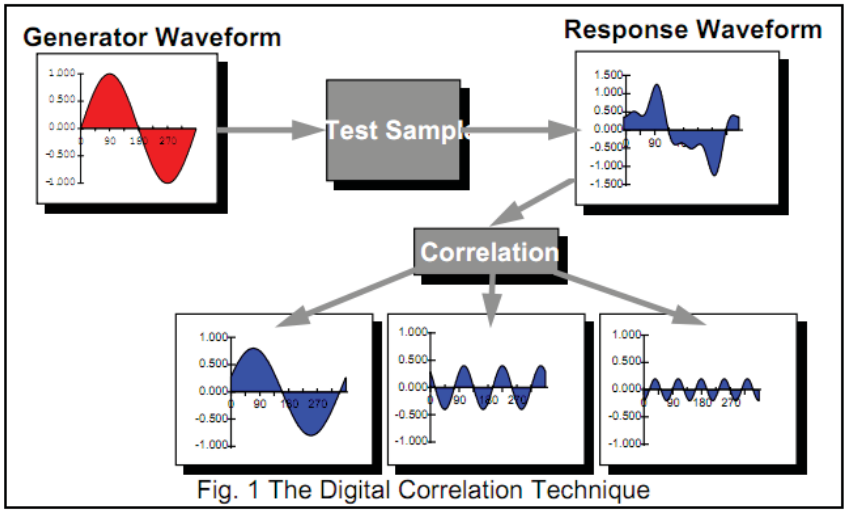


Fig. 1 The Digital Correlation Technique

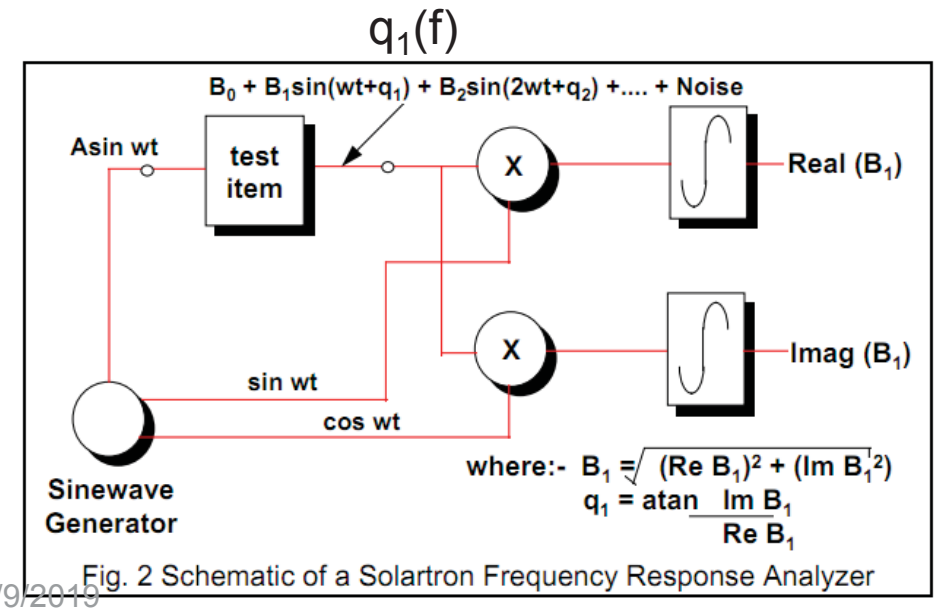


Fig. 2 Schematic of a Solartron Frequency Response Analyzer

Data EIS : freq, Zreal, Z im,
phase degree,
Z total,
σ (conductivity)

Basic Electrical Circuit Elements

EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as resistors, capacitors, and inductors. To be useful, the elements in the model should have a basis in the physical electrochemistry of the system. As an example, most models contain a resistor that models the cell's solution resistance.
Some knowledge of the impedance of the standard circuit components is therefore quite useful. The Table lists the common circuit elements, the equation for their current versus voltage relationship, and their impedance:

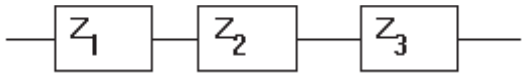
Component	Current Vs.Voltage	Impedance
resistor	E= IR	Z = R
inductor	E = L di/dt	Z = iωL
capacitor	I = C dE/dt	Z = 1/iωC

Notice that the impedance of a resistor is independent of frequency and has only a real component. Because there is no imaginary impedance, the current through a resistor is always in phase with the voltage.
The impedance of an inductor increases as frequency increases. Inductors have only an imaginary impedance component. As a result, an inductor's current is phase shifted 90 degrees with respect to the voltage.
The impedance versus frequency behavior of a capacitor is opposite to that of an inductor. A capacitor's impedance decreases as the frequency is raised. Capacitors also have only an imaginary impedance component. The current through a capacitor is phase shifted -90 degrees with respect to the voltage.

Serial and Parallel Combinations of Circuit Elements

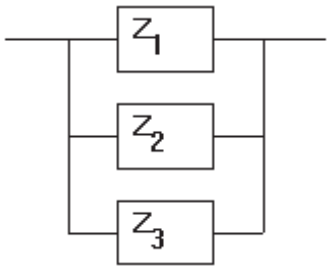
Very few electrochemical cells can be modeled using a single equivalent circuit element. Instead, EIS models usually consist of a number of elements in a network. Both serial and parallel combinations of elements occur.

Impedances in Series:



$$Z_{eq} = Z_1 + Z_2 + Z_3$$

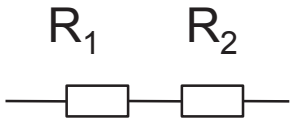
Impedances in Parallel



$$\frac{1}{Z_{eq}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3}$$

Serial and Parallel Combinations of Circuit Elements

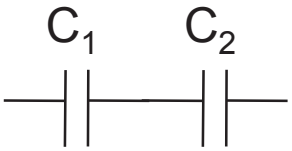
Suppose we have a 1Ω and a 4 Ω resistor is series. The impedance of a resistor is the same as its resistance (see Table 2-1). We thus calculate the total impedance Z_{eq}:



$$Z_{eq} = Z_1 + Z_2 = R_1 + R_2 = 1\Omega + 4\Omega = 5\Omega$$

Resistance and impedance both go up when resistors are combined in series.

Now suppose that we connect two 2 μF capacitors in series. The total capacitance of the combined capacitors is 1 μF



$$\frac{1}{Z_{eq}} = Z_1 + Z_2 = \frac{1}{i\omega C_1} + \frac{1}{i\omega C_2}$$

$$= \frac{1}{i\omega(2e^{-6})} + \frac{1}{i\omega(2e^{-6})} = \frac{1}{i\omega(1^{e-6})} = 1\ \mu\text{F}$$

Impedance goes up, but capacitance goes down when capacitors are connected in series. This is a consequence of the inverse relationship between capacitance and impedance.

Basic impedance : R,C,L

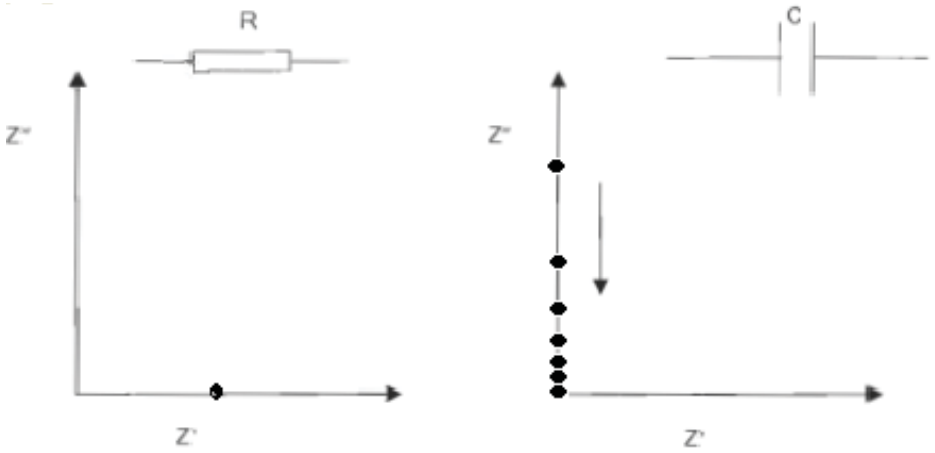
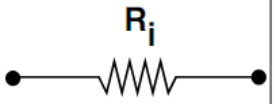
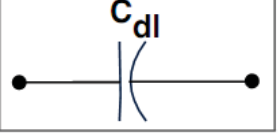


Fig. (2.3a)

mplex impedance plot for resistor only

Fig. (2.3b)

Complex impedance plot for capacitor only

Element	Impedance	Symbol
Resistor	$Z_{R_i}(\omega) = R_i$	
Capacitor	$Z_{C_i}(\omega) = -\frac{j}{\omega C}$	

Note: $j = \sqrt{-1}$

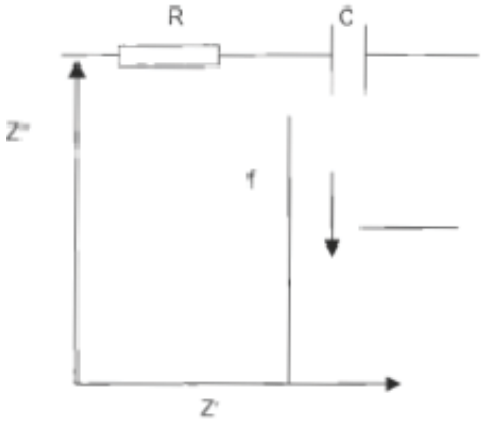


Fig. (2.4a)

Complex impedance plot for series circuit

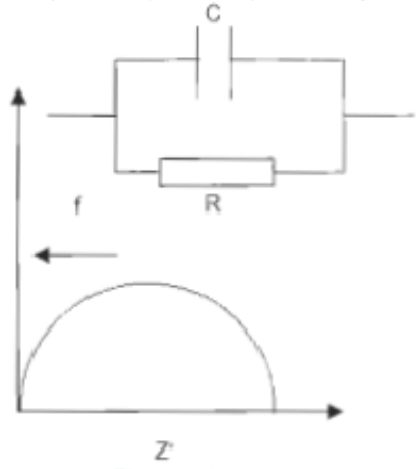
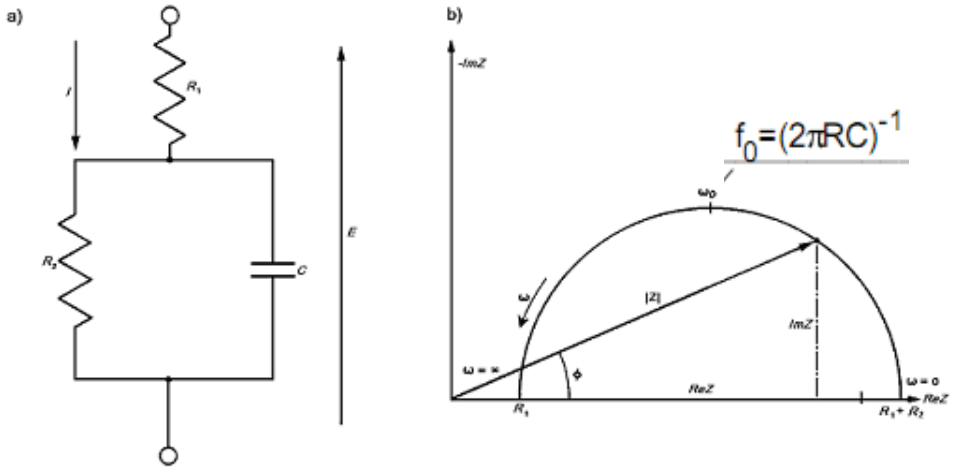
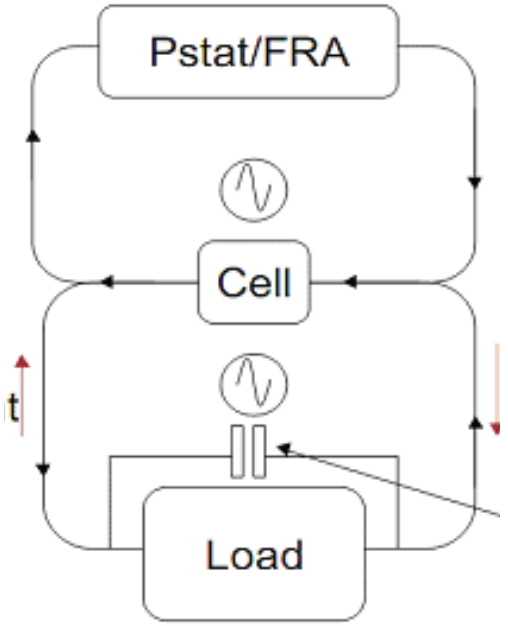


Fig. (2.4b)

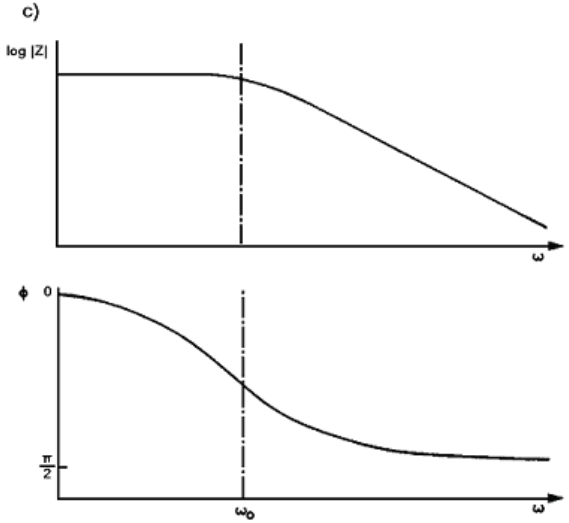
Complex impedance plot for parallel circuit

Single time constant



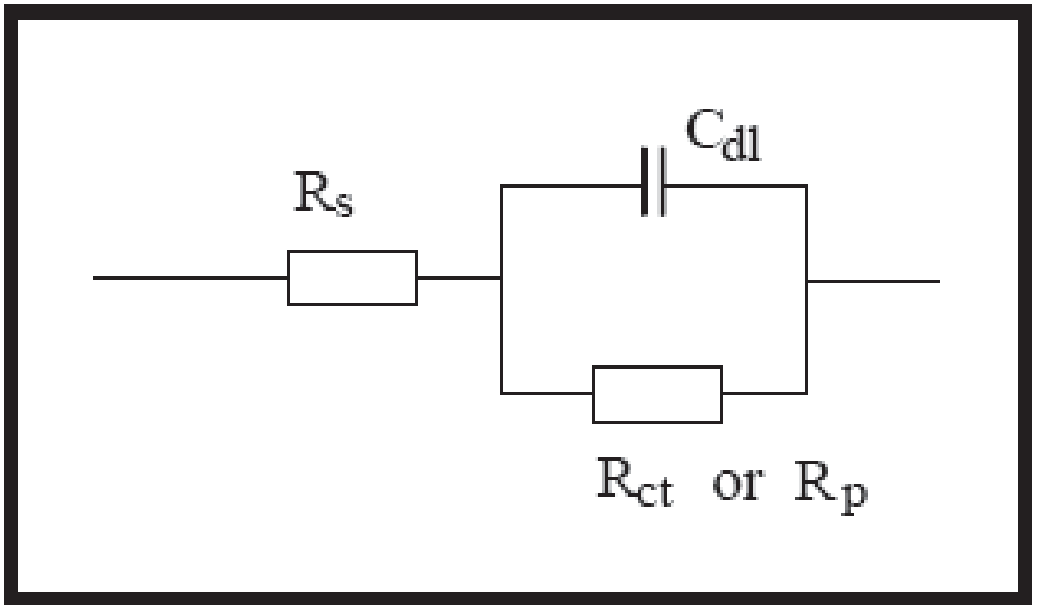


freq	Rs	X	σ	deg
4				
4.5				
5.1				
…				
…				
1 MHz	Ω	Ω	S/cm	θ°



Equivalent circuit : Randles

- Randles circuit for a simple corroding system

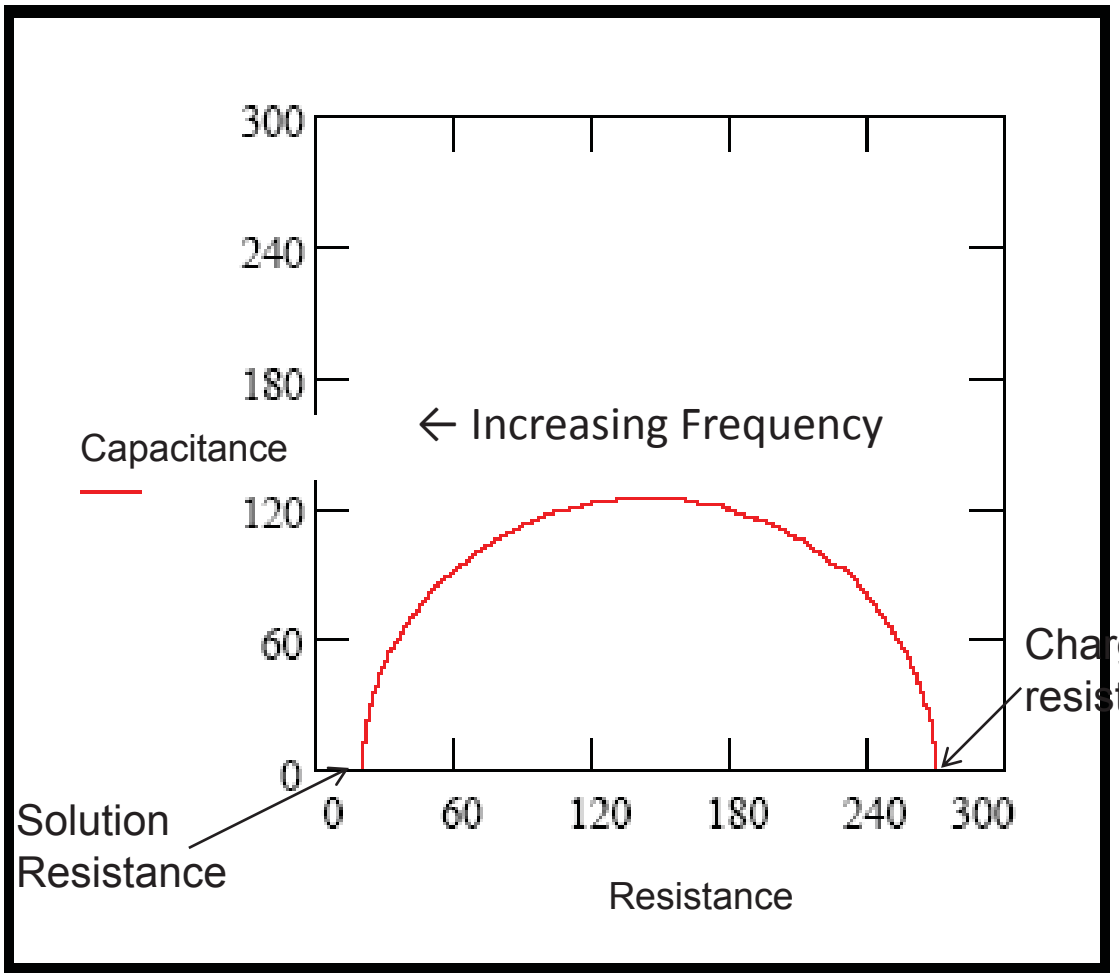


- R_s = the solution resistance
- R_{ct} = the charger transfer (polarisation resistance)
- C_{dl} = the double layer capacitance

LIPI

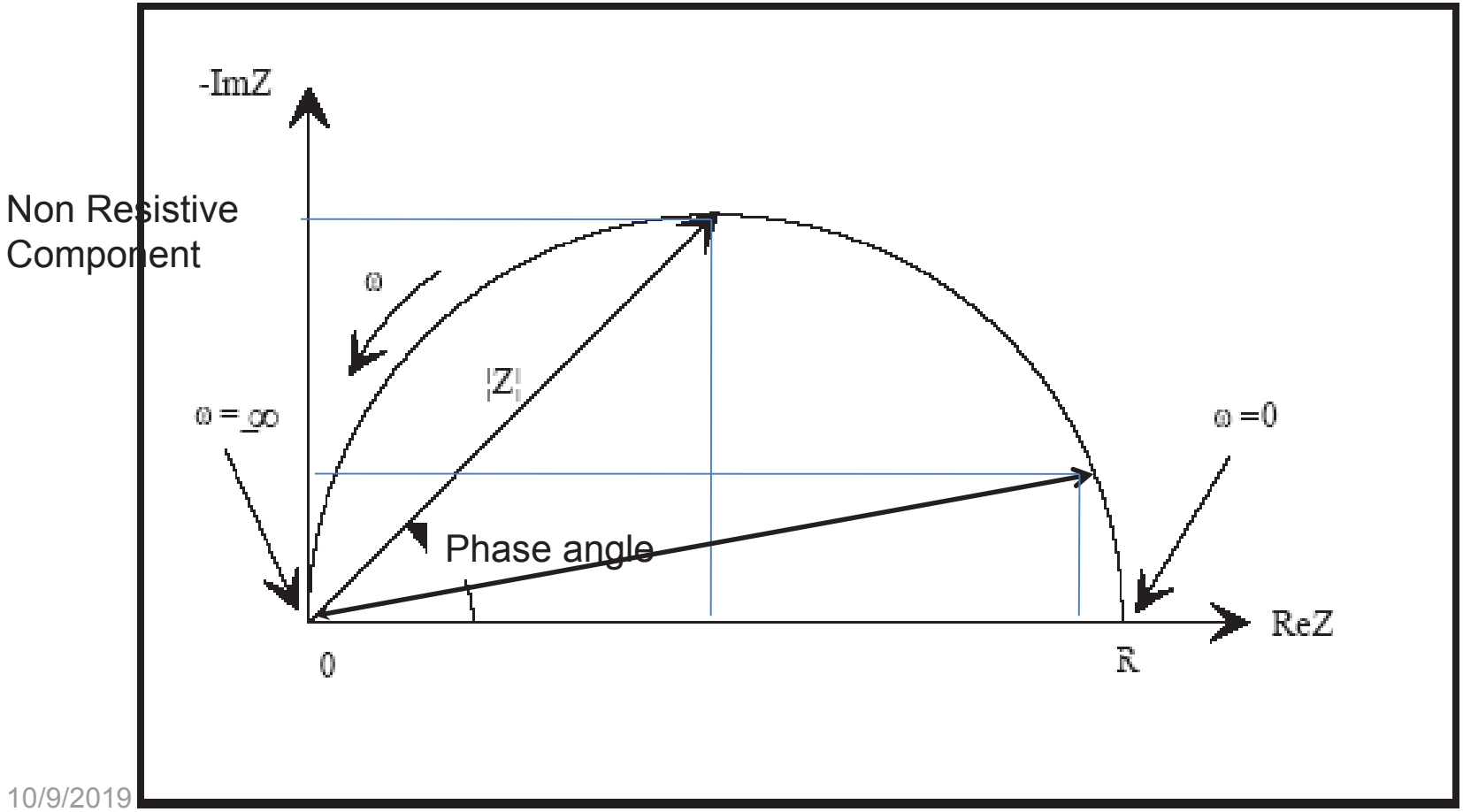
Electrochemical Impedance Spectroscopy

- Nyquist plot for the Randels circuit



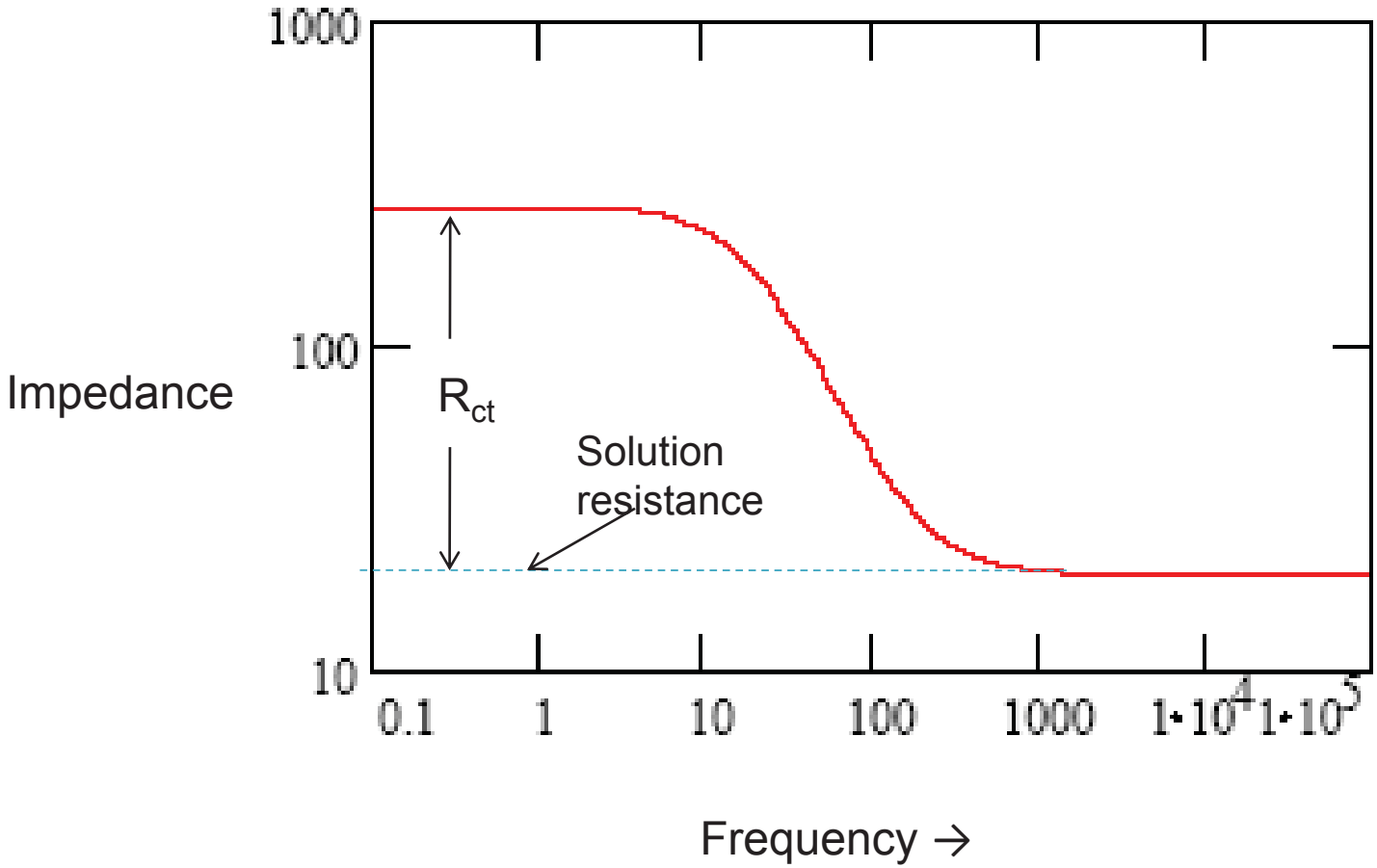
EIS Nyquist Plots

- A Nyquist plot is made up of a series of vectors representing the total magnitude of the resistance and capacitance components



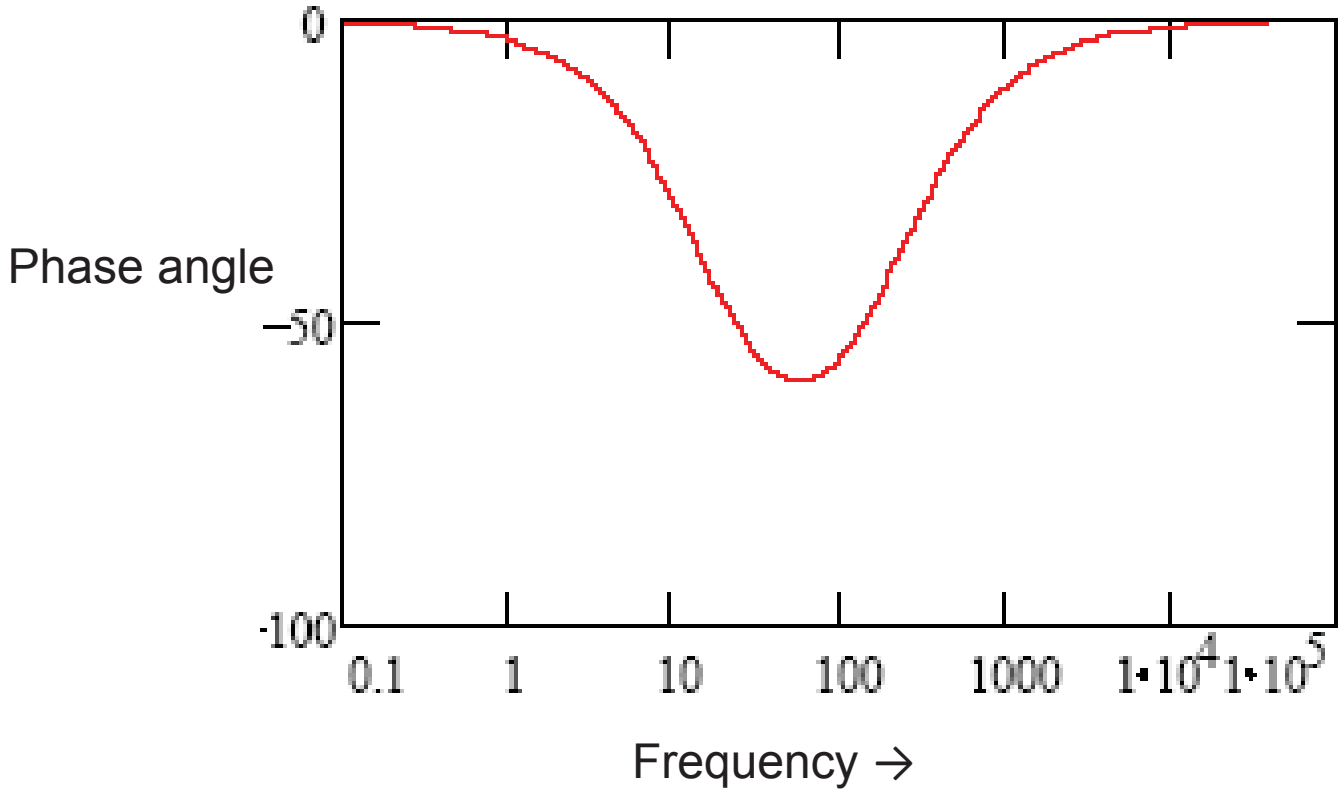
Electrochemical Impedance Spectroscopy

- Bode impedance plot

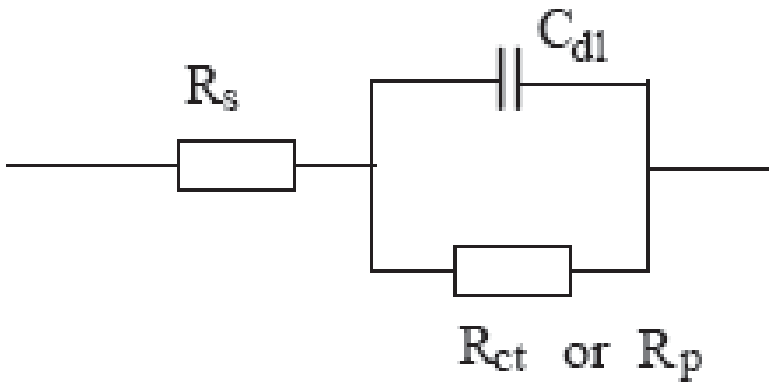


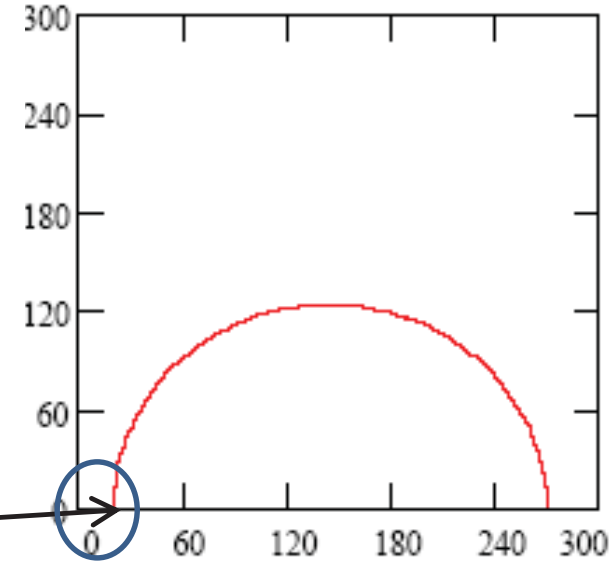
Electrochemical Impedance Spectroscopy

- Bode Phase plot

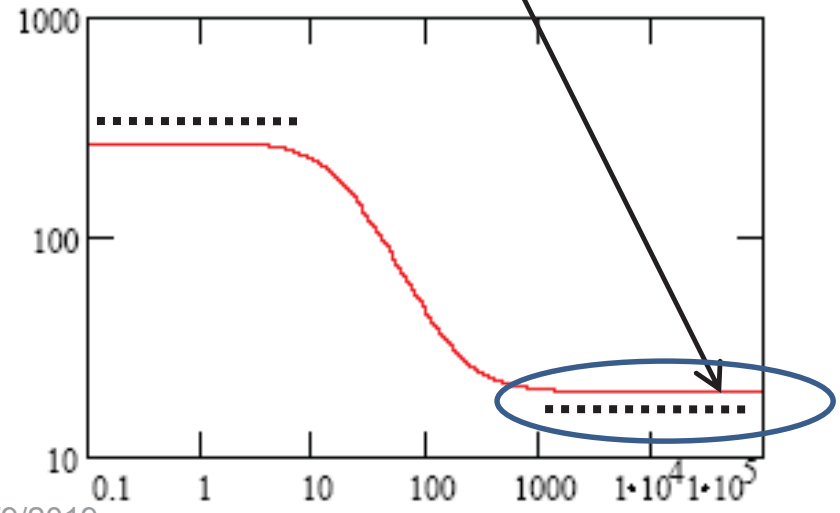


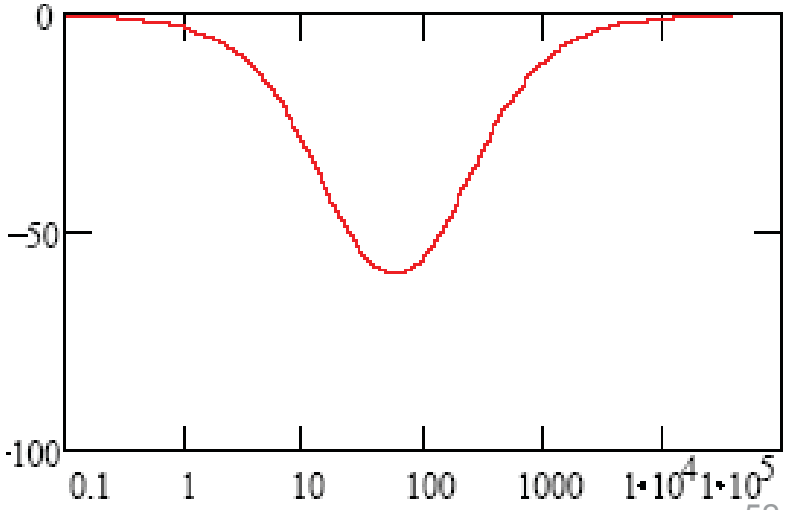
EIS (Summary)





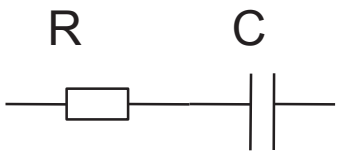
We start here at the high frequency

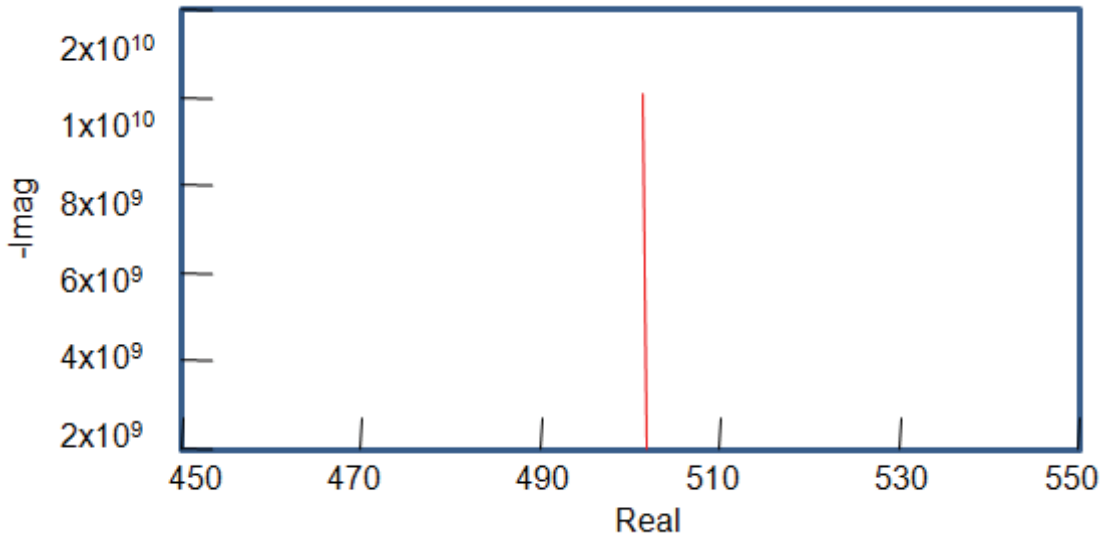




A Purely Capacitive Coating

A metal covered with an undamaged coating generally has a very high impedance. The equivalent circuit for such a situation is in the Figure:



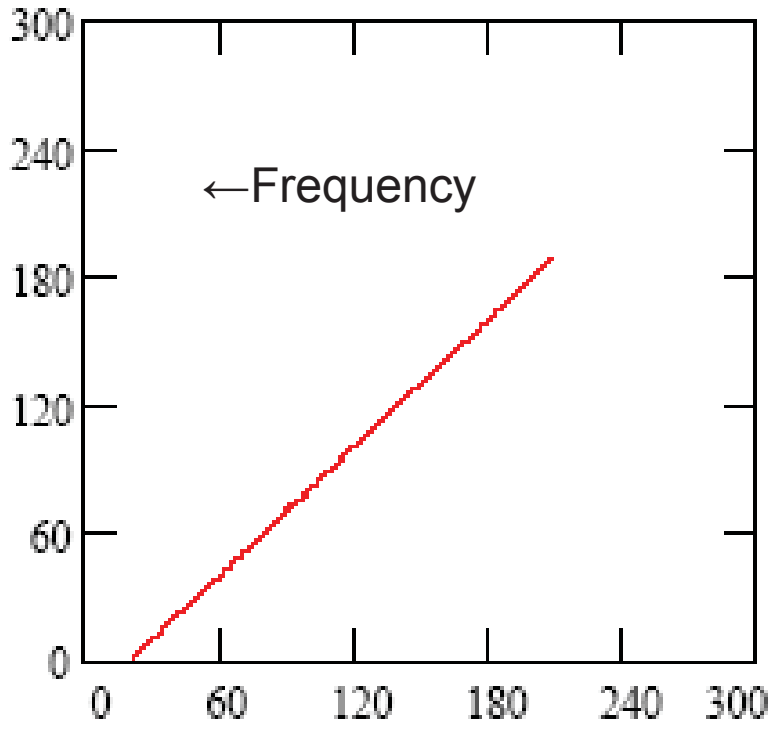


The model includes a resistor (due primarily to the electrolyte) and the coating capacitance in series.
A Nyquist plot for this model is shown in the Figure. In making this plot, the following values were assigned:
R = 500 Ω (a bit high but realistic for a poorly conductive solution)
C = 200 pF (realistic for a 1 cm^2 sample, a 25 μm coating, and ε_r = 6)
f_i = 0.1 Hz (lowest scan frequency -- a bit higher than typical)
f_f = 100 kHz (highest scan frequency)

The value of the capacitance cannot be determined from the Nyquist plot. It can be determined by a curve fit or from an examination of the data points. Notice that the intercept of the curve with the real axis gives an estimate of the solution resistance. The highest impedance on this graph is close to 10^{10} Ω . This is close to the limit of measurement of most EIS systems

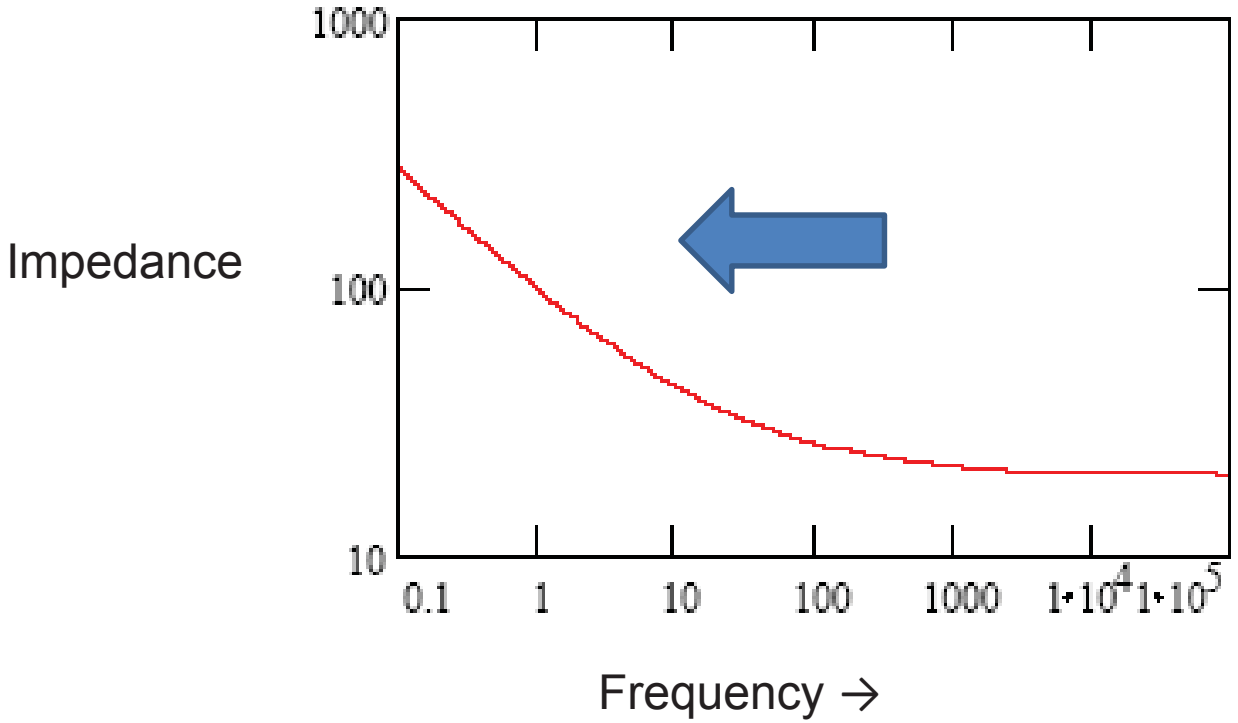
EIS

- Diffusion or Mass Transfer controlled process
- Nyquist plot - Warburg Impedance



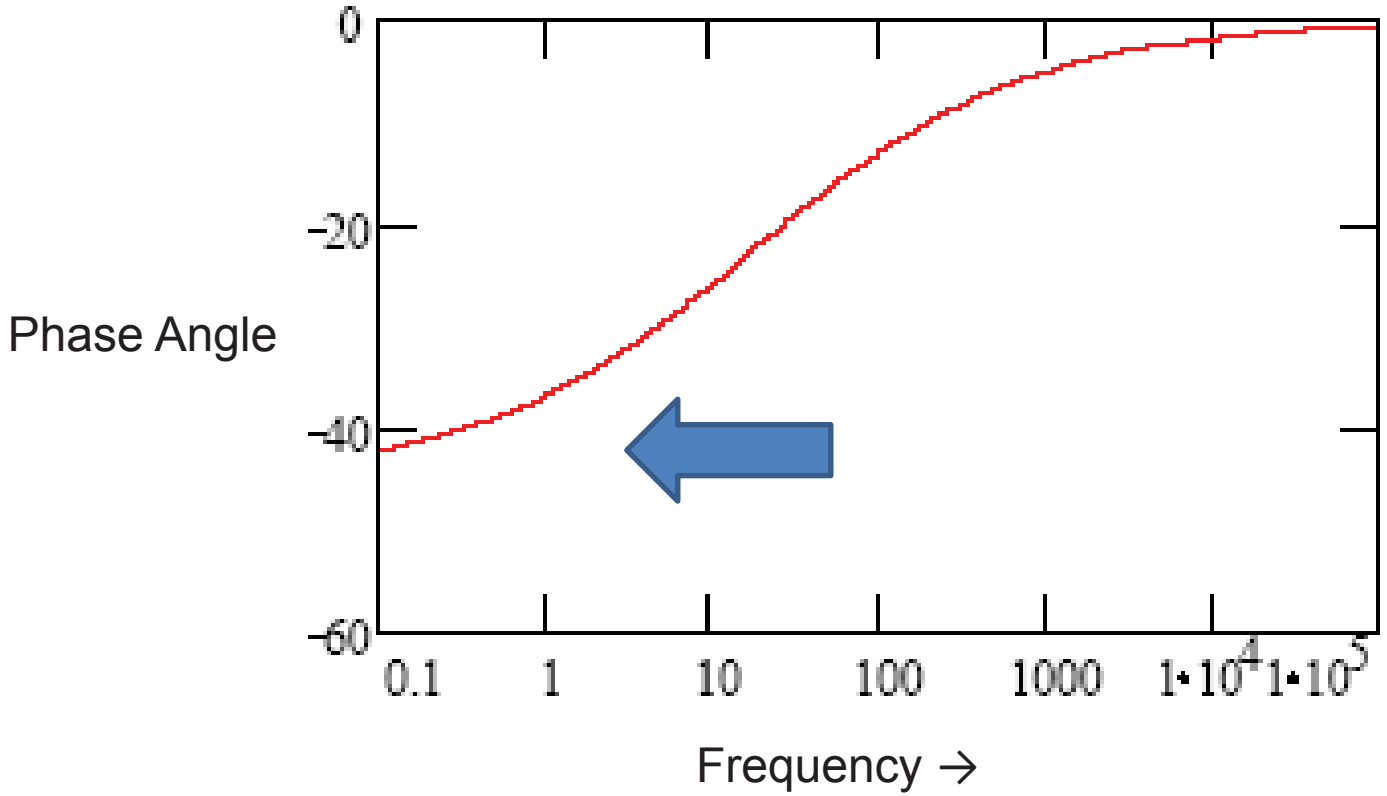
EIS

- Diffusion or Mass Transfer controlled process
- Bode Impedance plot

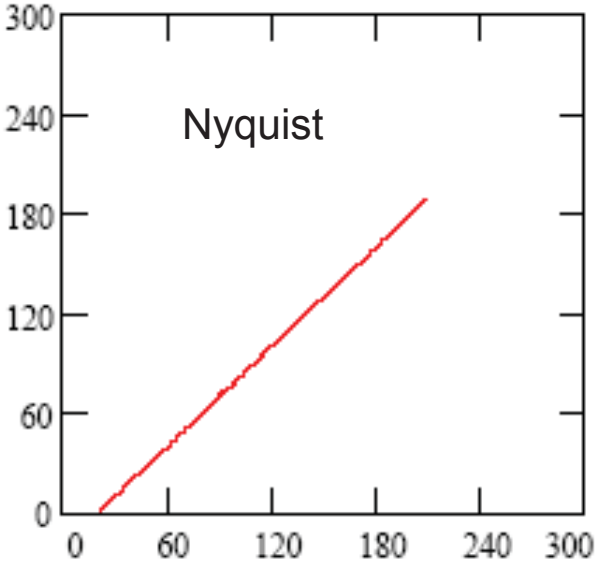


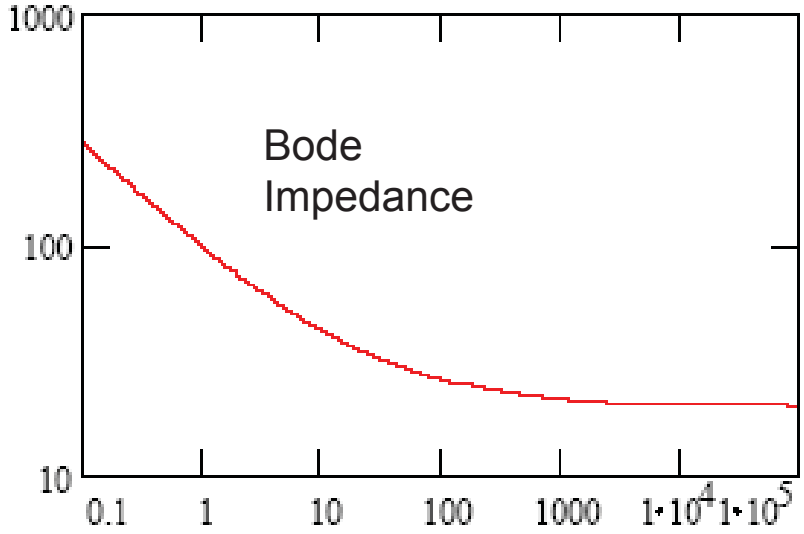
EIS

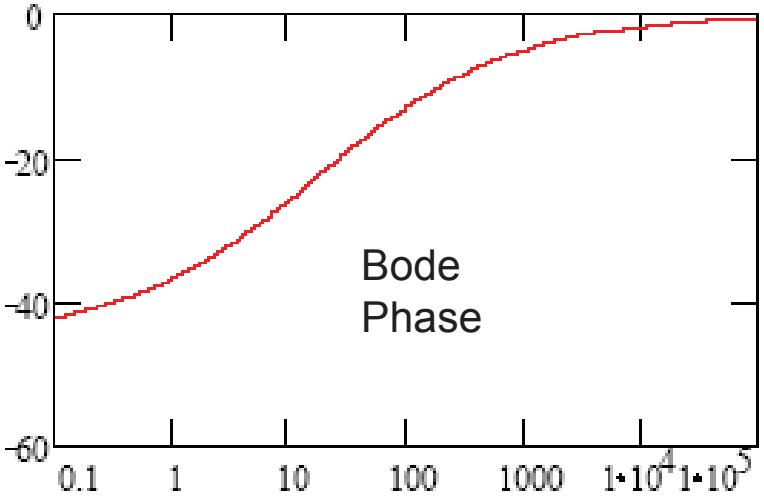
- Diffusion or Mass Transfer controlled process
- Bode Phase plot



EIS – Mass Transfer Controlled Process (Summary)

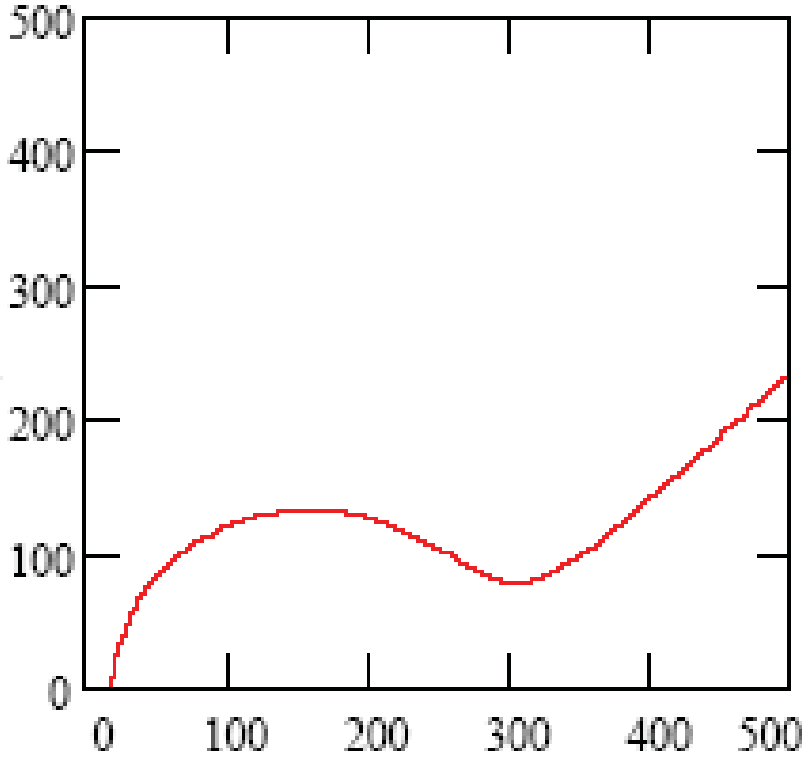


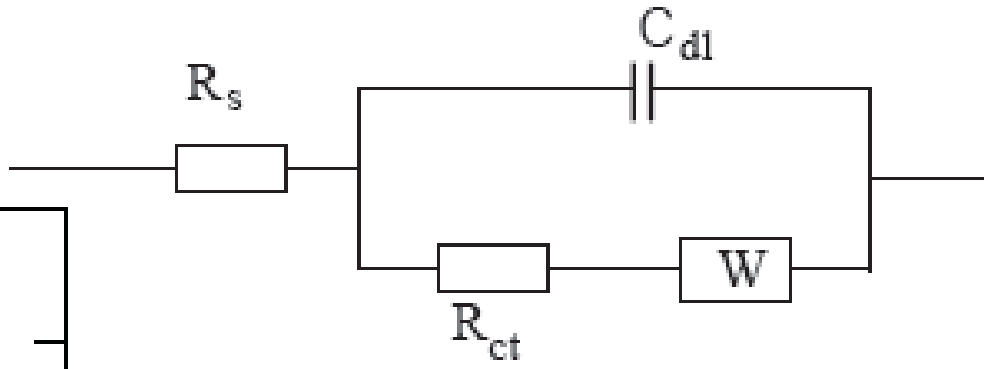




LIPI

EIS Equivalent Circuit for a Mixed Kinetic and Charge Transfer Controlled Process





LIPI

The electrolyte resistance

Standard chemical handbooks list σ values for specific solutions. For other solutions and solid materials, you can calculate σ from specific ion conductances. The units for σ are Siemens per meter (S/m). The Siemens is the reciprocal of the ohm, so 1 S = 1/ohm

Unfortunately, most electrochemical cells do not have uniform current distribution through a definite electrolyte area. The major problem in calculating solution resistance therefore concerns determination of the current flow path and the geometry of the electrolyte that carries the current. A comprehensive discussion of the approaches used to calculate practical resistances from ionic conductances is well beyond the scope of this manual.
Fortunately, you don't usually calculate solution resistance from ionic conductances. Instead, it is found when you fit a model to experimental EIS data.

Double Layer Capacitance

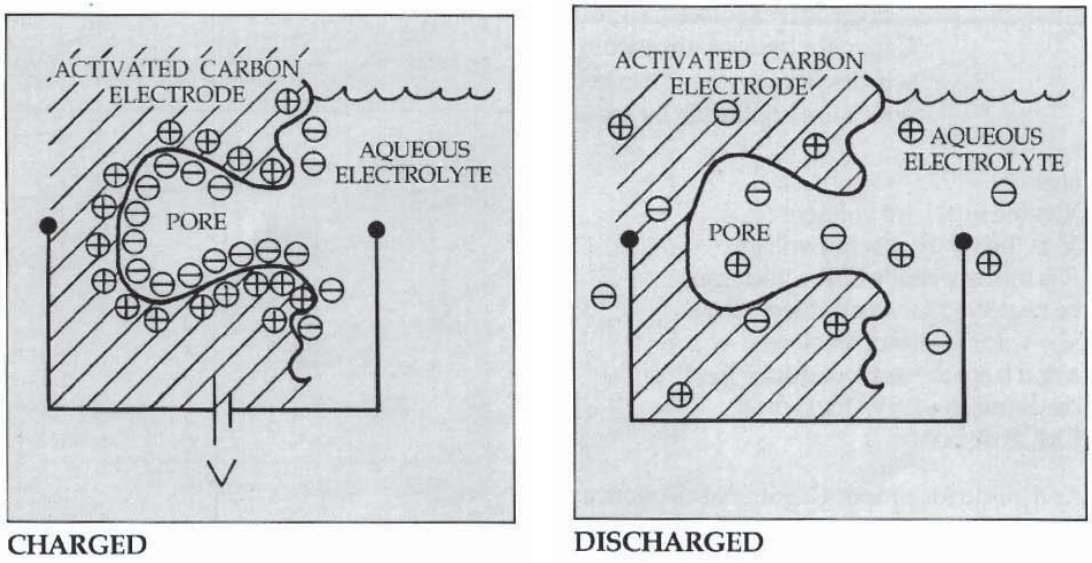
A electrical double layer exists at the interface between an electrode and its surrounding electrolyte.

This double layer is formed as ions from the solution "stick on" the electrode surface. Charges in the electrode are separated from the charges of these ions. The separation is very small, on the order of angstroms.

Charges separated by an insulator form a capacitor. On a bare metal immersed in an electrolyte, you can estimate that there will be approximately 30 μF of capacitance for every cm^2 of electrode area.

The value of the double layer capacitance depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

Principle of the Electric Double-Layer: Here C electrodes



LIPI

Polarization Resistance

Whenever the potential of an electrode is forced away from it's value at open circuit, that is referred to as polarizing the electrode.

When an electrode is polarized, it can cause current to flow via electrochemical reactions that occur at the electrode surface. The amount of current is controlled by the kinetics of the reactions and the diffusion of reactants both towards and away from the electrode.

In cells where an electrode undergoes uniform corrosion at open circuit, the open circuit potential is controlled by the equilibrium between two different electrochemical reactions.
One of the reactions generates cathodic current and the other anodic current. The open circuit potential ends up at the potential where the cathodic and anodic currents are equal. It is referred to as a mixed potential. The value of the current for either of the reactions is known as the corrosion current.

LIPI

The Butler Volmer equation: For the polarization resistance of simple reactions at electrodes

When there are two simple, kinetically controlled reactions occurring, the potential of the cell is related to the current by the following (known as the Butler-Volmer equation).

$$I = I_{corr}\left(10^{\frac{\left(E-Eoc\right)}{\beta a}} - 10^{\frac{-\left(E-Eoc\right)}{\beta c}}\right)$$

I is the measured cell current in amps,
I_{corr} is the corrosion current in amps,
E_{oc} is the open circuit potential in volts,
β_a is the anodic Beta coefficient in volts/decade,
β_c is the cathodic Beta coefficient in volts/decade

If we apply a small signal approximation ($E-E_{oc}$ is small) to the buler Volmer equation, we get the following:

$$I_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \cdot \left(\frac{1}{R_p}\right)$$

which introduces a new parameter, R_p, the polarization resistance. As you might guess from its name, the polarization resistance behaves like a resistor.
If the Tafel constants β_i are known, you can calculate the I_{corr} from R_p. The I_{corr} in turn can be used to calculate a corrosion rate.
We will further discuss the R_p parameter when we discuss cell models.

Charge Transfer Resistance

A similar resistance is formed by a single kinetically controlled electrochemical reaction. In this case we do not have a mixed potential, but rather a single reaction at equilibrium. Consider a metal substrate in contact with an electrolyte. The metal molecules can electrolytically dissolve into the electrolyte, according to:

$$Me \Leftrightarrow Me^{n+} + ne^{-}$$

or more generally:

$$Red \Leftrightarrow Ox + ne^{-}$$

In the forward reaction in the first equation, electrons enter the metal and metal ions diffuse into the electrolyte. Charge is being transferred.
This charge transfer reaction has a certain speed. The speed depends on the kind of reaction, the temperature, the concentration of the reaction products and the potential.
The general relation between the potential and the current holds:

$$i = i_0 \left[\frac{C_O}{C_O^*} e^{\left(\frac{\alpha n F \eta}{RT}\right)} - \frac{C_R}{C_R^*} e^{\frac{-(1-\alpha) n F \eta}{RT}} \right]$$

i_o = exchange current density
C_o = concentration of oxidant at the electrode surface
C_o^* = concentration of oxidant in the bulk
C_R = concentration of reductant at the electrode surface

F = Faradays constant
T = temperature
R = gas constant
a = reaction order
n = number of electrons involved
h = overpotential (E - E_0)

Diffusion: Warburg impedance with infinite thickness

Diffusion can create an impedance known as the Warburg impedance. This impedance depends on the frequency of the potential perturbation. At high frequencies the Warburg impedance is small since diffusing reactants don't have to move very far. At low frequencies the reactants have to diffuse farther, thereby increasing the Warburg impedance.
The equation for the "infinite" Warburg impedance

$$Z = \sigma(\omega)^{-1/2}(1 - j)$$

On a Nyquist plot the infinite Warburg impedance appears as a diagonal line with a slope of 0.5.
On a Bode plot, the Warburg impedance exhibits a phase shift of 45°.
In the above equation, *s* is the Warburg coefficient defined as:

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{C_O^*\sqrt{D_O}} + \frac{1}{C_R^*\sqrt{D_R}}\right)$$

ω = radial frequency
D_O = diffusion coefficient of the oxidant
D_R = diffusion coefficient of the reductant
A = surface area of the electrode
n = number of electrons transferred
C* = bulk concentration of the diffusing species (moles/cm^3)

Constant Phase Element (for double layer capacity in real electrochemical cells)

Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element (CPE) as defined below.

$$Z = A(i\omega)^{-\alpha}$$

When this equation describes a capacitor, the constant A = 1/C (the inverse of the capacitance) and the exponent α = 1. For a constant phase element, the exponent a is less than one.

The "double layer capacitor" on real cells often behaves like a CPE instead of like a capacitor. Several theories have been proposed to account for the non-ideal behavior of the double layer but none has been universally accepted. In most cases, you can safely treat α as an empirical constant and not worry about its physical basis.

LIPI

Common Equivalent Circuit Models

In the following section we show some common equivalent circuits models.

To elements used in the following equivalent circuits are presented in the Table. Equations for both the admittance and impedance are given for each element.

Resistor (R)

$Z = R$

Capacitor (C)

$Z = 1 / ((\sqrt{-1})*\omega*C)$

Constant Phase Element (CPE)

$Z = 1 / [T*((\sqrt{-1})*\omega)^P]$

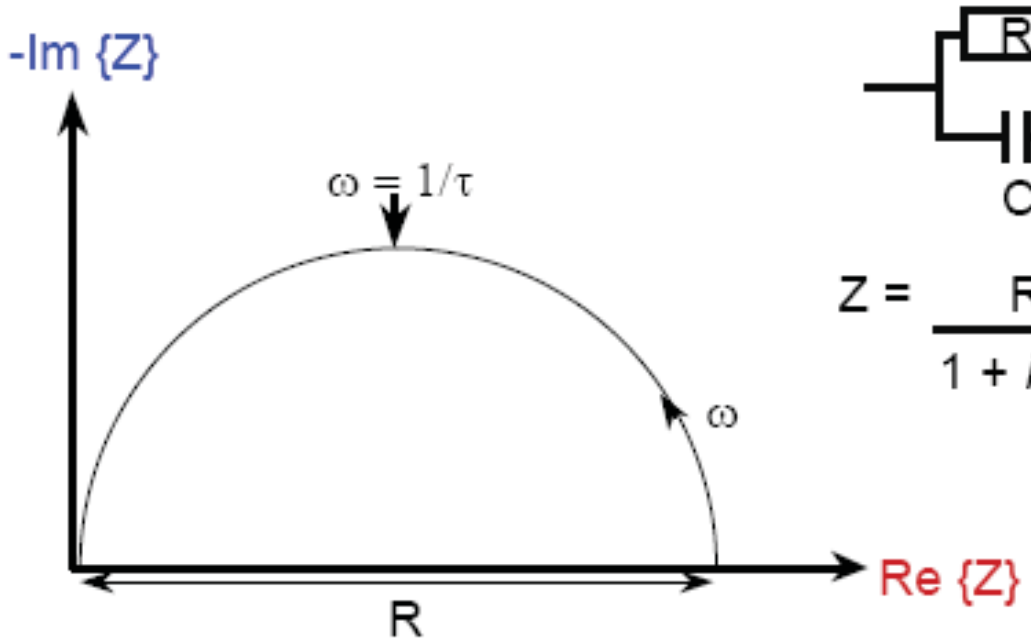
Warburg Element – Finite Length (W)

$Z = R*\tanh([(\sqrt{-1})*T*\omega]^P) / ((\sqrt{-1})*T*\omega)^P$

Equivalent element	Admittance	Impedance
R	1/R	R
C	$i\omega C$	$1/1/i\omega C$
L	$1/i\omega L$	$i\omega L$
W (infinite Warburg)	$Y_0(i\omega)^{1/2}$	$1/Y_0(i\omega)^{1/2}$
O (finite Warburg)	$Y_0\sqrt{i\omega}\coth(B\sqrt{i\omega})$	$\tanh(B\sqrt{i\omega})/\left[Y_0\sqrt{i\omega}\right]$
Q (CPE)	$Y_0(i\omega)^{\alpha}$	$1/Y_0(i\omega)^{\alpha}$

Cole-Cole Plots: Impedance Plots in the Complex Plane

When we plot the real and imaginary components of impedance in the complex plane (Argand diagram), we obtain a semicircle or partial semicircle for each parallel RC Voigt network:



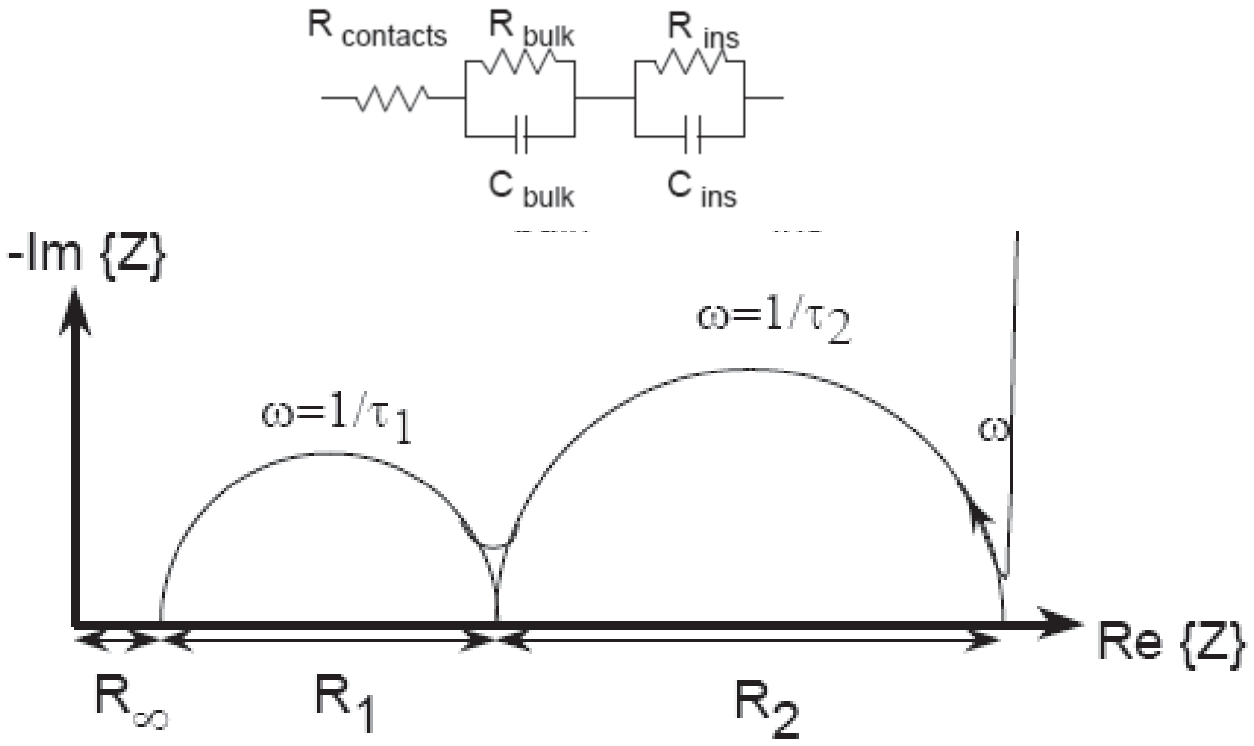
$$Z = \frac{R}{1 + i\,\omega\tau}$$

The diameter corresponds to the resistance R.
The frequency at the 90° position corresponds to 1/t = 1/RC

LIPI

Analyzing Circuits

By using the various Cole-Cole plots we can calculate values of the elements of the equivalent circuit for any applied bias voltage

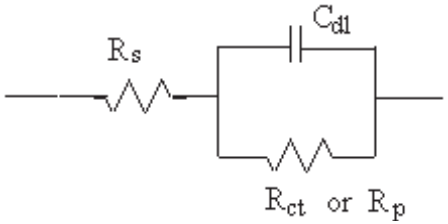


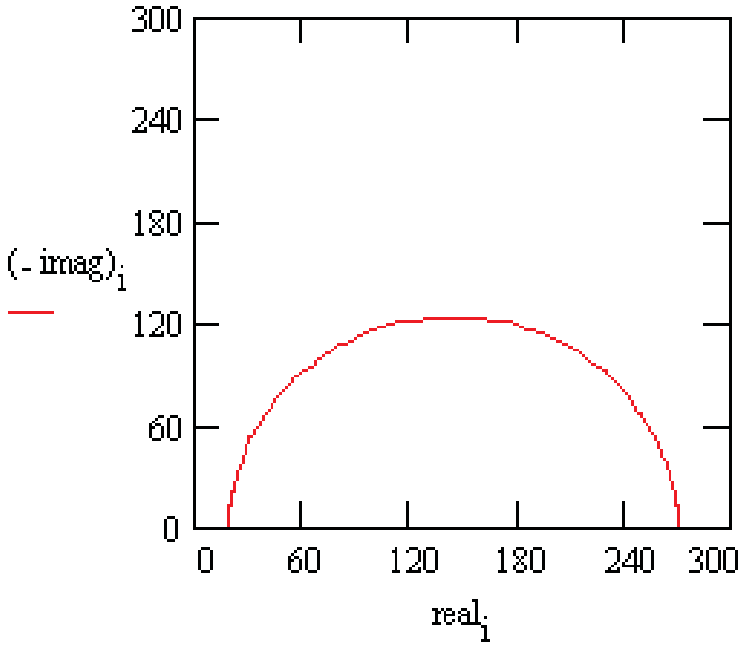
By doing this over a range of bias voltages, we can obtain:
the field distribution in the layers of the device (potential divider) and the relative widths of the layers, since C ~ 1/d

Randles Cell

The Randles cell is one of the simplest and most common cell models. It includes a solution resistance, a double layer capacitor and a charge transfer or polarization resistance. In addition to being a useful model in its own right, the Randles cell model is often the starting point for other more complex models.

The equivalent circuit for the Randles cell is shown in the Figure. The double layer capacity is in parallel with the impedance due to the charge transfer reaction





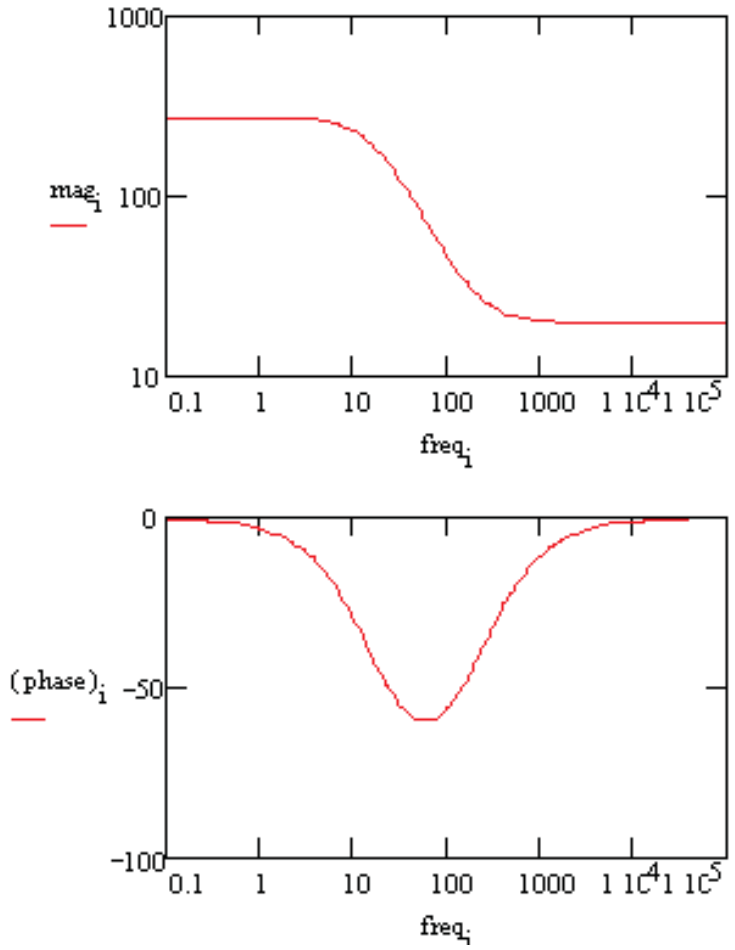
The Nyquist plot for a Randles cell is always a semicircle. The solution resistance can found by reading the real axis value at the high frequency intercept. This is the intercept near the origin of the plot. Remember this plot was generated assuming that R_s = 20 Ω and Rp= 250 Ω .

The real axis value at the other (low frequency) intercept is the sum of the polarization resistance and the solution resistance. The diameter of the semicircle is therefore equal to the polarization resistance (in this case 250Ω).

Bode Plot oft Randalls cell

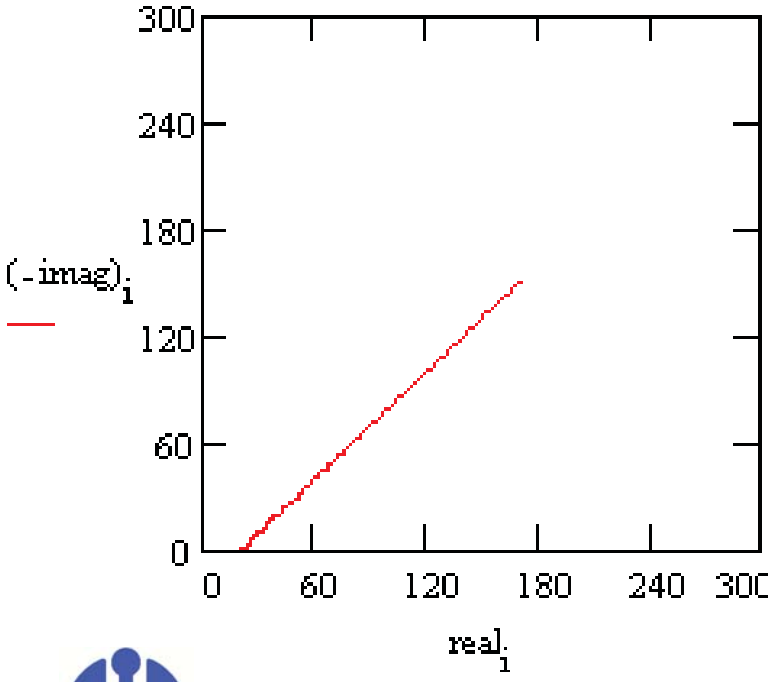
This Figure is the Bode plot for the same cell. The solution resistance and the sum of the solution resistance and the polarization resistance can be read from the magnitude plot. The phase angle does not reach 90˚ as it would for a pure capacitive impedance. If the values for R_s and R_p were more widely separated the phase would approach 90˚.

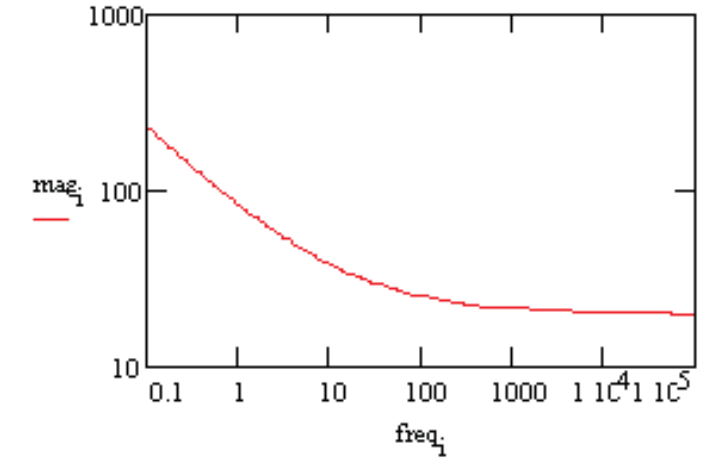
Bode Plot for 1 mm/year Corrosion Rate

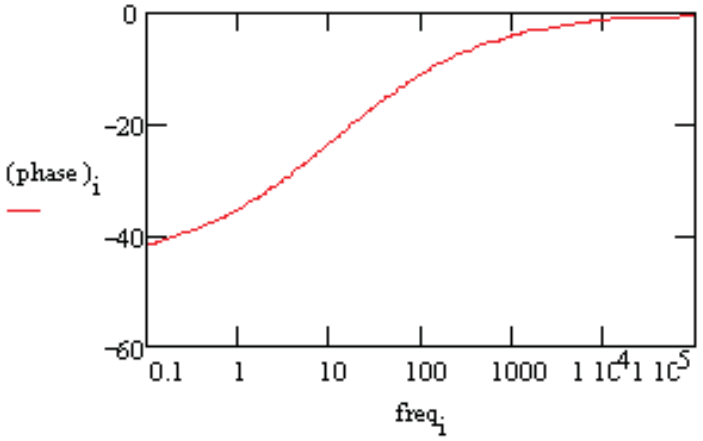


Mixed Kinetic and Diffusion Control

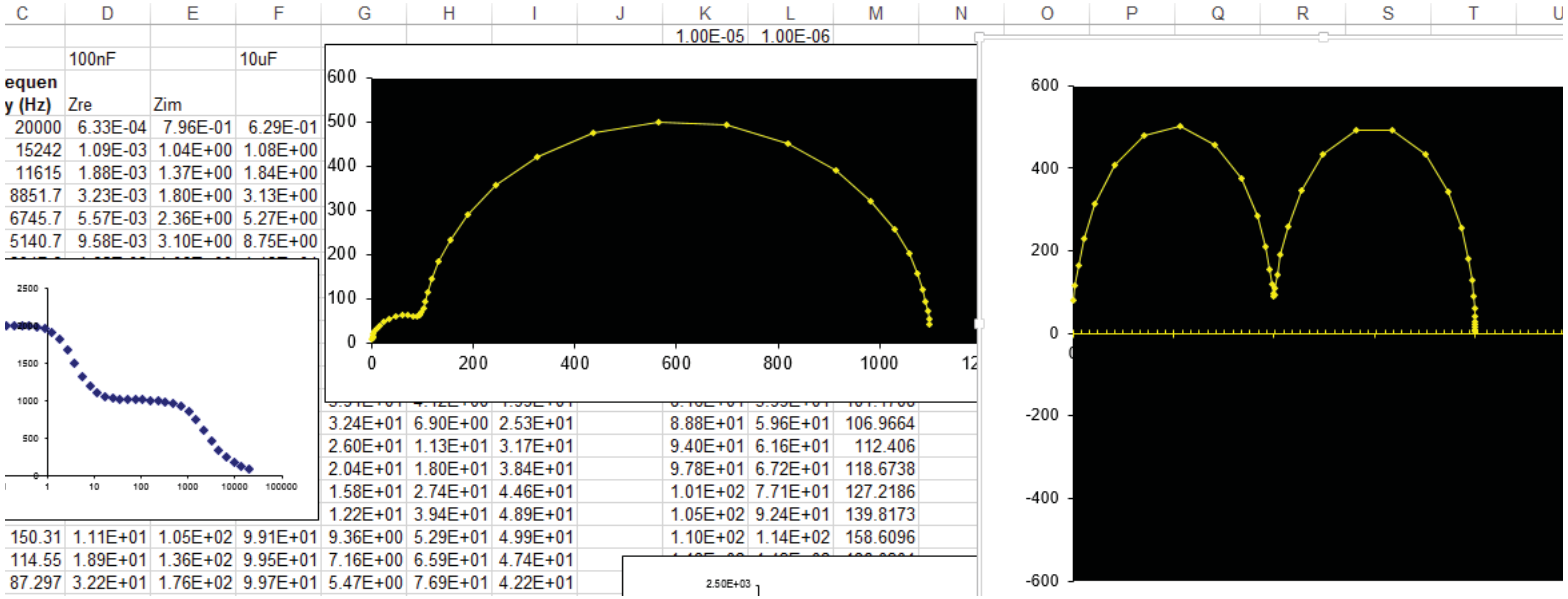
First consider a cell where semi-infinite diffusion is the rate determining step, with a series solution resistance as the only other cell impedance.
A Nyquist plot for this cell is shown in Figure 2-17. R_s was assumed to be 20 W. The Warburg coefficient calculated to be about 120 $\Omega sec^{-1/2}$ at room temperature for a two electron transfer, diffusion of a single species with a bulk concentration of 100 µM and a typical diffusion coefficient of 1.6 $x10^{-5}$ cm^2/sec. Notice that the Warburg Impedance appears as a straight line with a slope of 45°.







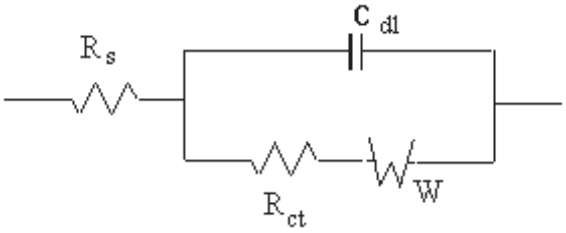
Simple simulation using excel :



	100nF		10uF
equen y (Hz)	Zre	Zim	
20000	6.33E-04	7.96E-01	6.29E-01
15242	1.09E-03	1.04E+00	1.08E+00
11615	1.88E-03	1.37E+00	1.84E+00
8851.7	3.23E-03	1.80E+00	3.13E+00
6745.7	5.57E-03	2.36E+00	5.27E+00
5140.7	9.58E-03	3.10E+00	8.75E+00
150.31	1.11E+01	1.05E+02	9.91E+01
114.55	1.89E+01	1.36E+02	9.95E+01
87.297	3.22E+01	1.76E+02	9.97E+01

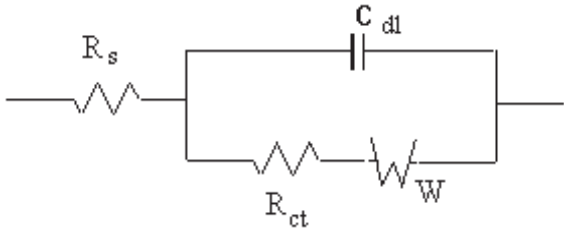
1.00E-05	1.00E-06	
3.24E+01	6.90E+00	2.53E+01
2.60E+01	1.13E+01	3.17E+01
2.04E+01	1.80E+01	3.84E+01
1.58E+01	2.74E+01	4.46E+01
1.22E+01	3.94E+01	4.89E+01
9.36E+00	5.29E+01	4.99E+01
7.16E+00	6.59E+01	4.74E+01
5.47E+00	7.69E+01	4.22E+01

8.88E+01	5.96E+01	106.9664
9.40E+01	6.16E+01	112.406
9.78E+01	6.72E+01	118.6738
1.01E+02	7.71E+01	127.2186
1.05E+02	9.24E+01	139.8173
1.10E+02	1.14E+02	158.6096

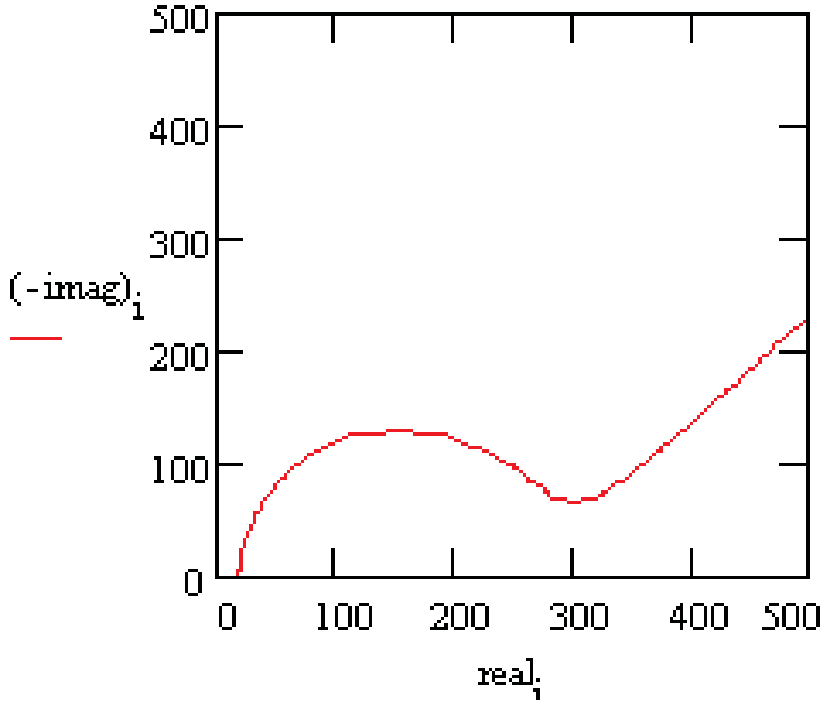


Example: Half a full cell

Adding to the previous example a double layer with capacitance and a charge transfer impedance, we get the equivalent circuit:

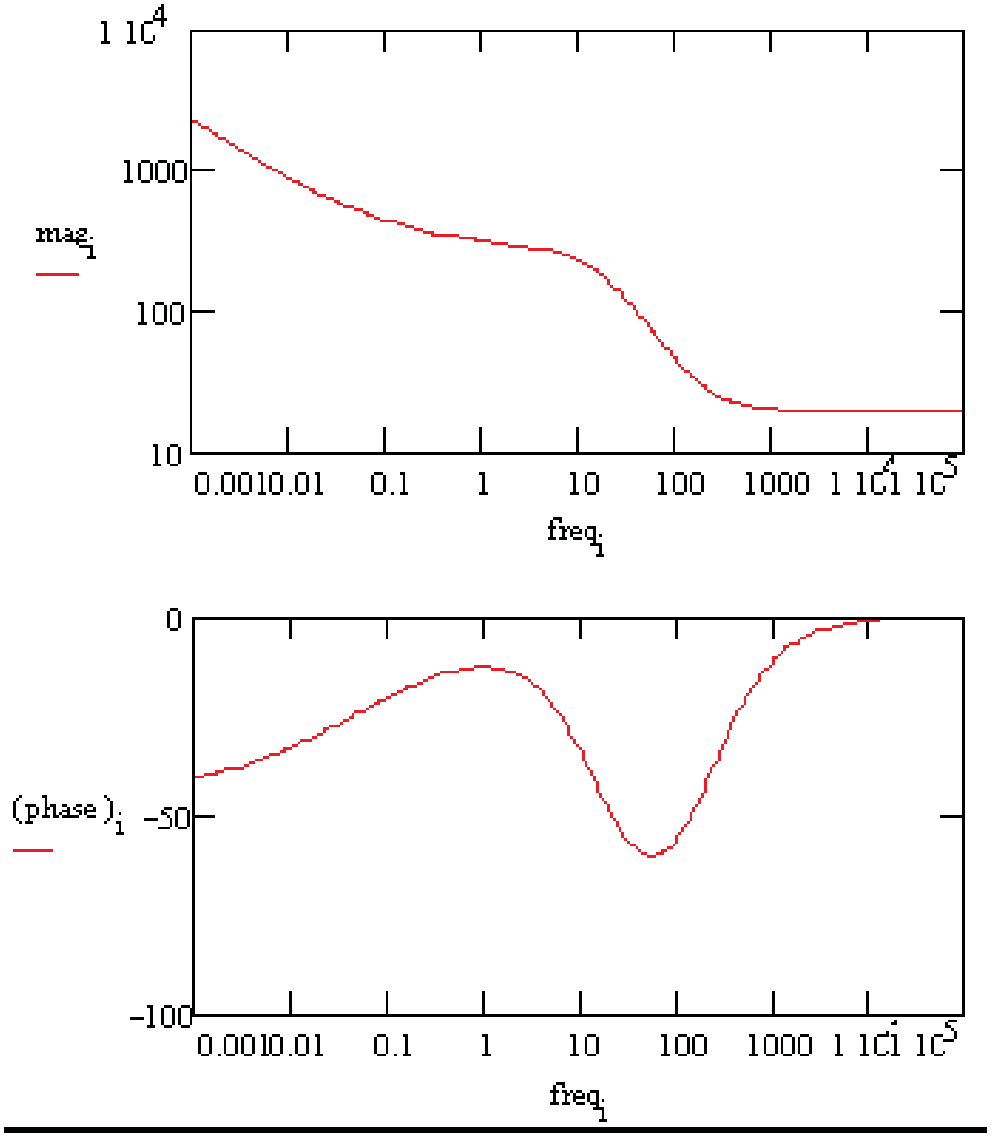


This circuit models a cell where polarization is due to a combination of kinetic and diffusion processes. The Nyquist plot for this circuit is shown in the Figure. As in the above example, the Warbug coefficient is assumed to be about 150 W $sec^{-1/2}$. Other assumptions: R_s = 20 Ω , R_{ct} = 250 Ω , and C_{dl} = 40 μF.



Bode plot

The Bode plot for the same data is shown here. The lower frequency limit was moved down to 1mHz to better illustrate the differences in the slope of the magnitude and in the phase between the capacitor and the Warburg impedance. Note that the phase approaches 45° at low frequency.



Some cases :

Preparation and electrochemical properties of Ca-doped $Li_4Ti_5O_{12}$ as anode materials in lithium-ion battery

Qianyu Zhang[a], Chengli Zhang[a], Bo Li[a], Shifei Kang[a], Xi Li[a,*], Yangang Wang[b,*]

Electrochemical tests were carried out by using the above coin-type half cells. Galvanostatic charge–discharge measurements were performed on Land CT2001A (Wuhan, China) tester at 1 C, 5 C and 10 C, respectively. For the rate performance measurement, the current was varied from 0.5 C to 20 C. Cyclic voltammetry (CV) was measured on an electrochemical workstation (CHI 660E) between 1.0 and 2.5 V (*vs.* Li/Li^+) at a scanning rate of 0.5 mV s^{-1}. Electrochemical impedance spectra (EIS) measurements were also measured at the electrochemical workstation with a ±5 mV AC signal and a frequency range from 10 mHz to 1 MHz. All experiments were carried out at room temperature (25 °C).

Fig. 9 shows the electrochemical impedance spectra (EIS) curves of the $Li_{4-x}Ca_xTi_5O_{12}$ ($0 \le x \le 0.2$) electrodes at the voltage of 1.55 V after the first cycle. EIS are fitted by using an equivalent circuit. All the EIS curves are composed of a depressed semicircle at the high to intermediate frequency range, and there is a straight line at lowest frequency region. The high frequency semicircle is related to the charge transfer resistance at the active material interface, while the sloping line at the low frequency end indicates the Warburg impedance caused by a semi-infinite diffusion of Li^+ ion in the electrode. In the equivalent circuit, R_s is the ohmic resistance of electrolyte; R_{ct} is the charge transfer resistance; CPE is placed to represent the double layer capacitance and passivation film capacitance; Z_w represents the Warburg impedance [24,36]. As seen from Fig. 9, the charge transfer resistance (R_{ct}) of Ca-doped electrodes is much lower than that of the pure LTO, indicating that Ca doping is favorable to improve the electronic conductivity. Moreover, the increased slope in the low frequency end for the Ca-doped samples demonstrates that Ca-doping can improve Li^+ migration in LTO. Some of the parameters fitted by ZView software are listed in Table 3. It can be seen that the exchange current density ($i^0 = R_T/nFR_{ct}$) of the $Li_{3.9}Ca_{0.1}Ti_5O_{12}$ sample is the highest among all samples. Thus, the charge

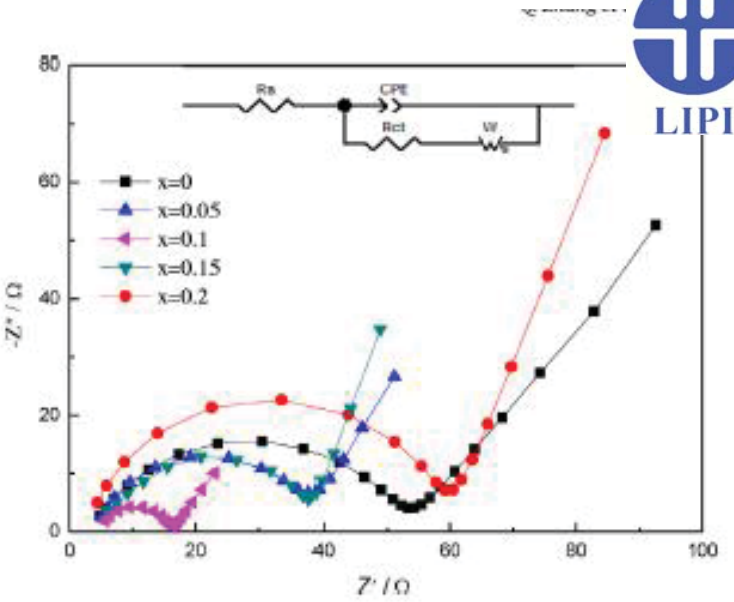


Fig. 9. Electrochemical impedance spectra of $Li_{4-x}Ca_xTi_5O_{12}$ ($0 \le x \le 0.2$) electrodes. Inset is the equivalent circuit.

pristine LTO, which indicate that Ca-doping is favorable for reducing the electrode polarization. Besides, the $Li_{3.9}Ca_{0.1}Ti_5O_{12}$ shows the least potential difference among all the doped samples, suggesting that too high amount of doping is adverse. Thus, the optimal ratio of Ca-doping is 0.1, which exhibits the lowest electrode polarization.

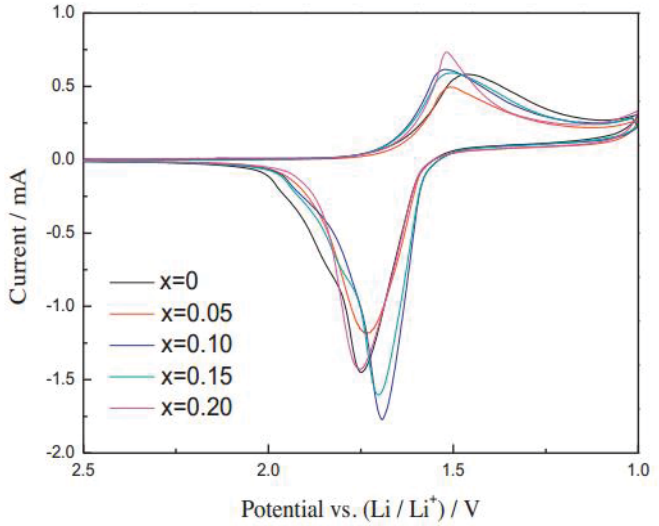


Fig. 7. Cyclic voltammograms of $Li_{4-x}Ca_xTi_5O_{12}$ ($0 \le x \le 0.2$) samples. Scan rate: 0.5 mV s^{-1}.

of all investigated electrodes are similar, suggesting that Ca-doping do not change the electrochemical reaction process of LTO. The oxi-

Ionics
https://doi.org/10.1007/s11581-018-2633-0

ORIGINAL PAPER

Effects of activated carbon treatment on $Li_4Ti_5O_{12}$ anode material synthesis for lithium-ion batteries

Achmad Subhan[1] · Ferensa Oemry[1] · Siti Nailul Khusna[2] · Erna Hastuti[2]

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Table 2 The impedance parameters of non-AC and AC-treated $Li_4Ti_5O_{12}$ samples

wt% AC	R_o (Ω)	R_{ct} (Ω)	σ_w (Ω cm^2 s$^{-1/2}$)	D_{Li} (cm^2 s^{-1})
NL-1 (0)	9.46	90.50	81.59	6.91×10^{-14}
NL-2 (3)	23.74	86.26	82.70	6.73×10^{-14}
NL-3 (6)	10.89	69.31	54.86	1.53×10^{-13}
NL-4 (10)	4.83	62.17	61.82	1.20×10^{-13}

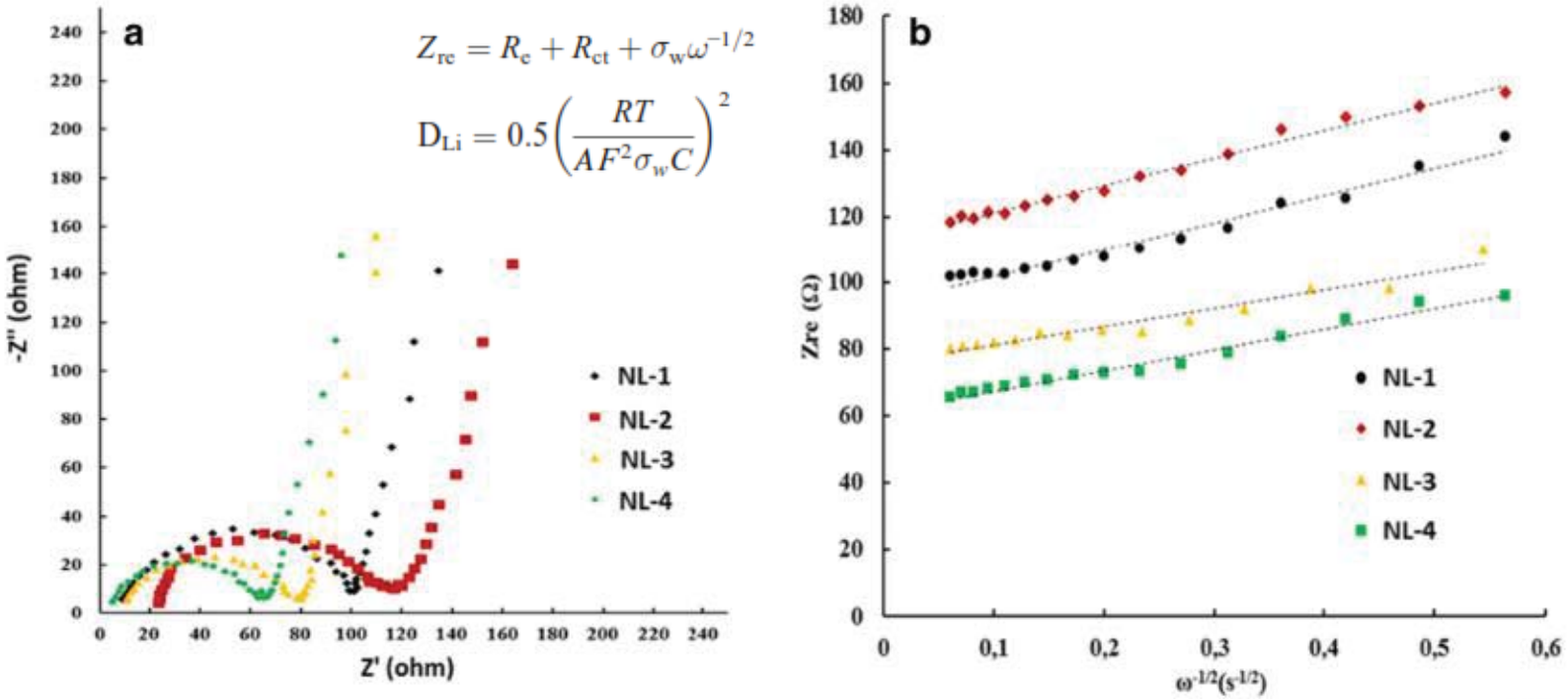
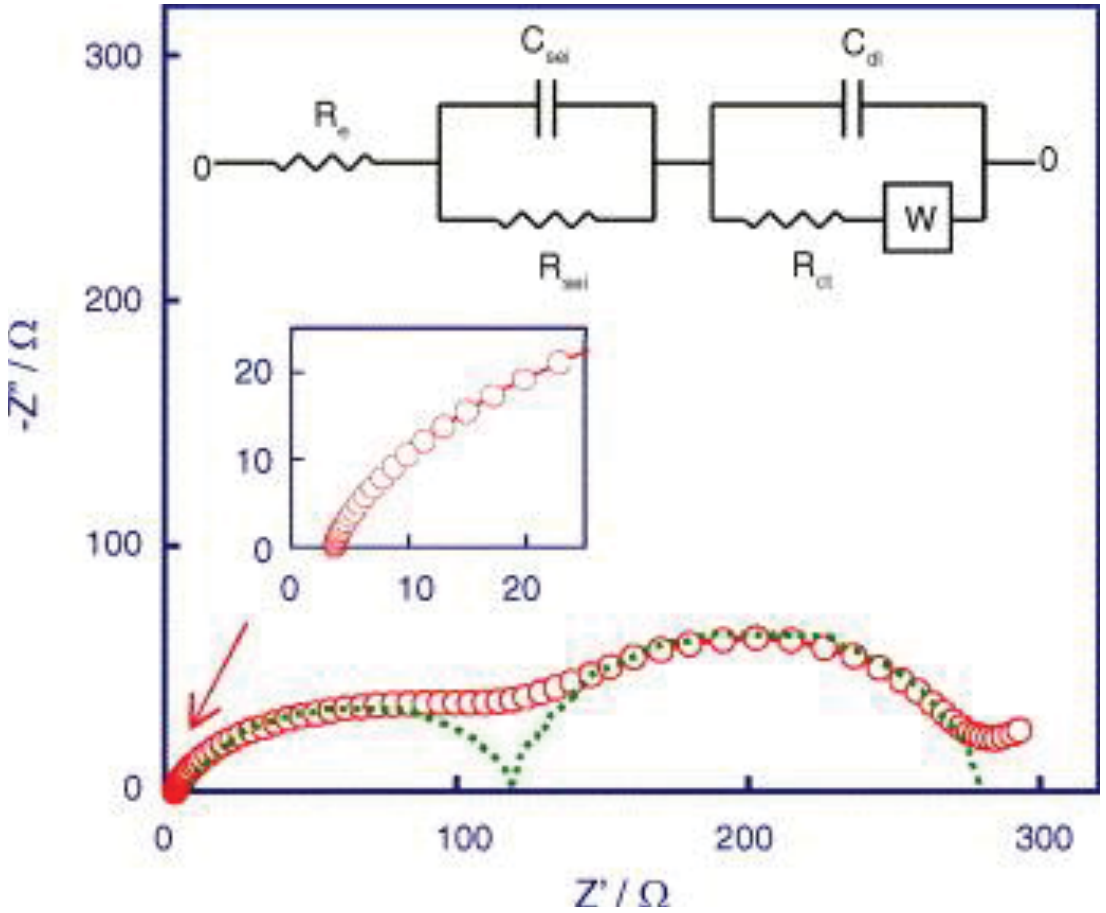
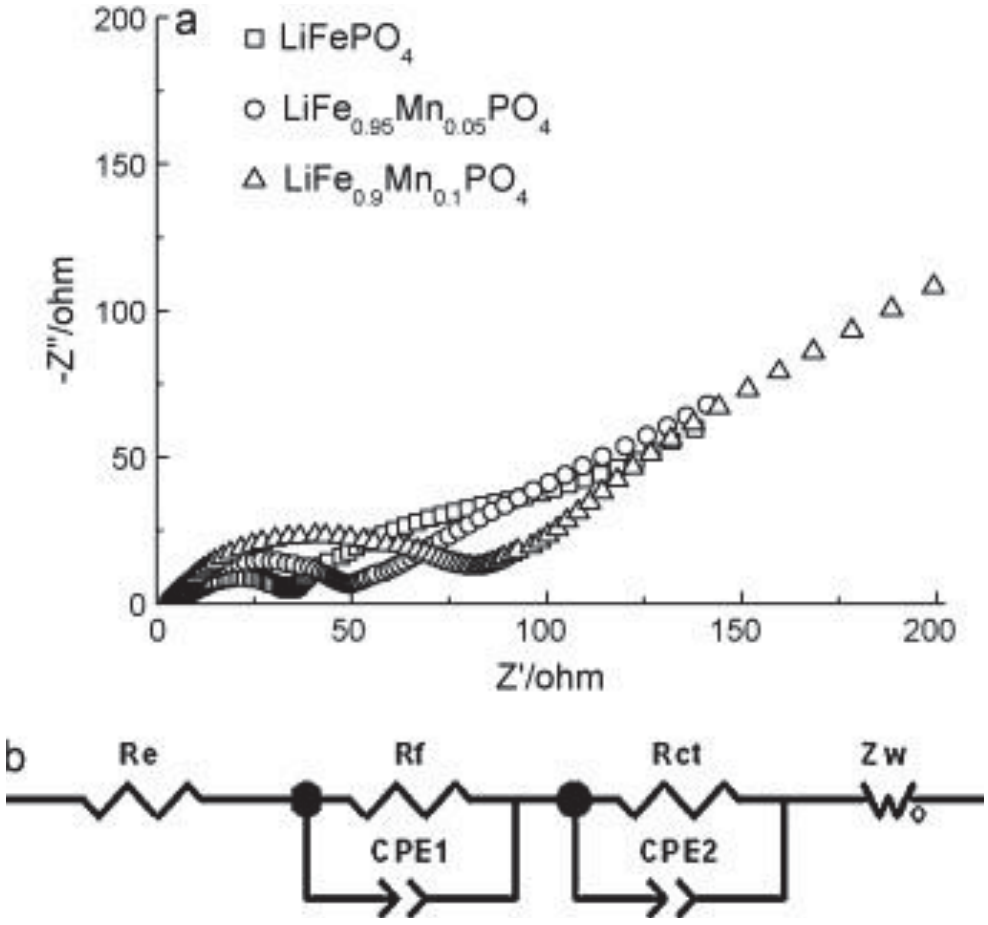
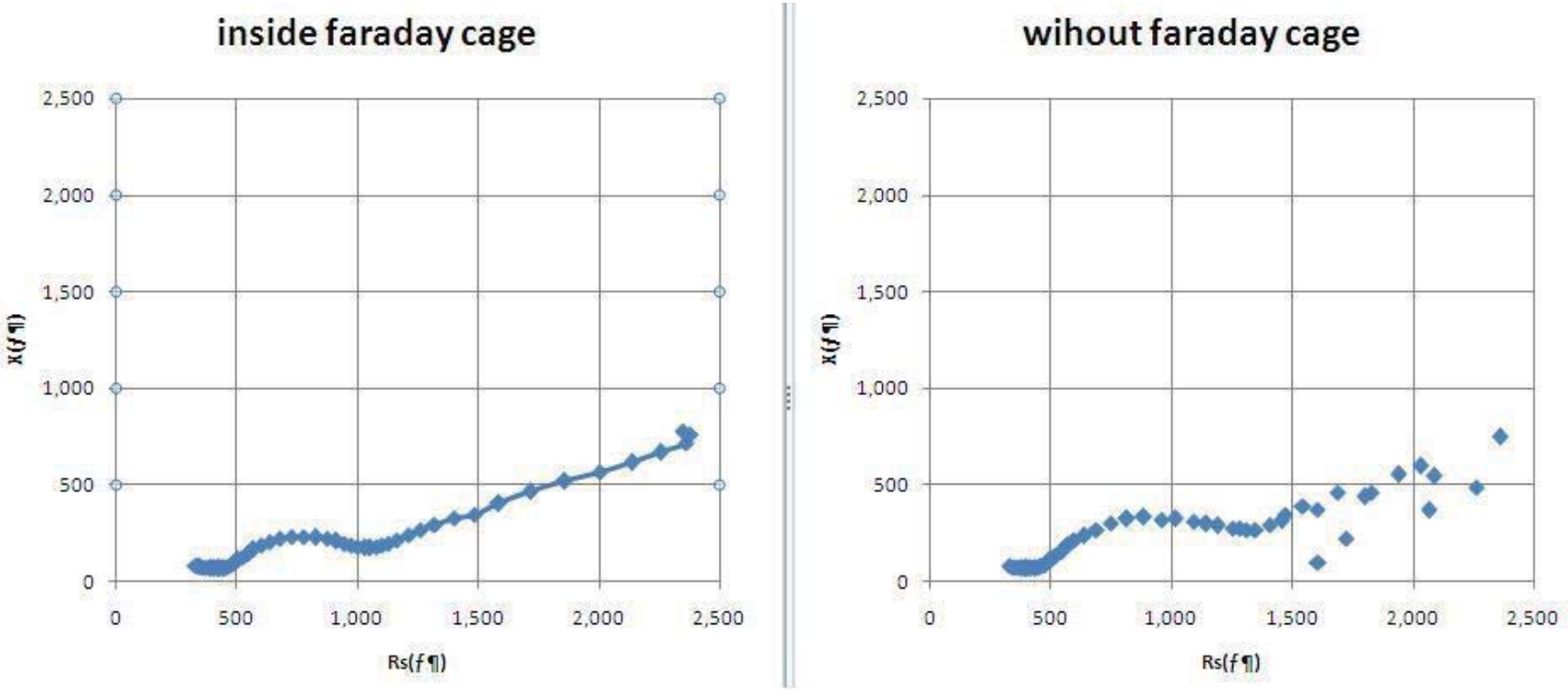


Fig. 6 **a** Nyquist plot of samples NL-1, NL-2, NL-3, and NL-4 obtained from EIS measurement and **b** relationship between real impedance and $\omega^{-1/2}$ at low-frequency region


300
200
100
0
-Z'' / Ω
0
100
200
300
Z' / Ω
20
10
0
0
10
20
W
0
0

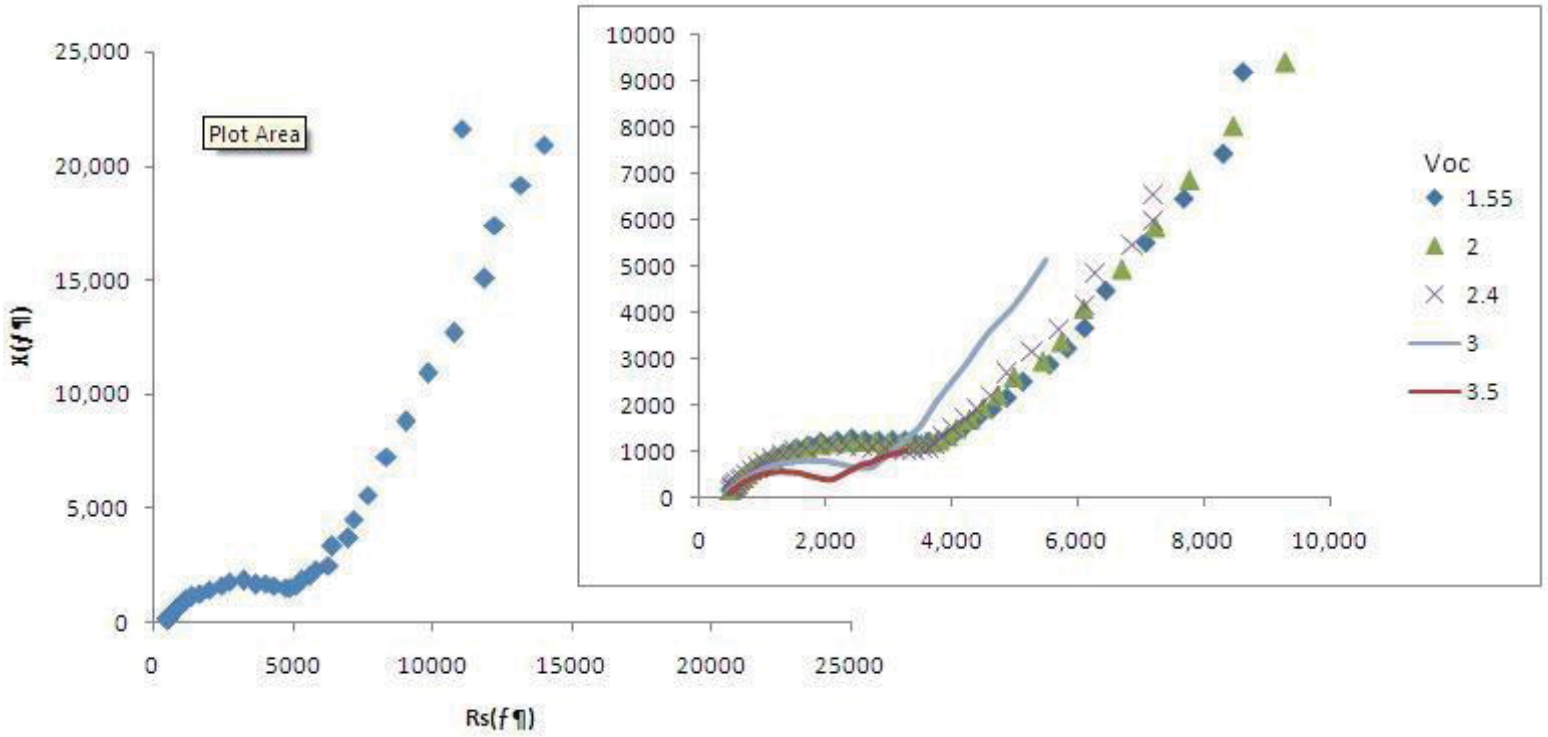

a
LiFePO4
LiFe0.95Mn0.05PO4
LiFe0.9Mn0.1PO4
-Z''/ohm
Z'/ohm
0
50
100
150
200
b
Re
Rf
Rct
Zw
CPE1
CPE2

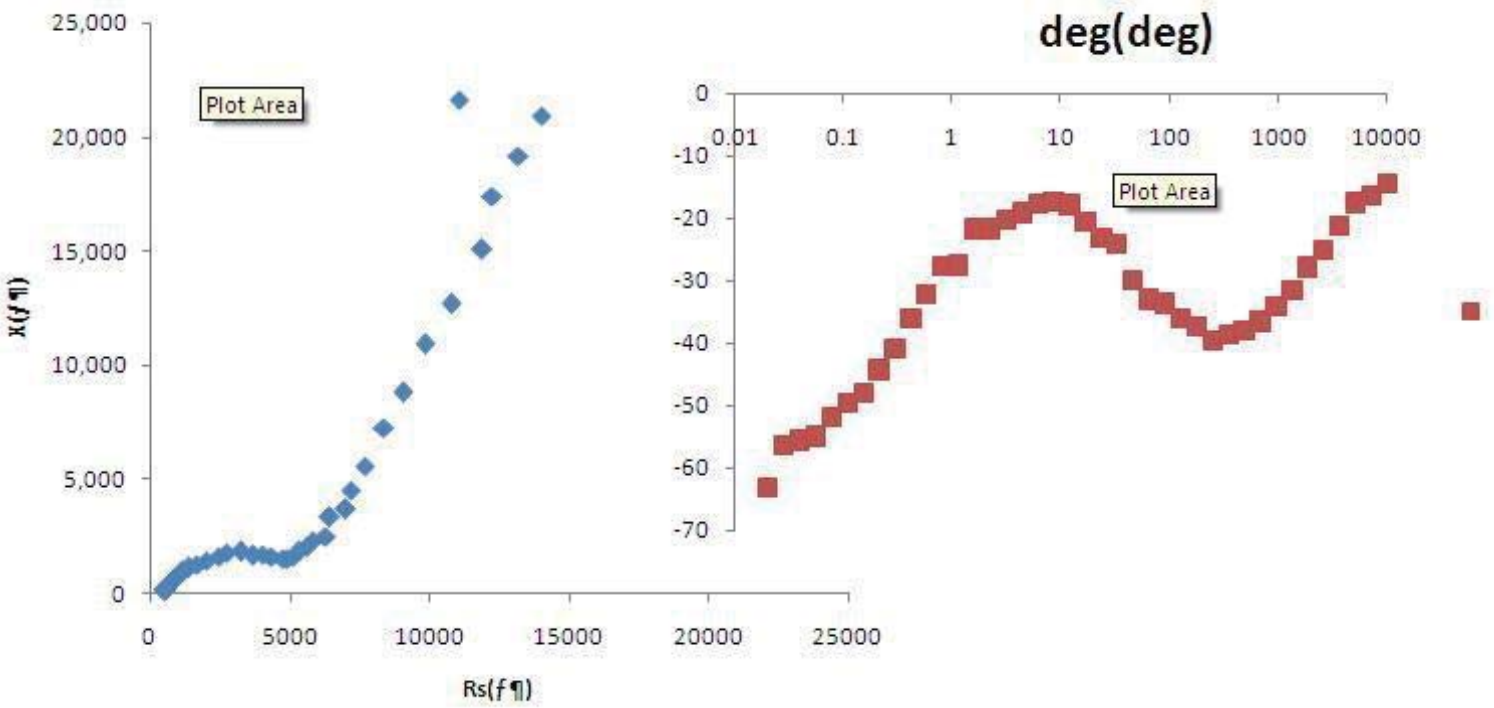
Faraday cage



Sample pouch cell 80 mAh.

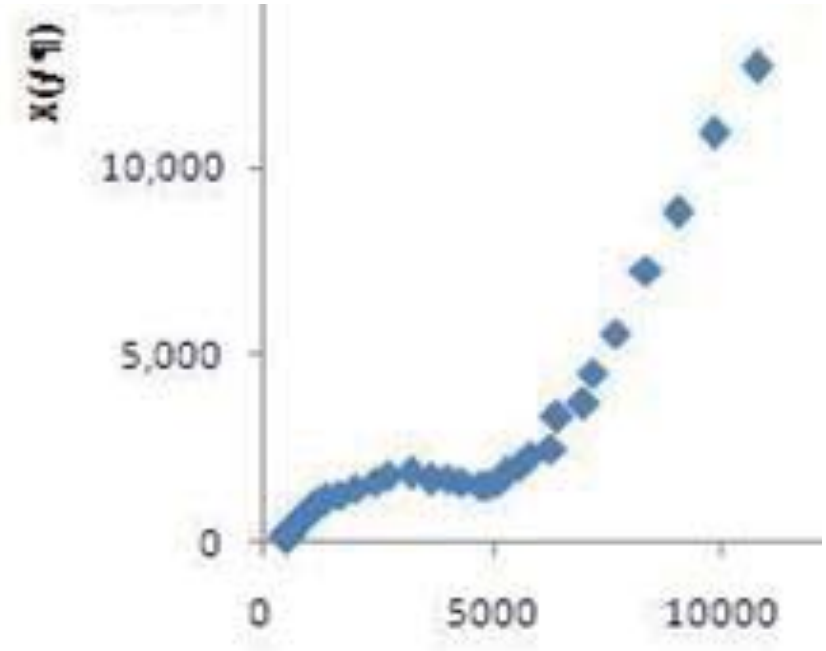
Hioki vs AutoLab



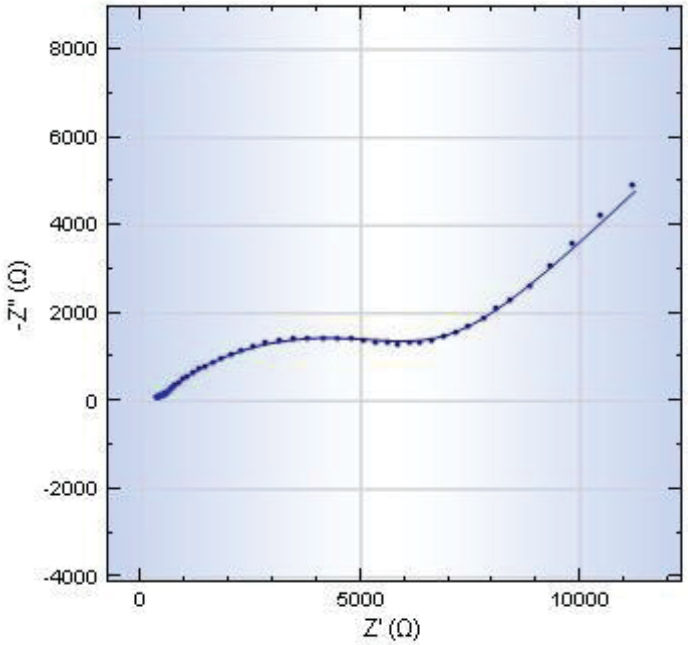

25,000
20,000
15,000
10,000
5,000
0
X(f¶)
Plot Area
0
5000
10000
15000
20000
25000
Rs(f¶)
deg(deg)
0
-10
-20
-30
-40
-50
-60
-70
0.01
0.1
1
10
100
1000
10000
Plot Area

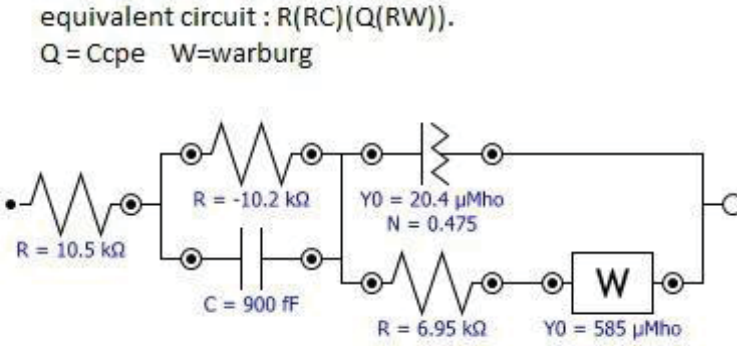
Hioki 3522

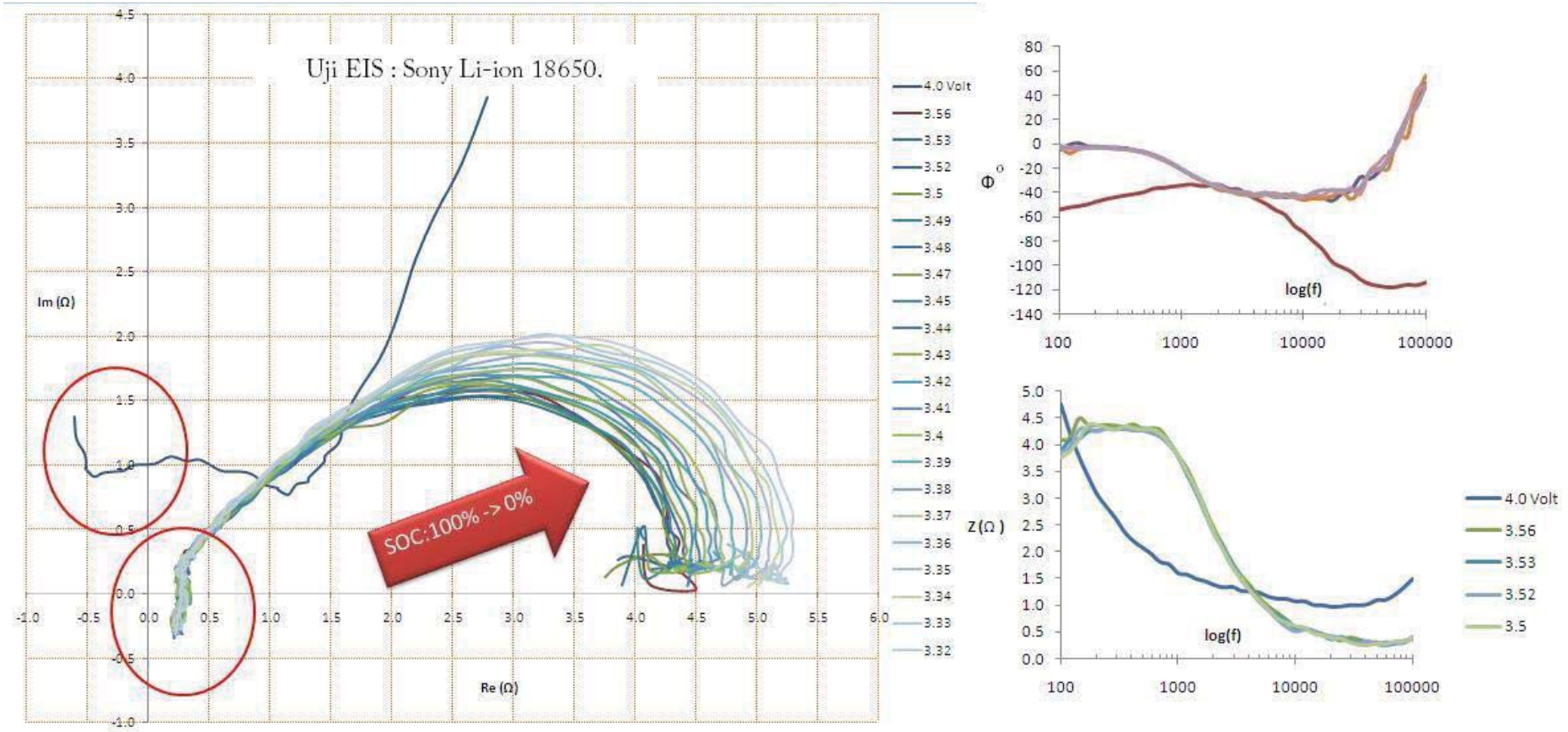
*) Metalurgi UI.



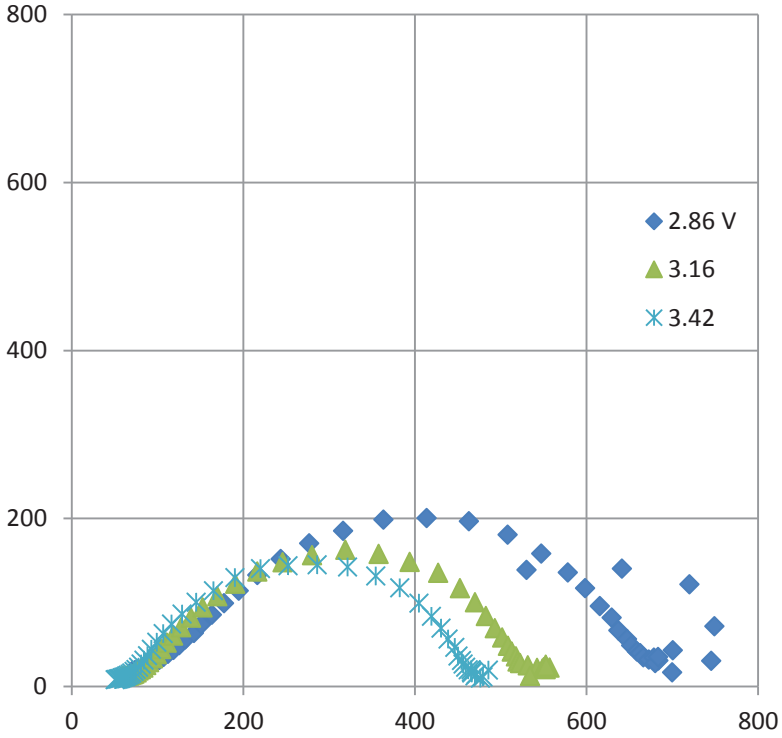
Autolab



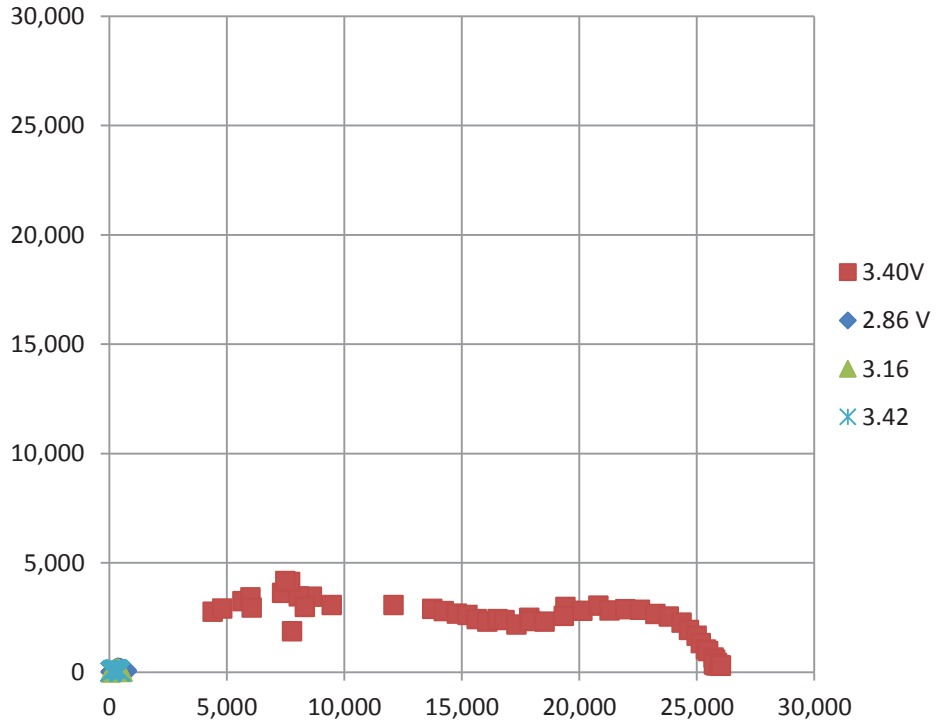



Uji EIS : Sony Li-ion 18650.
Im (Ω)
Re (Ω)
SOC:100% -> 0%
4.0 Volt
3.56
3.53
3.52
3.5
3.49
3.48
3.47
3.45
3.44
3.43
3.42
3.41
3.4
3.39
3.38
3.37
3.36
3.35
3.34
3.33
3.32
Φ °
log(f)
Z (Ω)
log(f)
4.0 Volt
3.56
3.53
3.52
3.5

Same Voc, but impedance ?



JK-20



JK-23

3.Charge-Discharge Schedule Li-ion

- CC- CV. Power, energy, C-rates, load (± r ohm).
- Voltage range.
- Rate capacity.
- Sampling time.
- Temperature < 50^{o}C.

Result

• Show result in graphical form, Voltage vs capacity . Capacity vs cycle time, etc.

$$C_{total} = \sum_{i}^{j} \Delta t_i . i_i$$

• Internal resistance

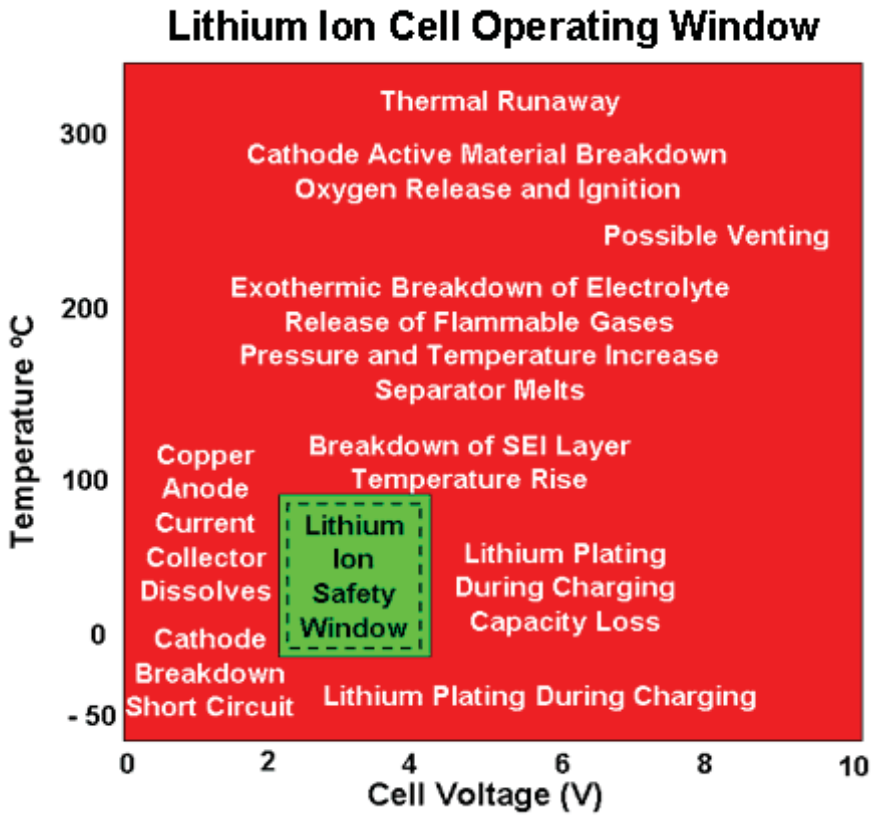
•C-rates.

LIPI

Temperature & Safety

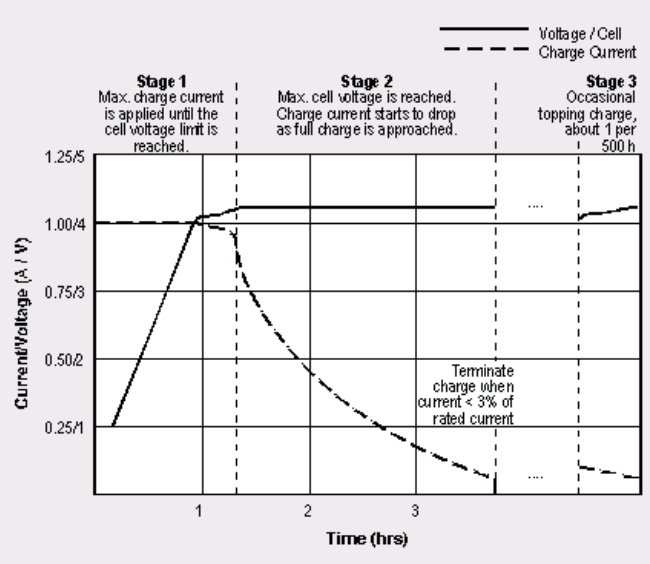
Lithium Fire (UPS Flight 1307)Source US National Transportation Safety Board

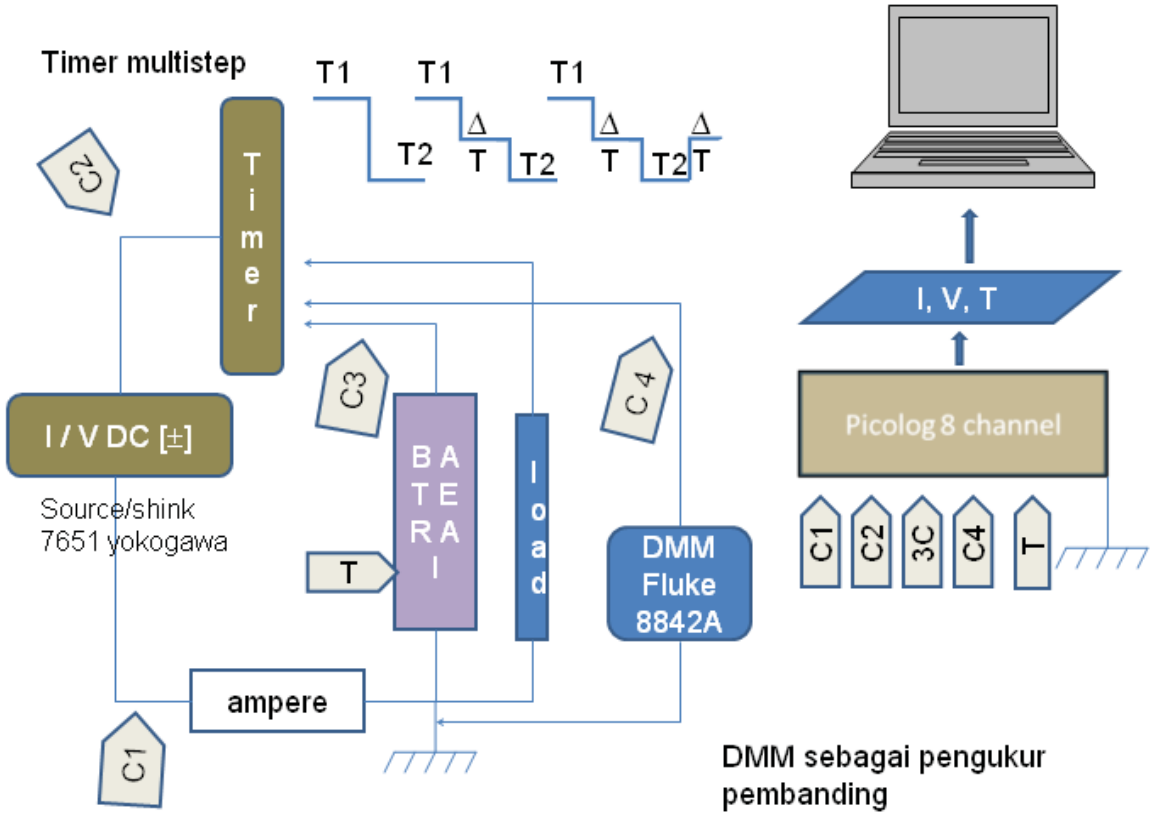
Figure 1.5 Remains of a Prius PHEV after its Li-Ion traction pack caught fire.

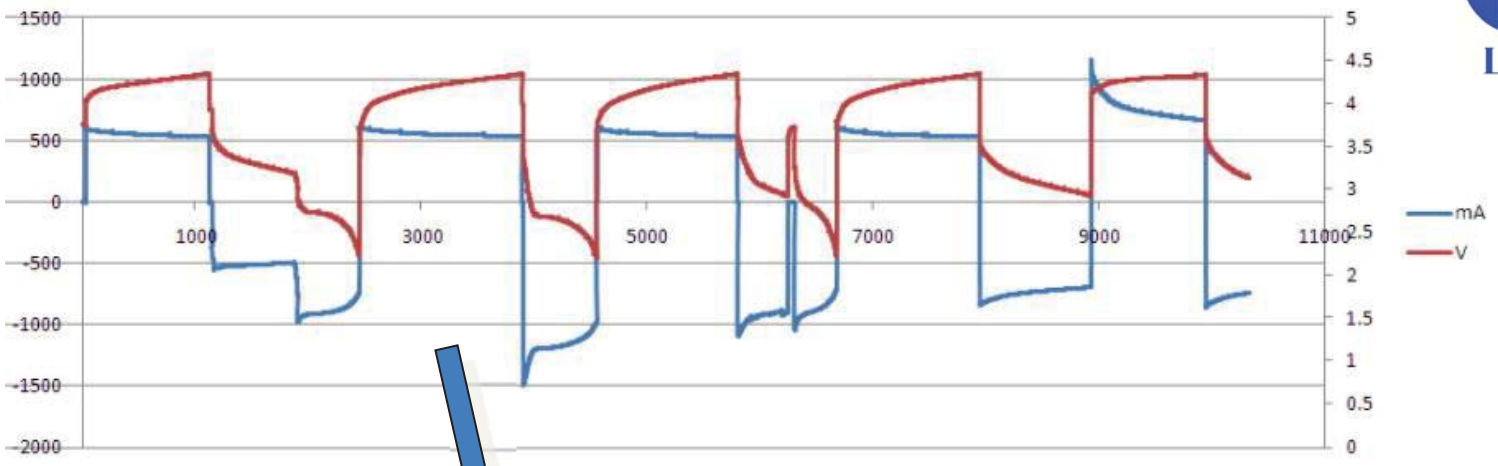


http://www.mpoweruk.com/lithium_failures.htm#lifetime

Uji charge discharge/CV using Yokogawa 7651.

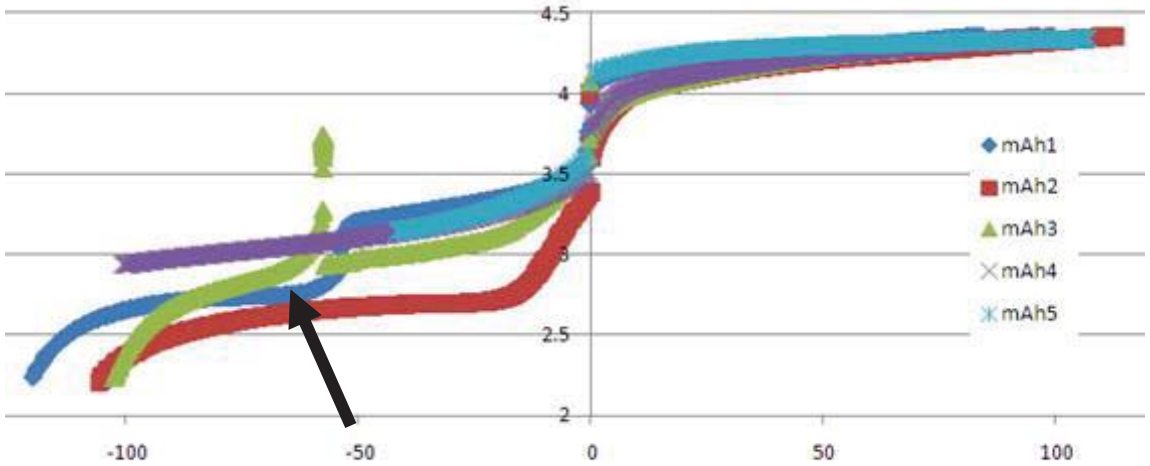






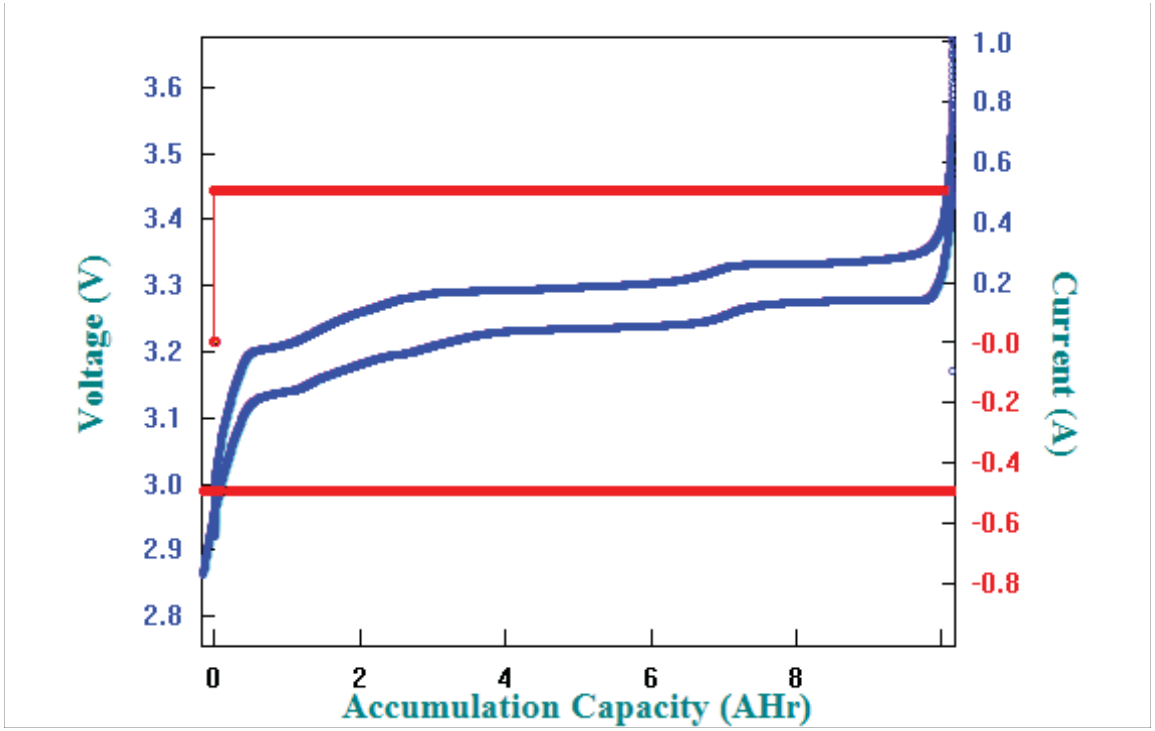
Kapasitas Nokia

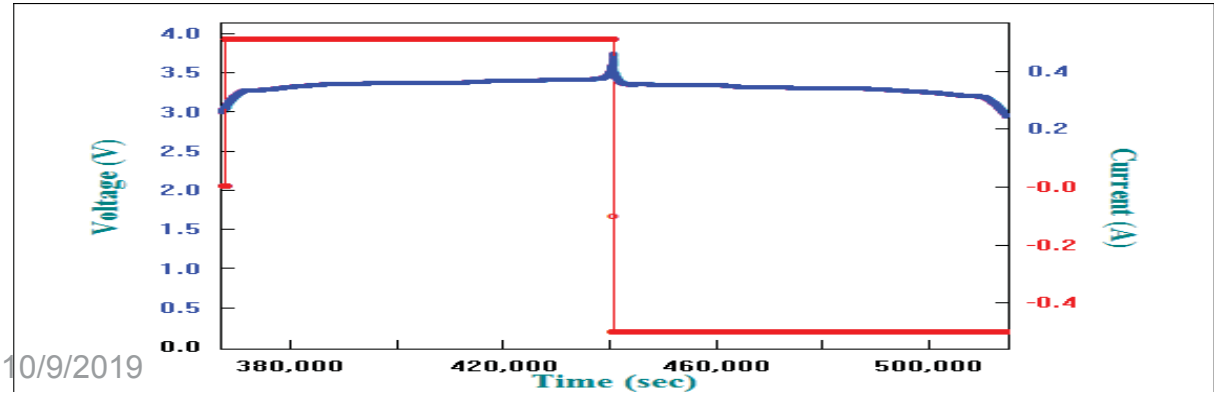
BA2-600 mAh



Not recommended for high rates/power battery

Using wbcs 3000





V_1= 3.3248V
V_2=3.2647

ΔV = 0.1601 V
V_{work} = 3.34 V

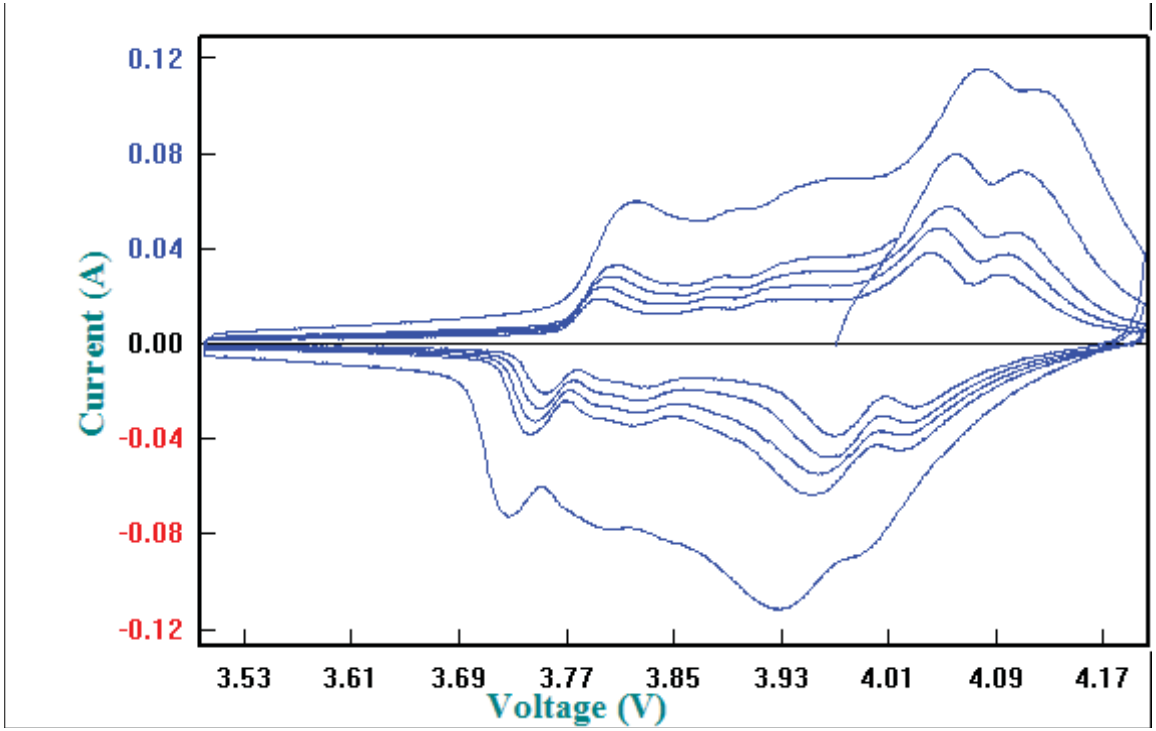
I = 0.5 A
T = 20.2 jam

C = 10Ah

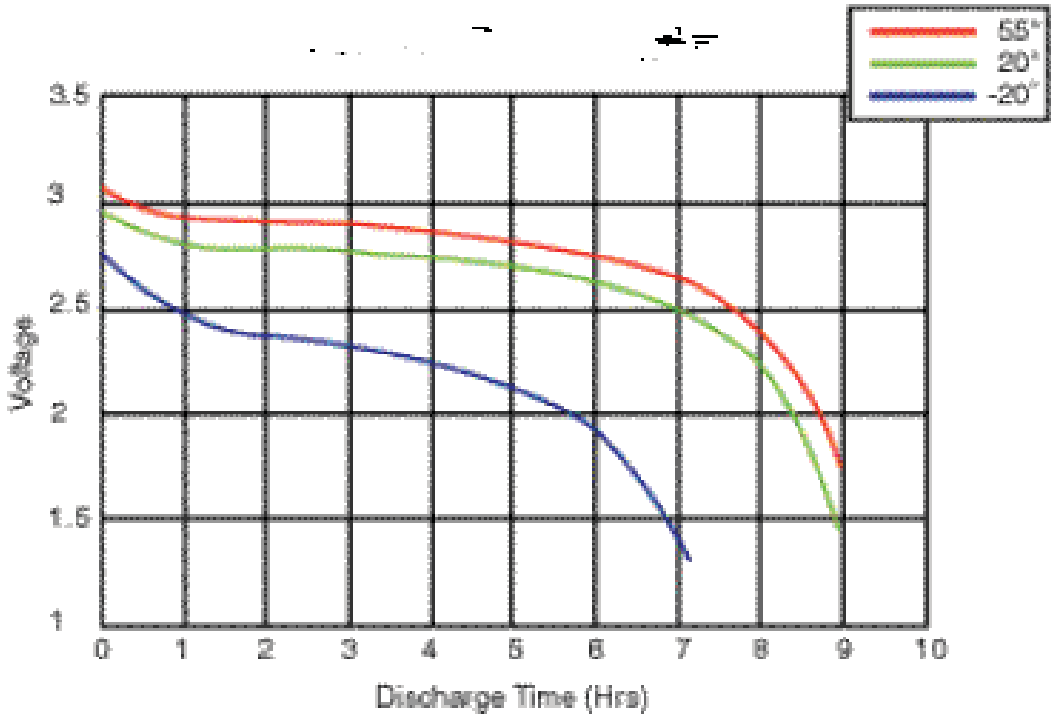
i=Crates = $C_{1/20}$

Indikasi :
3 plateu – 3 phase.

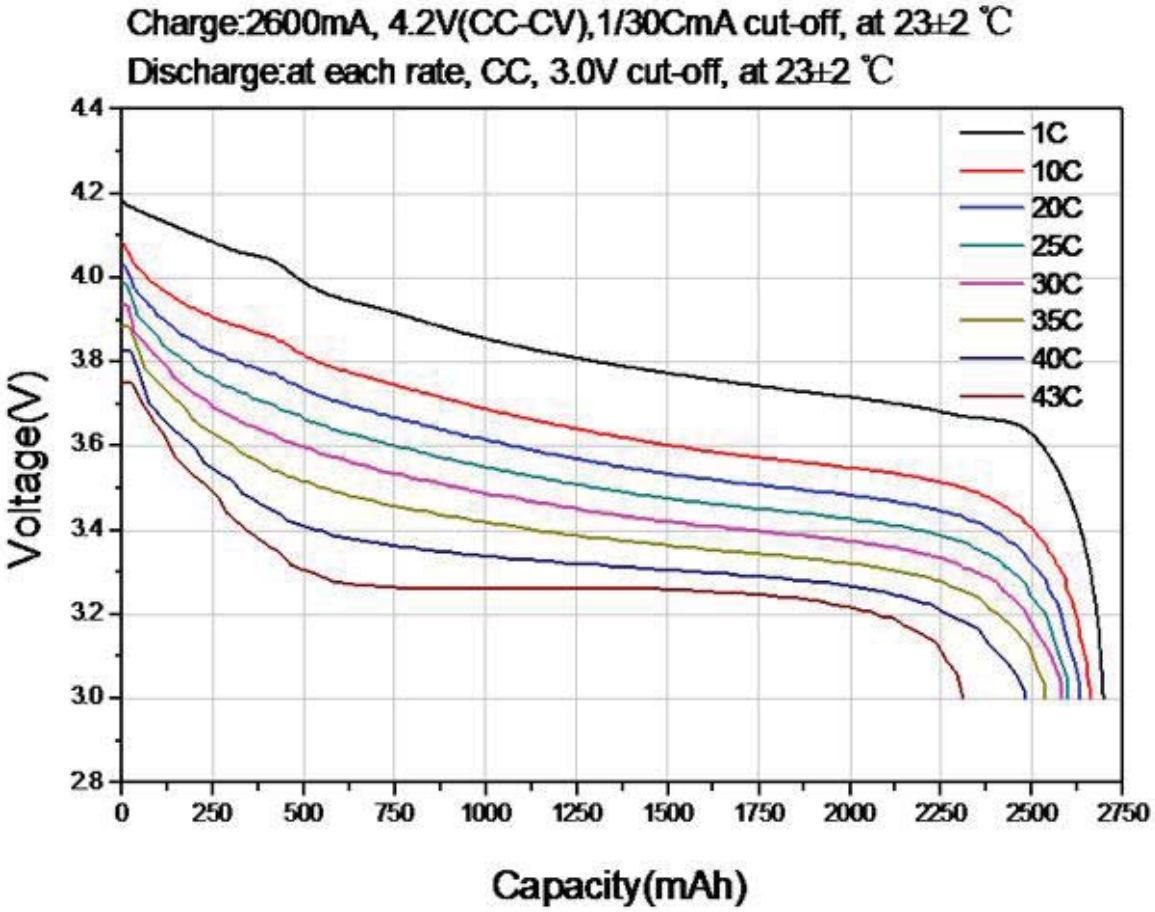
3 peak redox


0.12
0.08
0.04
0.00
-0.04
-0.08
-0.12
Current (A)
3.53
3.61
3.69
3.77
3.85
3.93
4.01
4.09
4.17
Voltage (V)

Temperature influence : capacity fade.



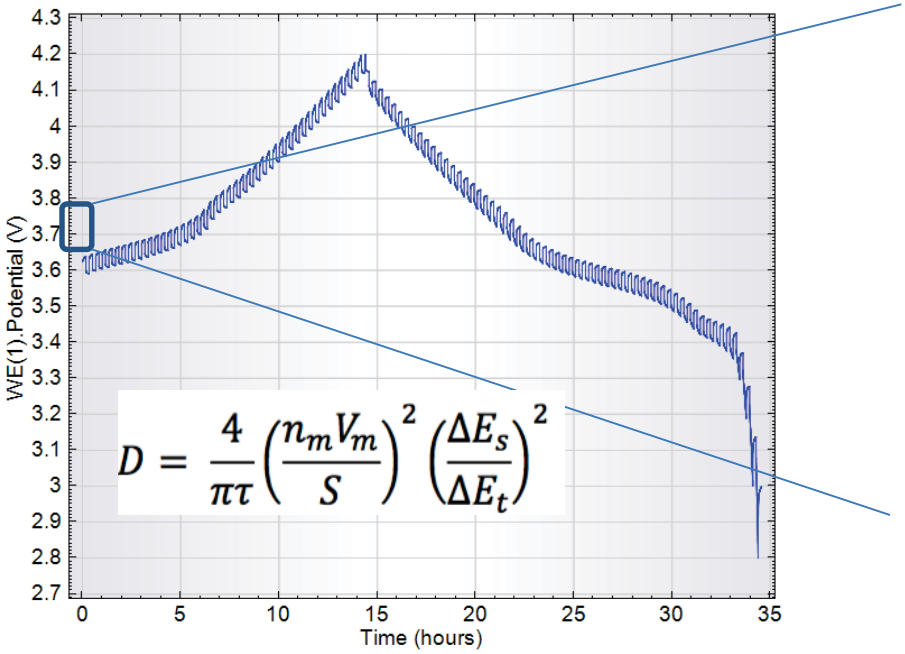
LIPI

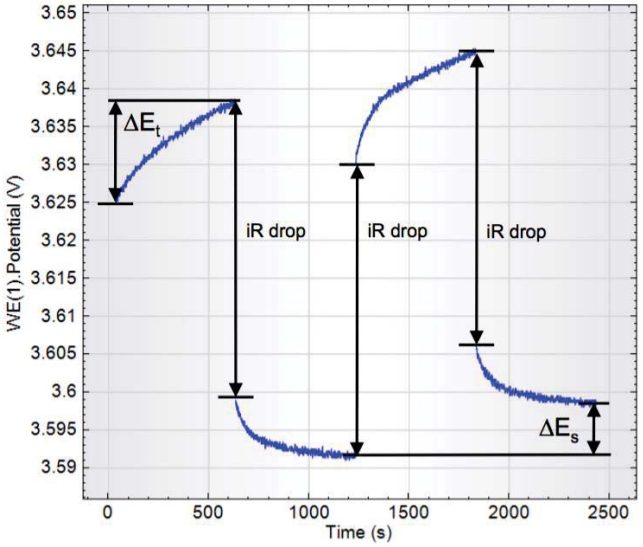


Capacity = current x discharge time

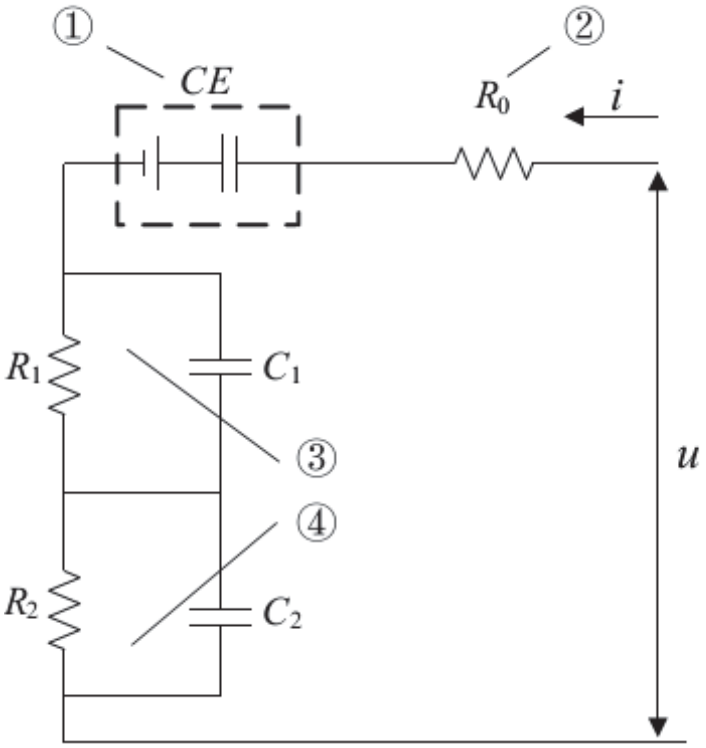
Lithium diffusion coefficient calculation: GITT

GITT : Galvanostatic Intermittent Titration Technique….. What is this?





Internal resistance :



① Battery capacity

② Ohm resistance

③ Concentration polarization

④ Electrochemical polarization

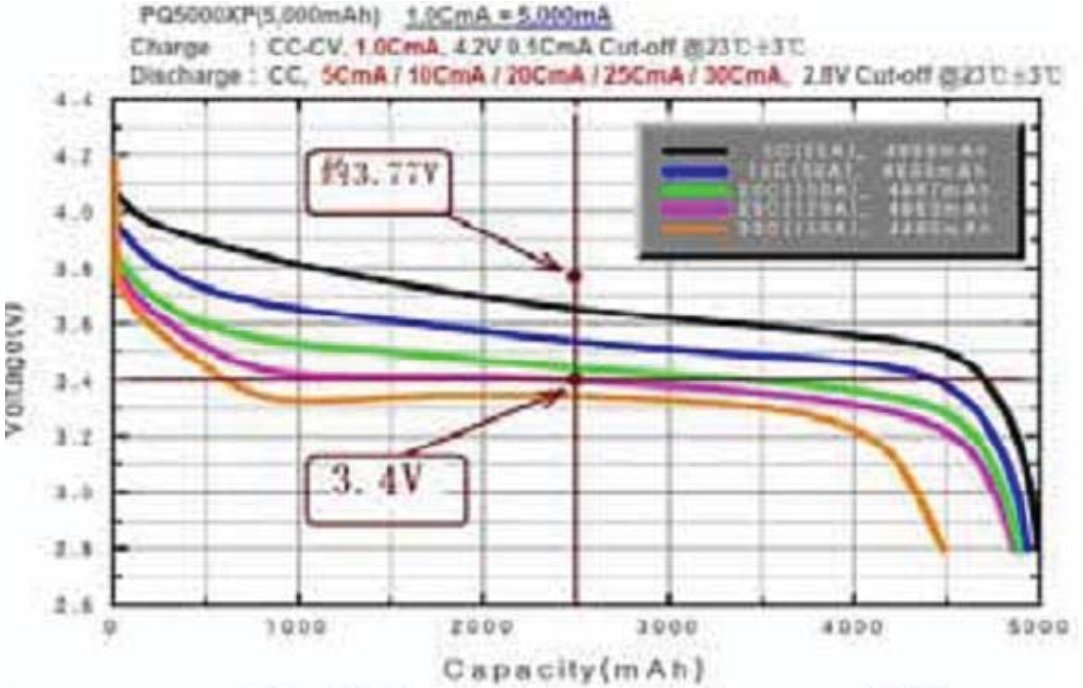


Fig. 1 Discharge curves clusters of LiPo

S in series

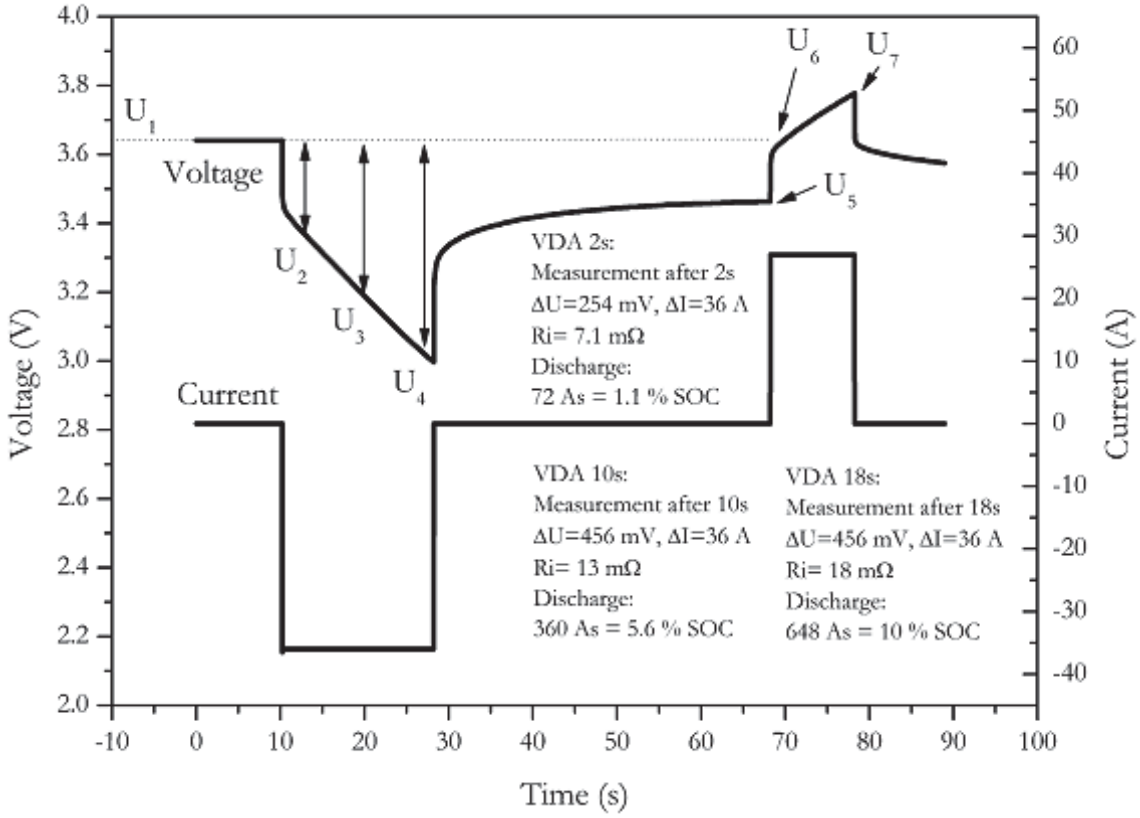
gh C is $R_i \le (370 \times S)/(C \times Ah)$ Unit: mΩ (23°C)

LiPo's 3.7V 5Ah, 25C.
1C =5000mA
Ch : CC-CV 1C, 4.2 V, 0.1C cut off 23±3oC
Ds : CC, 5C,10C,20C,25C,30C, 2.8V cut off

*) Huai, measurement and analysis…, Procedia Enginering 15 (2011).

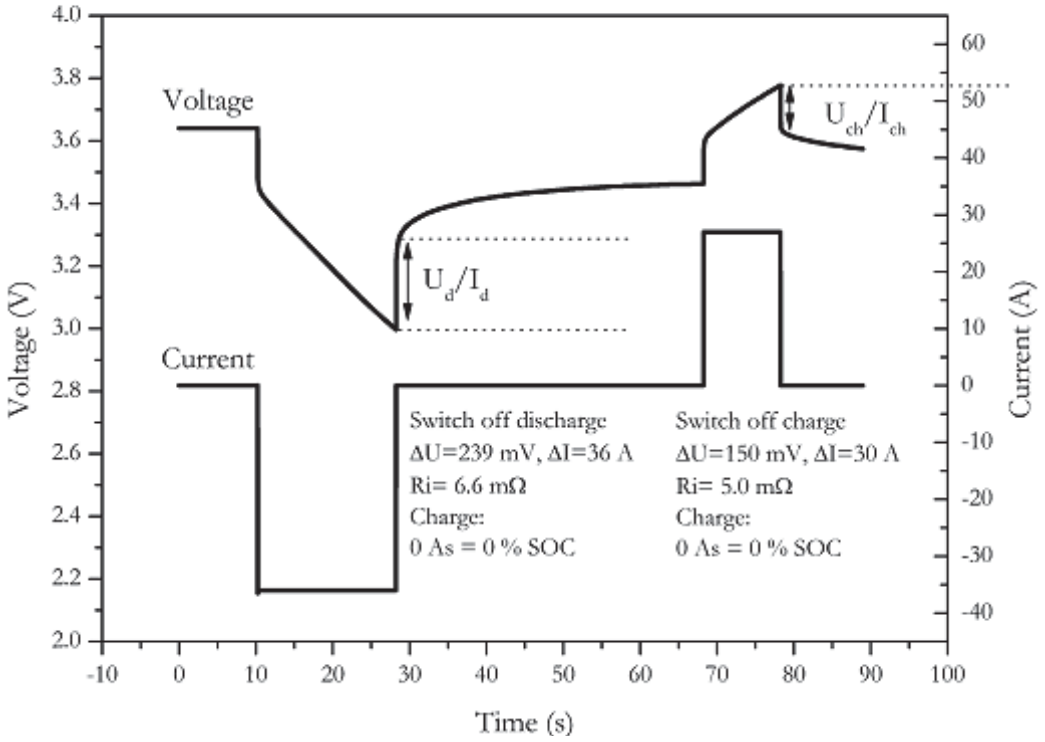
Step current

$$Ri_{discharge,2s} = \left| \frac{U_1 - U_2}{I_{discharge}} \right|$$



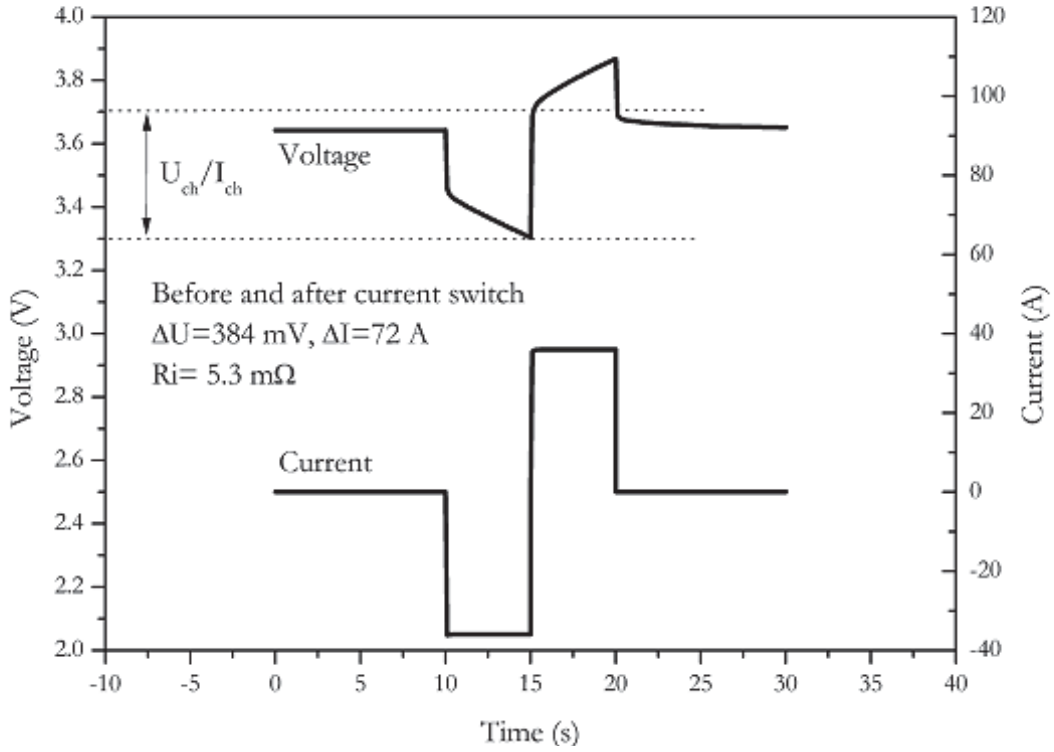
Current-off method

Figure 7. Measurement of internal resistance by switching off the pulse current.



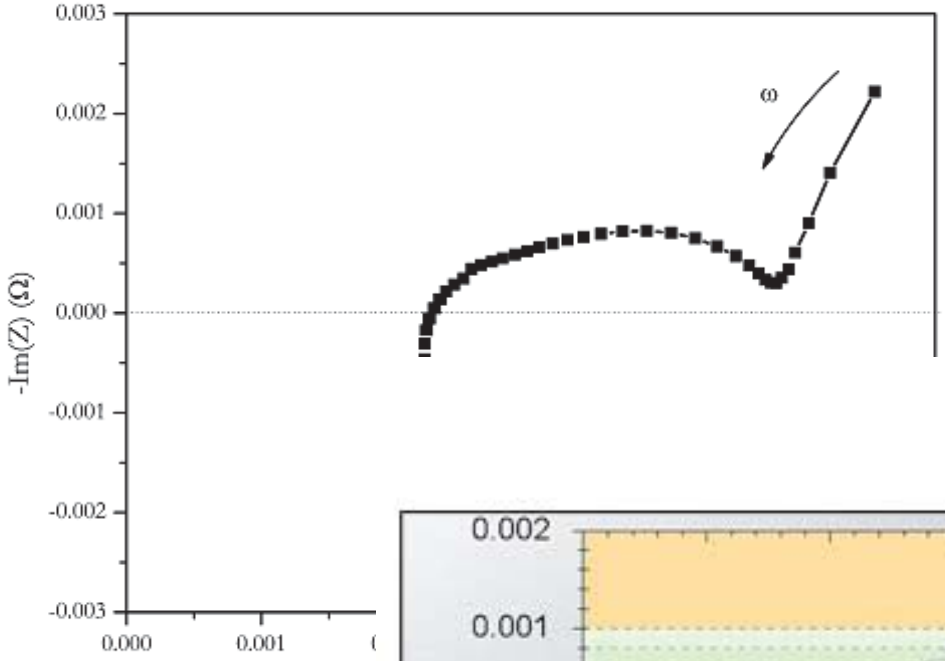
Current switch method

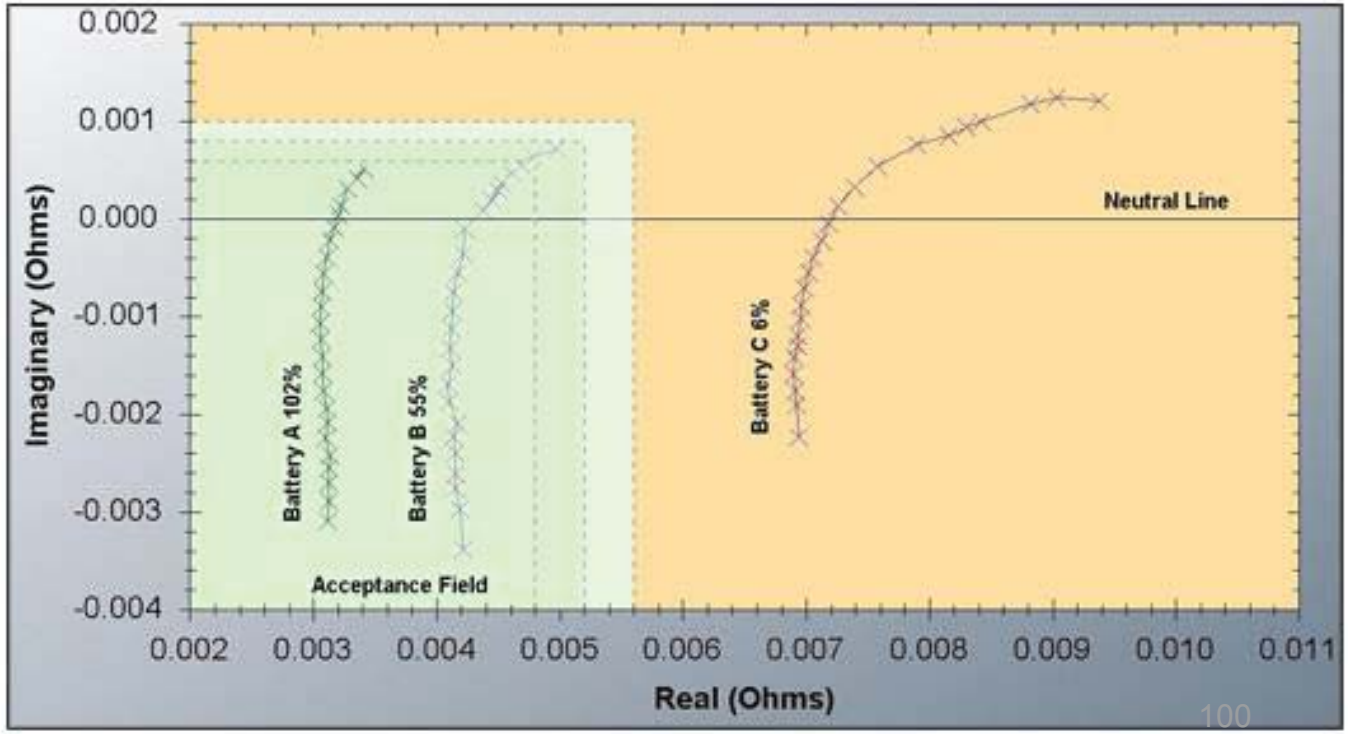
Figure 8. Measurement of internal resistance by switching current from discharge to charge.



EIS

Figure 11. Nyquist plot of the NX2P0M cell.

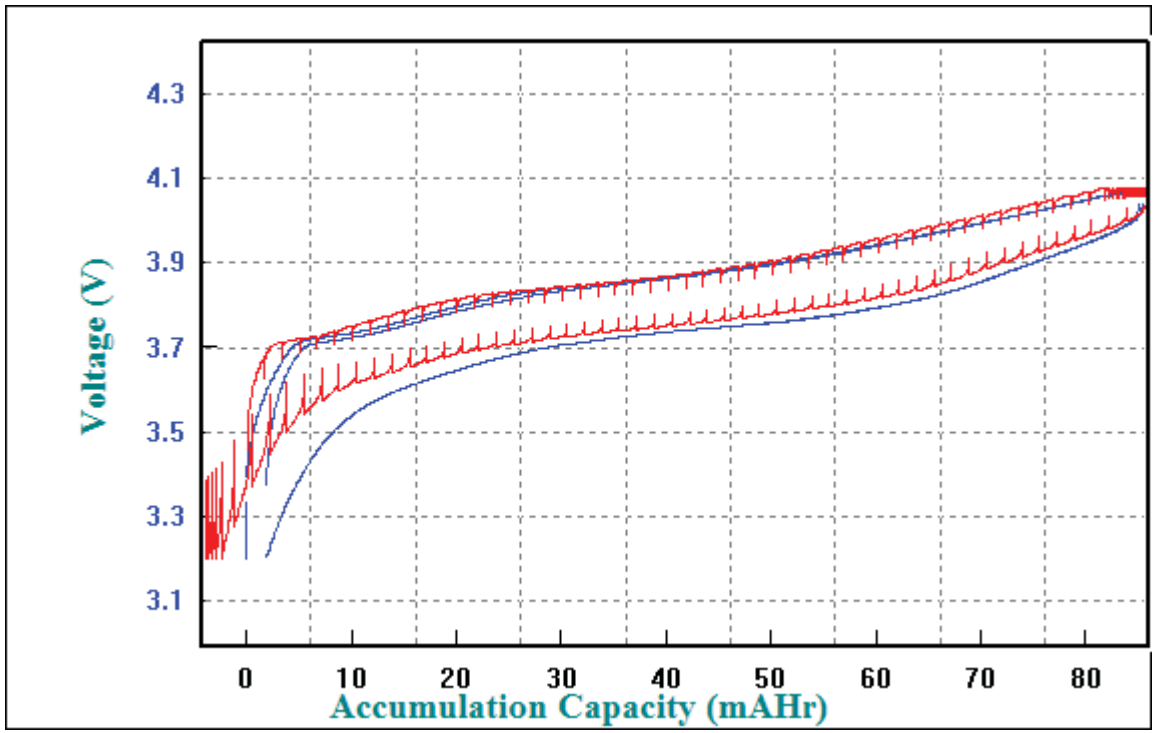


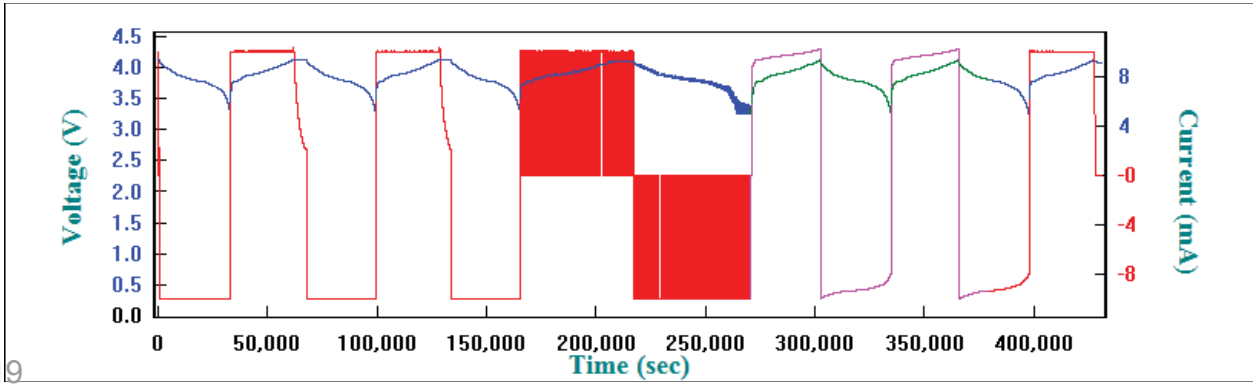


Cadex **Spectro CA-12 battery tester**

f : 20 - 2000 Hz.

Pulse charge/dis :

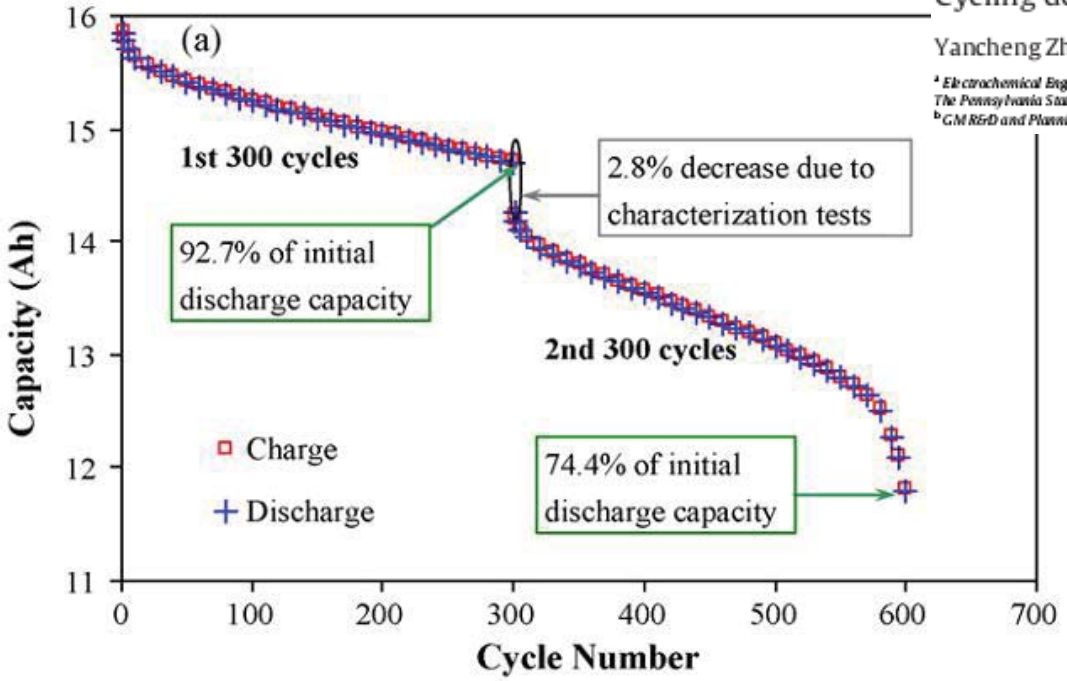




Cycling degradation of an automotive $LiFePO_4$ lithium-ion battery

Yancheng Zhang [a], Chao-Yang Wang [a,*], Xidong Tang [b]

[a] Electrochemical Engine Center (ECEC), Department of Materials Science and Engineering, and Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[b] GM R&D and Planning, General Motors, Mail Code: 480-106-390, 30500 Mound Road, Warren, MI 48090-9055, USA



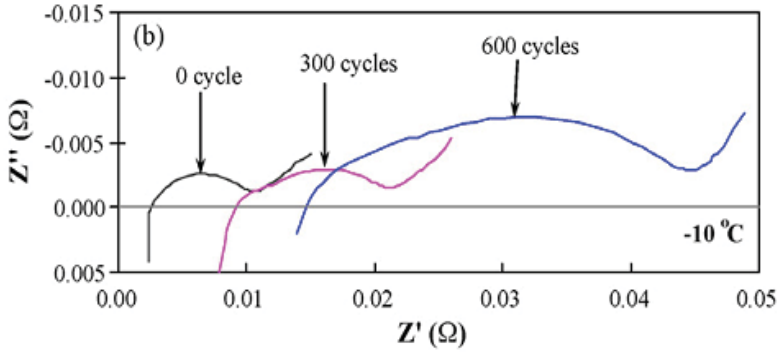
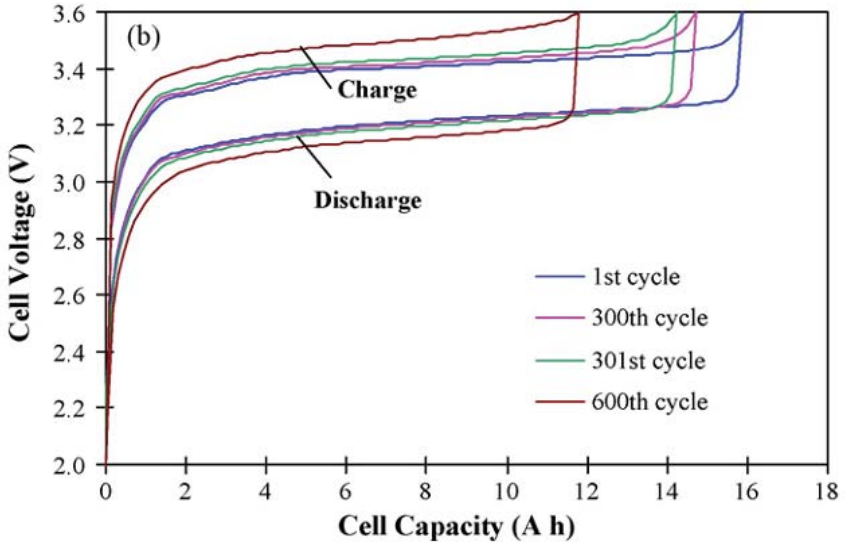
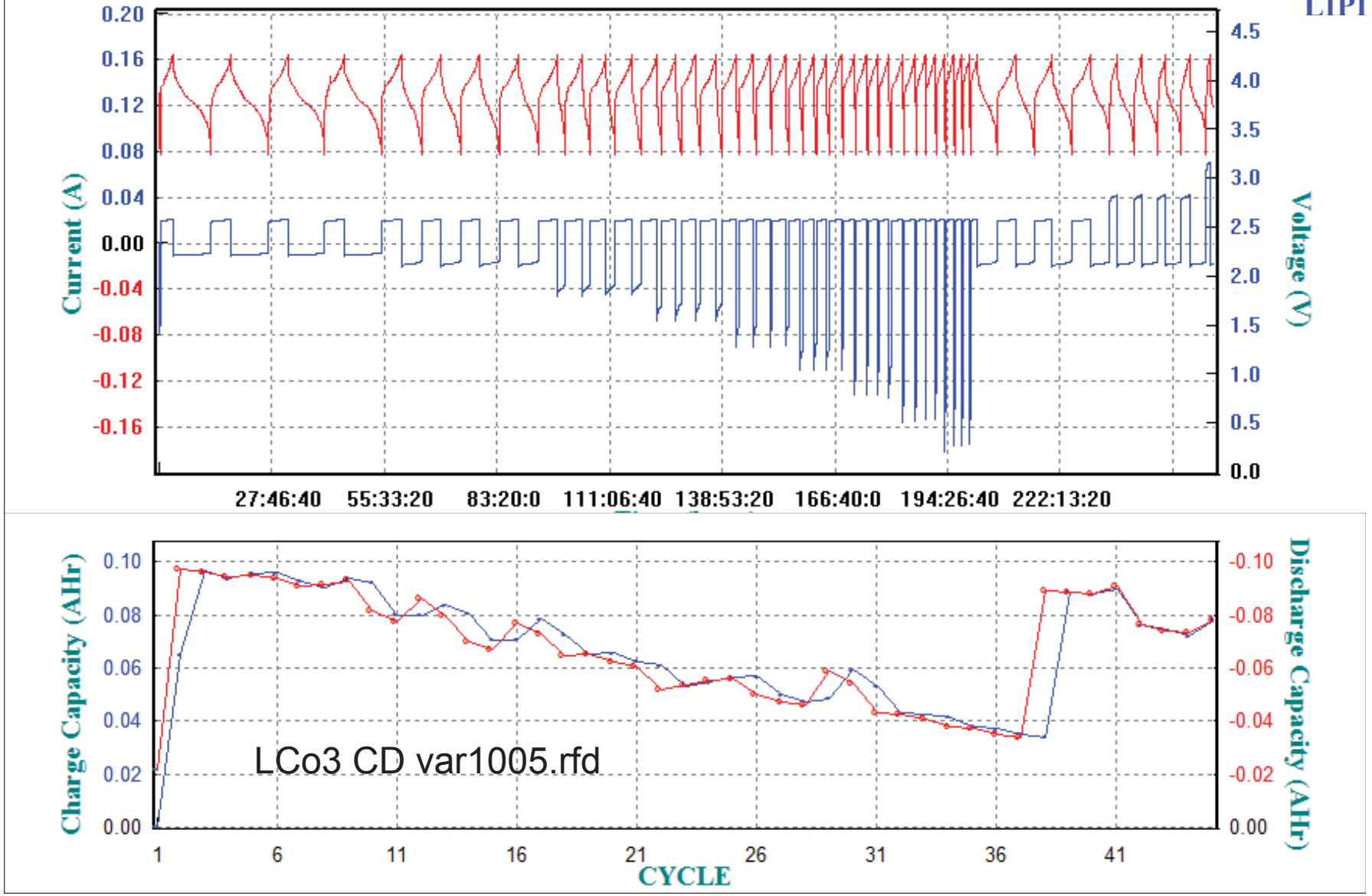
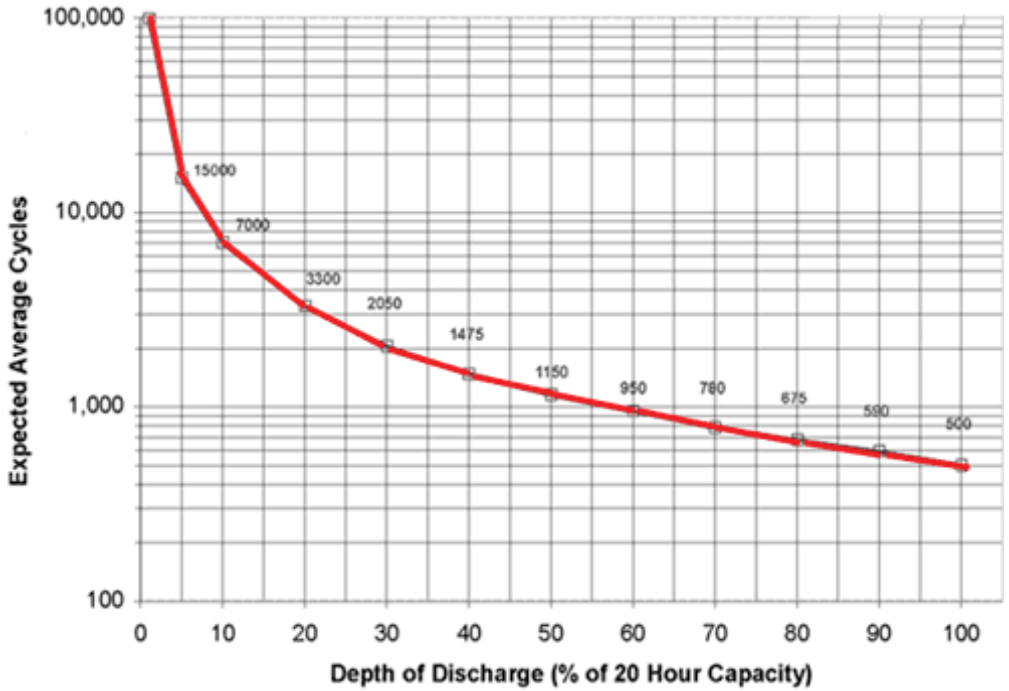


Fig. 9. Nyquist plots of electrochemical impedance spectra measured at 70% SOC



C-rate : capacity loss.





Over voltage problem ….

Additional important information

Calculating full cell capacity

$$C_t = \frac{C_a}{1 + (C_a/C_c)}$$

C_t = Total capacity

C_a = capacity of the anode

C_c = capacity of the cathode

Example #1: Si//NMC

$$C_t = \frac{4200}{1 + (4200/200)} = 190 \text{ mAh/g}$$

Improving anode capacity to >10 times

Example #2: Graphite//another cathode

$$C_t = \frac{372}{1 + (372/400)} = 193 \text{ mAh/g}$$

Improving cathode capacity ONLY 2 times

That's why many attempts are being done to improve cathode material than anode

CONCLUSION

- Maximum capacity is not the sole factor for a great battery material
- Good cathode has a plateau in high voltage region
- Good anode has a plateau in low voltage region (nearly zero is desirable)
- Lithium-ion diffusion coefficient can be calculated from CV and GITT
- CV can be used to determine material type: battery
  - Sharp peaks in CV denotes a battery-type material
  - Parallelogram denotes a capacitor-type material
- Equivalent circuit of the EIS for each material is different
- Improving cathode material is more practicable

- **Terima kasih**

http://www.mpoweruk.com/bms.htm#gas