ZMAN™
Getting Started with ZMAN

June 2010

WonATech Co., Ltd.

What is ZMAN?

- Impedance Spectroscopy Analysis and Presentation Software

- We have to know about:
  1. Electrochemical Impedance Spectroscopy(EIS)
  2. Analysis
     - K-K consistency
     - Modeling of Data
       - Initial Guessing: Circular Fit, Genetic Algorithm
       - Complex Non-linear Least Square Fit
  3. Presentation
     - Nyquist, Bode, Black-Nichols, and 3D Curve/Surface Plots
     - Parameter Plot

EIS

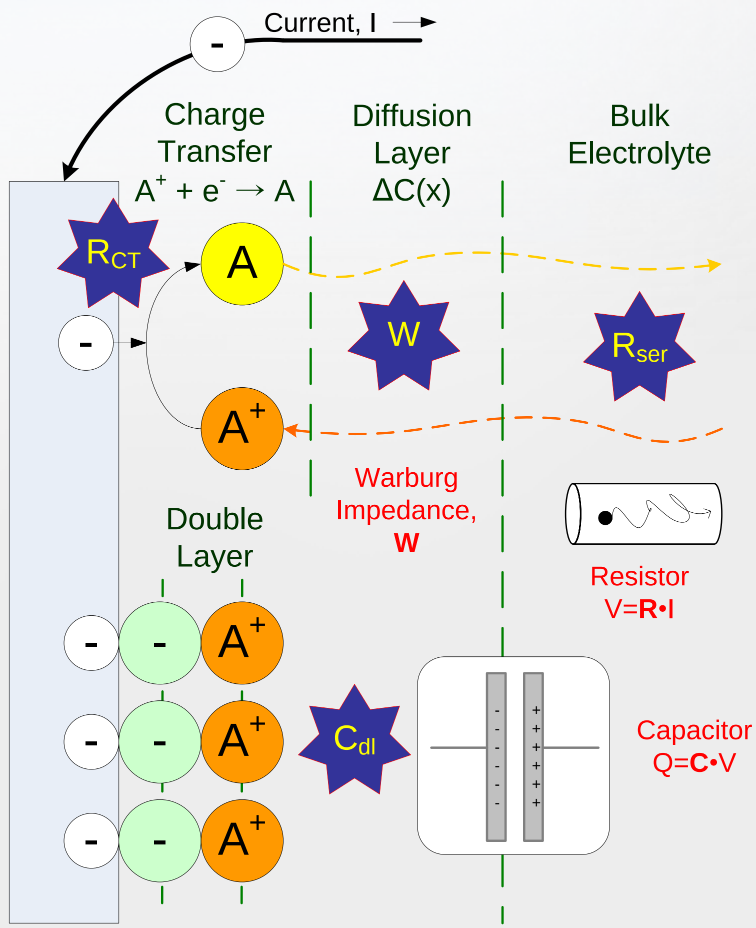
Nomenclature : EIS

- Electrochemical?
  - In electrochemistry, everything of interest takes place at the interface between electrode & electrolyte!
  - Controlling REDOX by Potentiostat/galvanostat

- Impedance?
  - AC circuit theory describes the response of a circuit to an alternating current or voltage as a function of frequency
  - Impedance is a totally complex resistance encountered when a current flows through a circuit made of resistors, capacitors, or inductors, or any combination of these
  - Ohm's Law, $V = R \times I \rightarrow V = Z \times I$ (complex number Z)

- Spectroscopy?
  - No Quantum Process
  - Small Perturbation → Response

Electrochemical Interface



- A potentiostat is an instrument which measures the current / voltage characteristics of an electrochemical (electrode/solution) interface. *Everything* happens at the interface.

Process of Energy Storage in Electrochemical System

Common Steps

- Ionic charge conduction through electrolyte in pores of active layer
- Electronic charge conduction through conductive part of active layer
- Electrochemical reaction on the interface of active material particles including electron transfer
- Diffusion of ions or neutral species into or out of electrochemical reaction zone.

$\vec{P}(\mathrm{SOC}, \mathrm{SOH}, \mathrm{T})$

Ex) R_s, R_{ct}, C_{dl}, W …

?

- Discharge Process
- Polarization Curve
- CV

EIS

Z(SOC,SOH,T;ω)

Study of Mechanism

Evaluation & Diagnosis

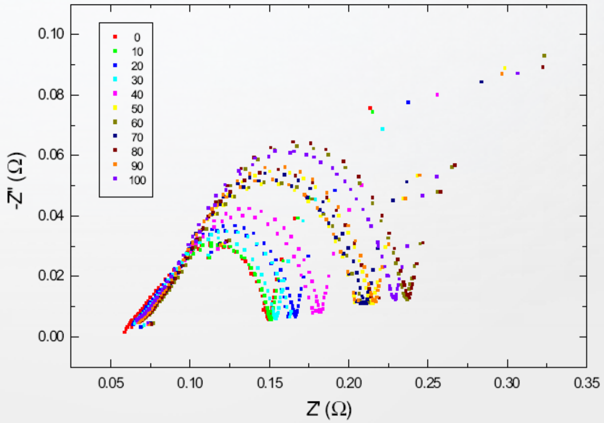
- *CO poisoning*
- *Water flooding in FC*

Performance Simulation

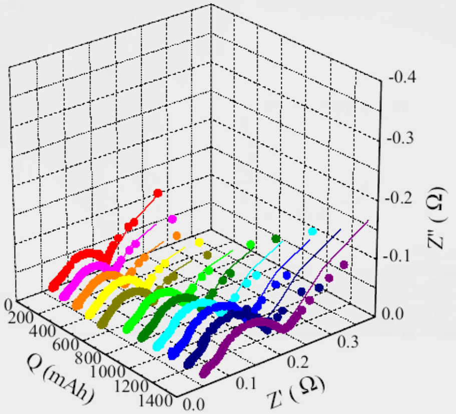
- *Arbitrary Load*
- *DC/AC/Transient*
- *Power/Energy*

Impedance Spectra of a Li-ion battery

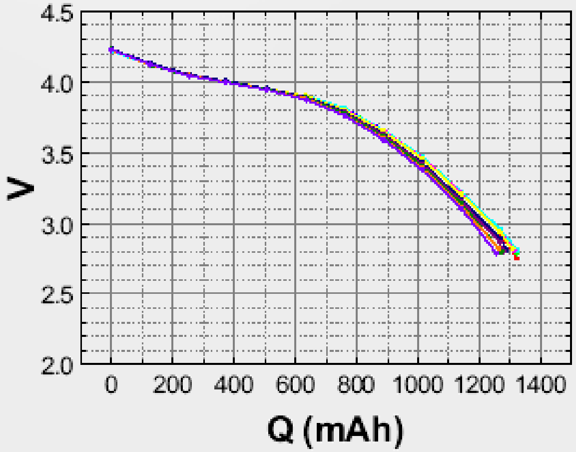
Impedance Spectra upon cycling



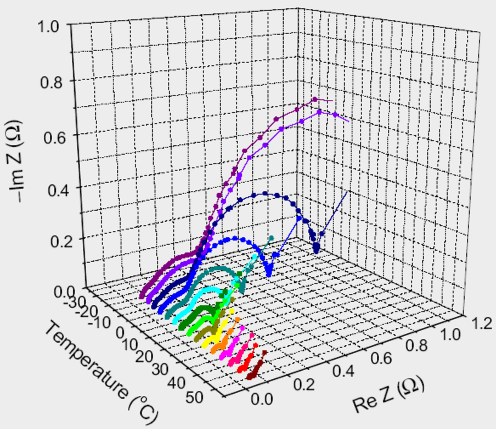
Nyquist Plot vs. level of discharge



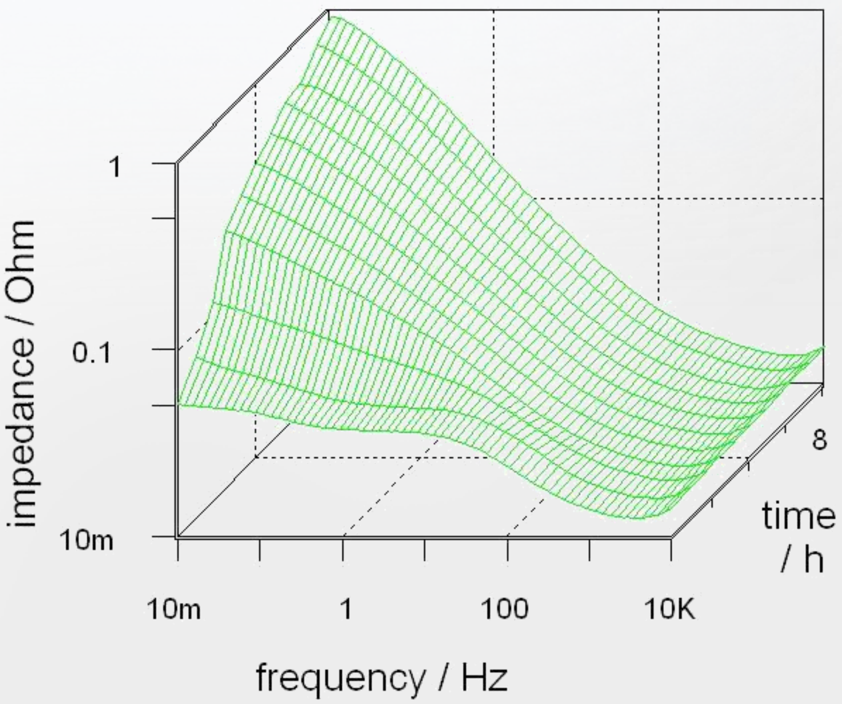
CF)Discharge curve upon cycling

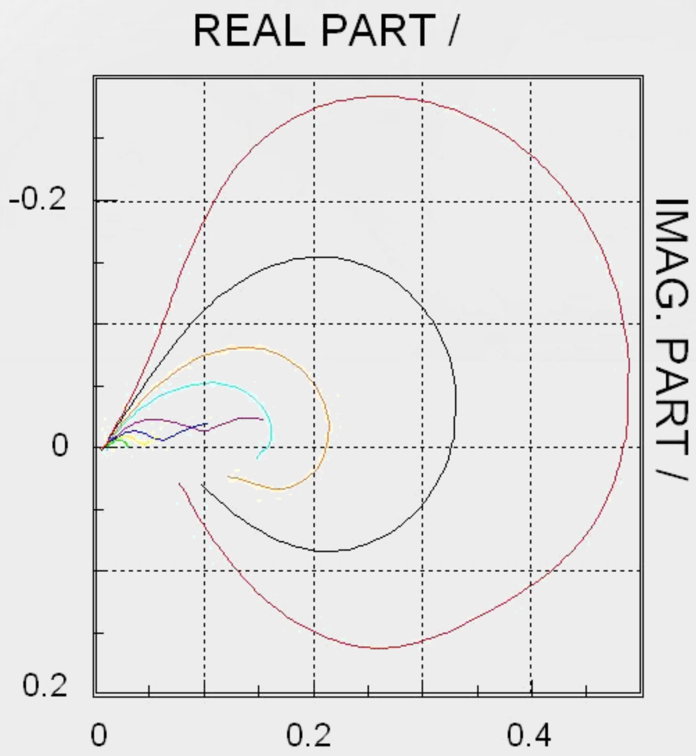


Effect of temperature



PEMFC





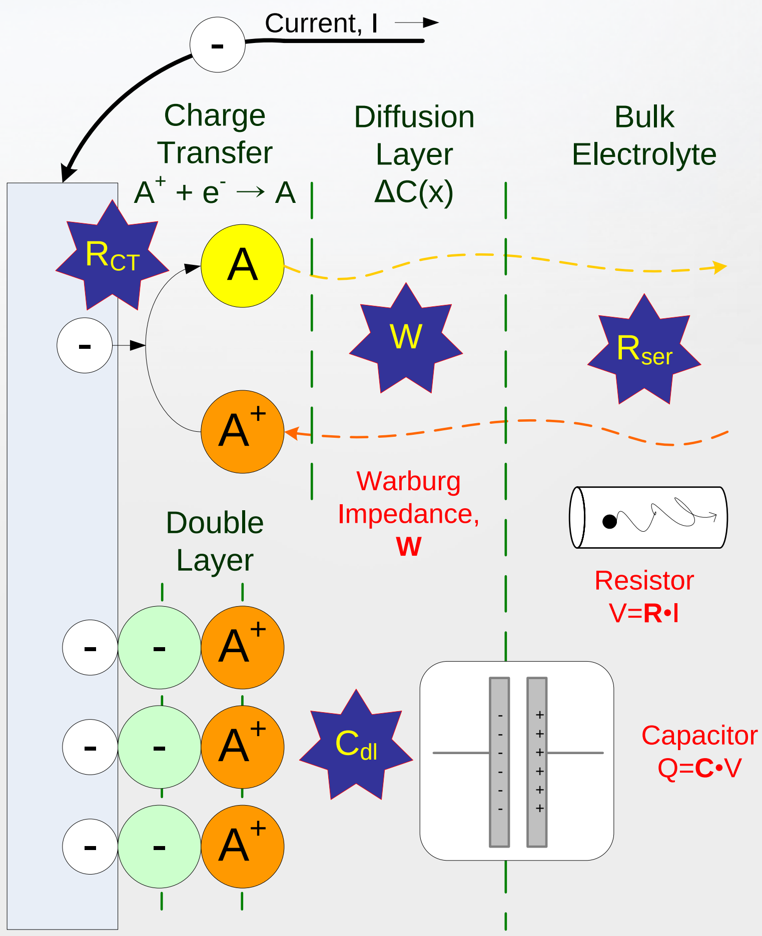
A. PEMFC Under Dead End

(H_2O outlet in cathode closed)

B. PEMFC Under CO Poisoning

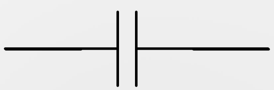
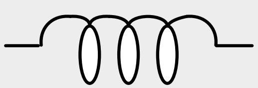
(H_2 + 100ppm CO as fuel gas)

Back to the e'Chem Interface

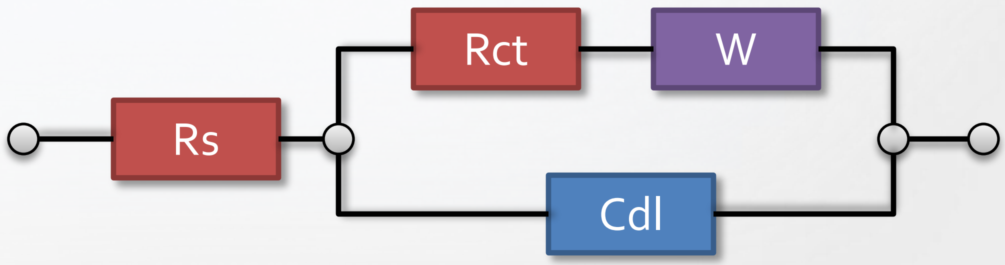


- Charge Transfer ⇒ R_{ct}, R_p
  - $R_{ct} \sim 1/\,i_o$
  - Butler-Volmer Equation
- Diffusion Layer ⇒ W
  - No energy loss
- Bulk Electrolyte ⇒ R_s, R_Ω
- Double Layer ⇒ C_{dl}
  - Non-Faradaic Process

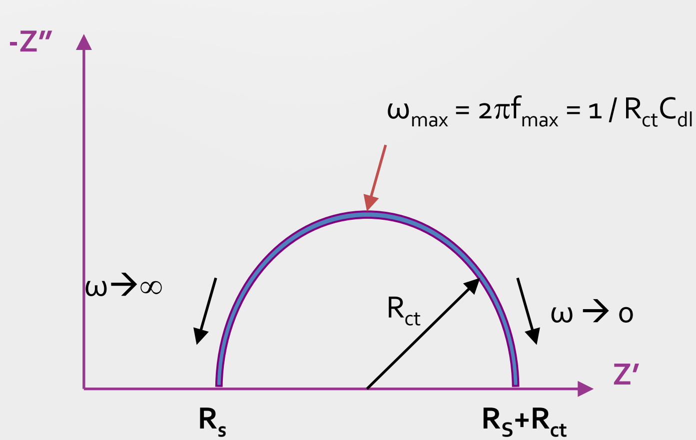
Basic Circuit Elements

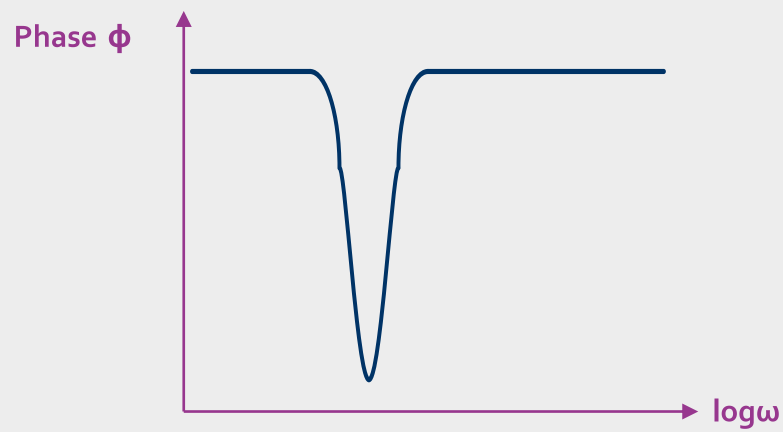
Resistor 	$V = RI$	$I(t) = I_0 e^{j\omega t}$ $\rightarrow$ $V = Z \times I$	$Z = R$
Capacitor 	$V = \frac{Q}{C} = \frac{1}{C}\int I dt$	$I(t) = I_0 e^{j\omega t}$ $\rightarrow$ $V = Z \times I$	$Z = \frac{1}{j\omega C}$
Inductor 	$V = L\frac{dI}{dt}$	$I(t) = I_0 e^{j\omega t}$ $V = Z \times I$	$Z = j\omega L$

Randles' Circuit



Rs-(Rct-W)|Cdl





Basic Circuit Elements 1

	Description	Parameters	Formula	Note
R	Resistive Element	R	R	R
C	Capacitive Element	C	$\frac{1}{sC}$	1/s/C
L	Inductive Element	L	sL	s*L
W	Warburg Diffusion	W	$\frac{1}{W\sqrt{s}}$	1/W/sqrt(s)
Q	Constant Phase Element	Qy Qa	$\frac{1}{Q_y}\frac{1}{s^{Q_a}}$	1/Qy/pow(s, Qa)

* where $s = j\omega = 2\pi f$

Basic Circuit Elements 2

	Description	Parameters	Formula	Note
O	Nernst Impedance	Oy Ob	$\frac{1}{O_y\sqrt{s}}\tanh(O_b\sqrt{s})$	
T	Finite Diffusion	Ty Tb	$\frac{1}{T_y\sqrt{s}}\coth(T_b\sqrt{s})$	
G	Homogeneous Reaction (Gerischer)	Gy Gk	$\frac{1}{G_y\sqrt{G_k+s}}$	
S	Spherical Diffusion	Sy Sk	$\frac{1}{S_y}\frac{1}{\sqrt{S_k}+\sqrt{s}}$	

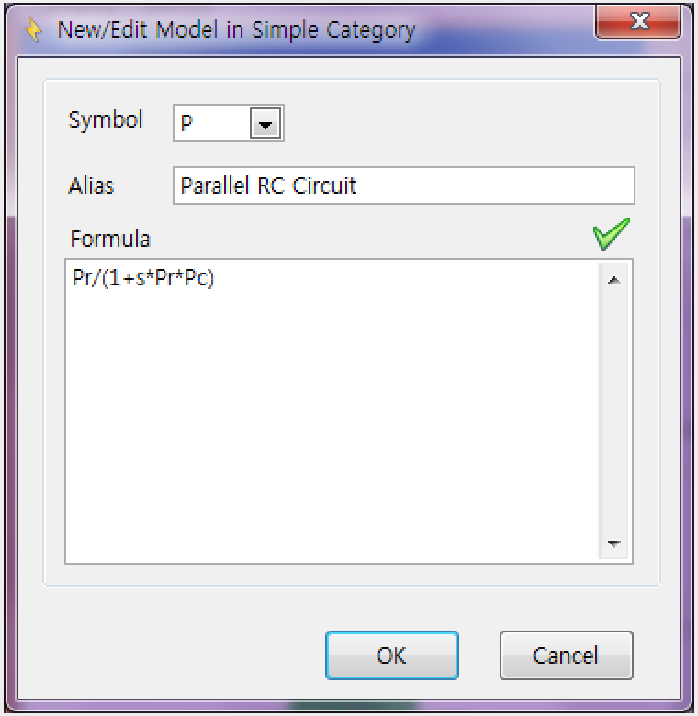
Basic Circuit Elements 3

	Description	Parameters	Formula	Note
X	Finite-length diffusion at planar particles	Xr Xc	$\sqrt{\frac{3X_r}{X_c s}}\tanh(\sqrt{3X_r X_c s})$	*a
Y	Finite-length diffusion at spherical particles	Yr Yc	$\frac{\tanh(\sqrt{3Y_r Y_c s})}{\sqrt{\frac{3Y_c s}{Y_r}} - \frac{1}{Y_r}\tanh(\sqrt{3Y_r Y_c s})}$	*a
Z	Finite-length diffusion at cylindrical particles	Zr Zc	$\frac{I_0(\sqrt{2Z_r Z_c s})}{\sqrt{2Z_r Z_c s} \cdot I_1(\sqrt{2Z_r Z_c s})} Z_r$	*a,*b

a. Impedance Spectroscopy: Theory, Experiment, and Applications, 2^{nd} ed., Ed. E. Barsoukov, and J. R. Macdonald, John Wiley & Sons, Inc., Hoboken, New Jersey, 2005
b. $I_0(x)$ and $I_1(x)$ are Bessel-functions of the first kind, with 0 and 1 order correspondingly.

Simple Circuit Elements

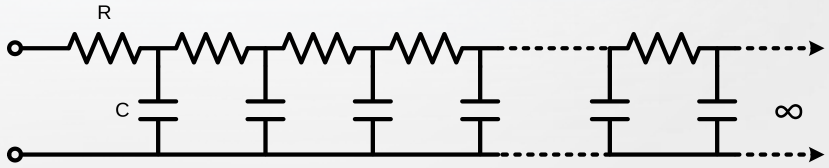
<table>
<tr><th></th><th>Description</th><th>Parameters</th><th>Formula</th><th>Note</th></tr>
<tr><td>P</td><td>Parallel RC Circuit
R|C</td><td>Pr
Pc</td><td>Pr/(1+s*Pr*Pc)</td><td></td></tr>
</table>



Diffusion

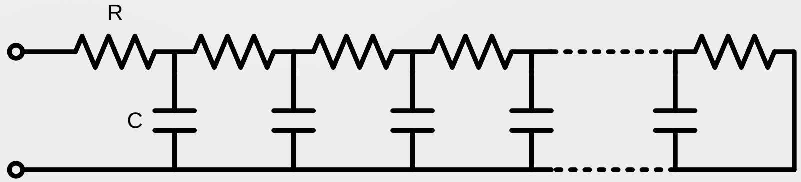
- Transmission Line Model

W: Warburg



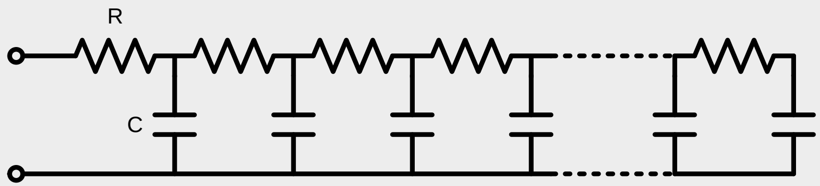
$$Z = \frac{\sigma}{\sqrt{\omega}}(1 - j)$$

O: Nernstian Impedance: Diffusion by Constant Concentration



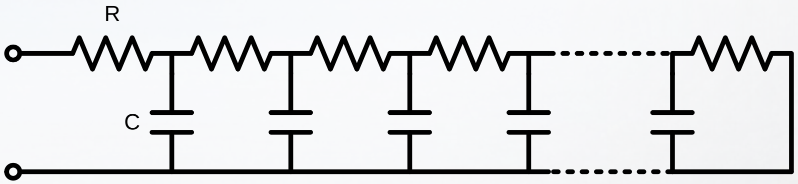
$$Z = \frac{\sigma}{\sqrt{\omega}}(1 - j)\tanh\left(\delta\sqrt{j\omega / D}\right)$$

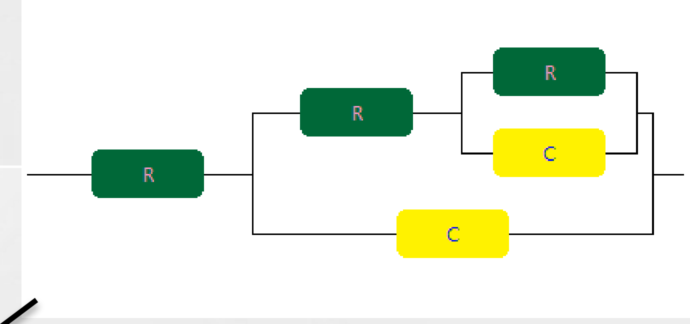
T: Finite Diffusion Impedance: Diffusion by Phase Boundary

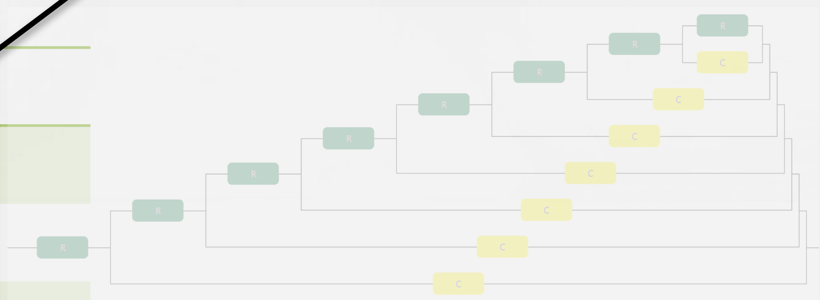


$$Z = \frac{\sigma}{\sqrt{\omega}}(1 - j)\coth\left(\delta\sqrt{j\omega / D}\right)$$

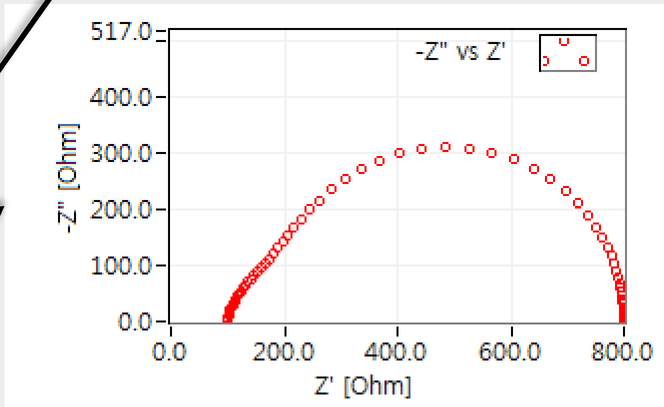
Transmission Line





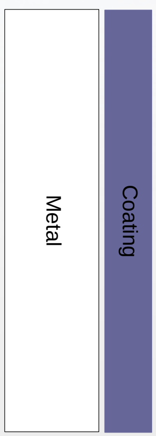


n	Model
1	R
2	R-R|C
3	R-(R-(R|C))|C
4	R-(R-(R-R|C)|C)|C
5	R-(R-(R-(R-R|C)|C)|C)|C
6	R-(R-(R-(R-(R-R|C)|C)|C)|C)|C
7	R-(R-(R-(R-(R-(R-R|C)|C)|C)|C)|C)|C
8	R-(R-(R-(R-(R-(R-(R-R|C)|C)|C)|C)|C)|C)|C

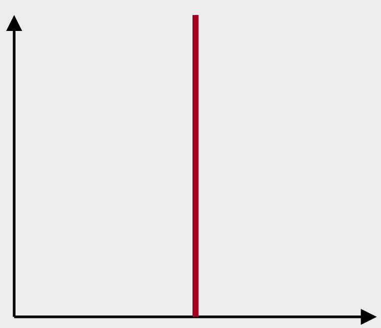


Coating Capacitance

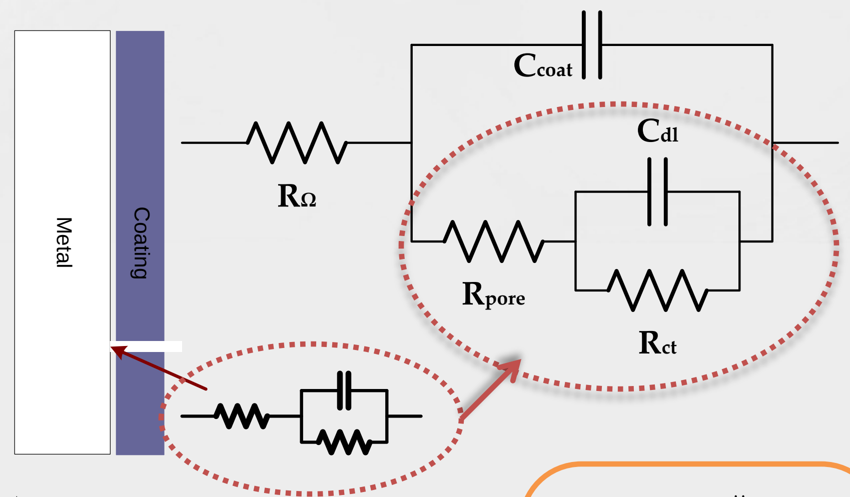
- Ideal Coating

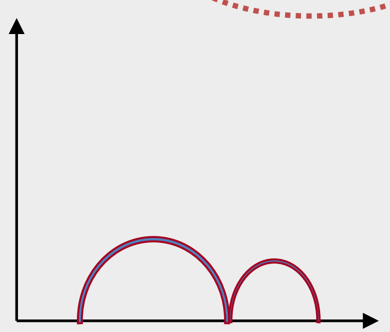


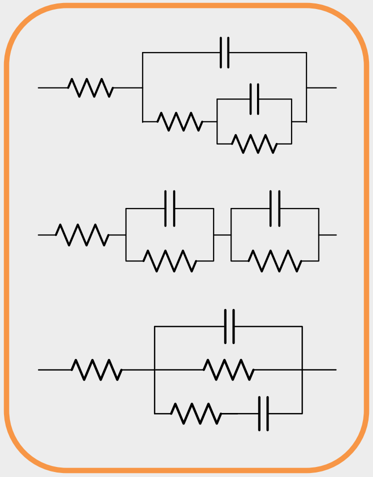
$$C_{coat} = \varepsilon \frac{A}{d}$$



- Imperfect Coating







Installation and Activation

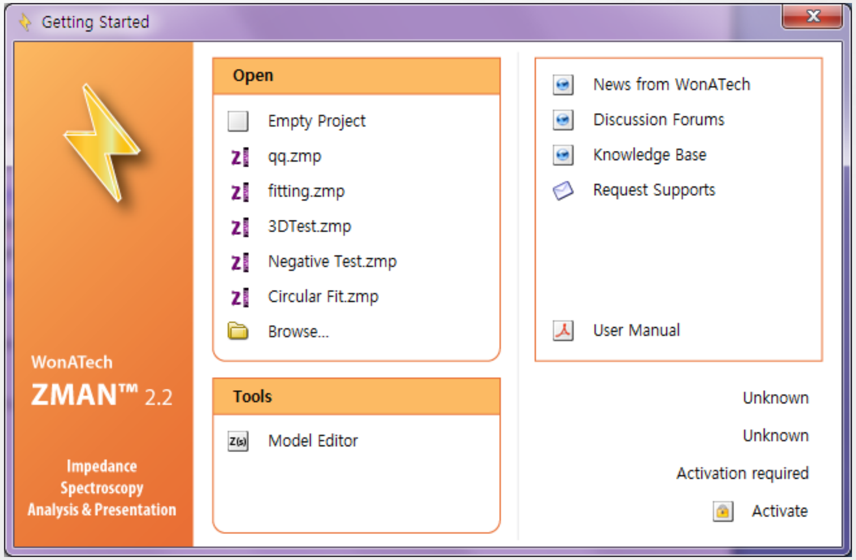
Installation and Activation

1. Setup "LabVIEW Run-Time Engine 2009 SP1"
   - How to get? Install CD or NI website (www.ni.com)
   - http://joule.ni.com/nidu/cds/view/p/lang/ko/id/1600

2. Setup "ZMAN 2.2"
   - How to get? Install CD or WonATech website (www.wonatech.com)
   - http://www.xenosystem.com/zman/korindex.htm

3. Activate ZMAN 2.2
   - Is it necessary? Once activated, you can open any ASCII files.
   - How to activate? Click **Activate** button in **Getting Started Window**

Launching ZMAN



- The **Getting Started** window appears when you launch ZMAN

a. Create new project
b. Select among the most recently opened ZMAN project files
c. Access information and resources to help you learn about ZMAN and resources on the WonATech Web site, wonatech.com
d. Launch the ZMAN User Manual
e. Manage Model Editor

Overall Procedure

Overall Procedure

1. Selecting Data Files

- Available File Formats
  - WonATech Binary Files:
    - *.wdf(WEIS Series), *wis(Z# Series)
    - No activation required
  - 3rd Party Binary Files:
    - *.ism(Zarner)
  - 3rd Party ASCII Files:
    - *.dta(Gamry), *.z(Solartron) *.dfr(AutoLab)
  - General ASCII Files:
    - *.txt, *.dat, *.csv, *etc*.
    - Delimiter: space, tab, comma(,), colon(:), semicolon(;)
    - The Order of Columns: f(or w), Z'(or |Z|), Z"(or Phase)

- Editing, Removing Bad Data, Interpolation...
- Set Column Value

Set Column Value: Available Functions

- pi

- abs(x)
- acos(x)
- acosh(x)
- acot(x)
- acoth(x)
- asin(x)
- asinh(x)
- atan(x)
- atan2(x,y)
- atanh(x)
- ceil(x)
- cos(x)
- cosh(x)
- cot(x)
- coth(x)
- csc(x)
- csch(x)
- deg(x)
- e(x)
- erf(x)
- erfc(x)
- exp(x)
- factr(x)
- floor(x)
- fract(x)
- gamma(x)
- gammai(a,x)
- getexp(x)
- getman(x)
- int(x)
- ldexp(m,e)
- ln(x)
- log(x,y)
- log10(x)
- log2(x)
- pi(x)
- pow(x,y)
- pow10(x)
- pow2(x)
- rad(x)
- random(x,y)
- sec(x)
- sech(x)
- sign(x)
- sin(x)
- sinc(x)
- sinh(x)
- spike(x)
- sqrt(x)
- square(x)
- step(x)
- tan(x)
- tanh(x)

2. Making ZMAN Project File

- Binary File Format: *.zmp
- 3 Control Variables Available
- Manipulation Items: Editing, Removing Bad Data, Interpolation…

3. Analysis Items

- **KK Consistency** for Validation
- **Modeling:**
  - Initial Guessing: **Circular Fit**, Genetic Algorithm
  - **Model Searching**
- **Model Subtraction**
- **Model Editor:** Manage Library, **Model Simulation**

Validation of IS Data

- Ideal impedance data must fulfill:
  - **Causality**: The output must be exclusively a result of the input
  - **Linearity**: The response must be a linear fn. of the perturbation
  - **Stability**: The system must not be changing during measurement
    → a serious problem for corroding systems
  - **Finite-Valued**: Impedance must be finite value at any frequency

- Kramers-Kronig Relation:
  - Validation Test
    → Artifact or true Z?
  - Low Frequency Extrapolation
  - Calculation: Maclaurin Method
  - The integration range includes the frequencies zero and infinity
    → **USE Z-HIT Approximation**

a. $Z'' \rightarrow Z'$

$$Z'(\omega) = Z'(\infty) + \frac{2}{\pi}\int_0^{\infty} \frac{xZ''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx$$

b. $Z' \rightarrow Z''$

$$Z''(\omega) = -\frac{2\omega}{\pi}\int_0^{\infty} \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx$$

Modeling of Data

- The model to be fitted is

$$y = y(x; \vec{p})$$

and the merit function is

$$\chi^2(\vec{p}) = \sum_{i=0}^{N-1} \left[\frac{y_i - y(x_i; \vec{p})}{\sigma_i} \right]^2$$

- **Problem**: Given a set of N empirical datum pairs of independent and dependent variables, optimize the parameters of the model curve so that χ^2 becomes minimal.

- **Algorithm**: Levenberg-Marquardt Method

Modeling of Data

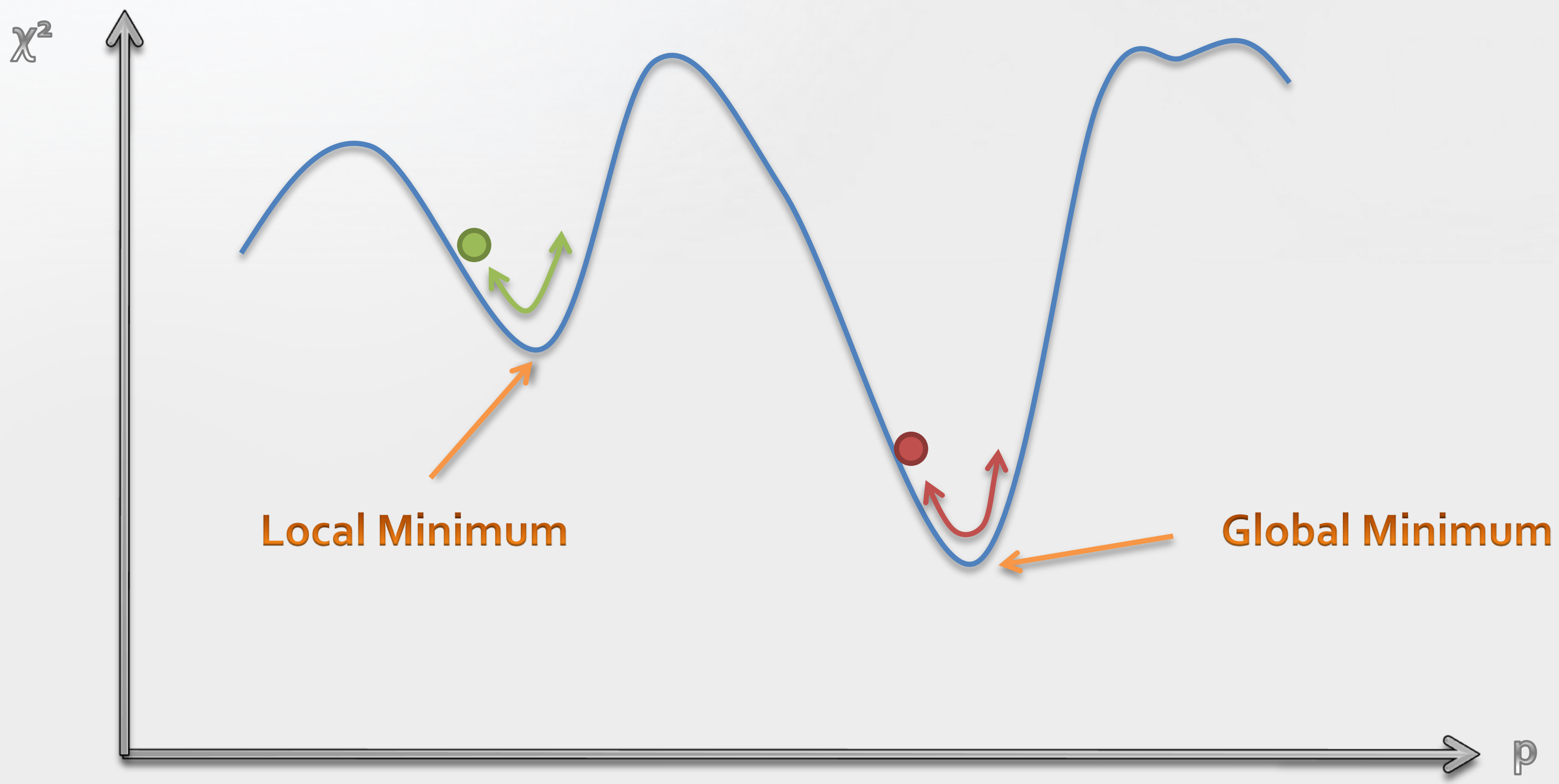
- 26 Data Sequence

Z′ + Z″	Z′	Z″	$\|Z\| + \phi_Z$	$\|Z\|$	ϕ_Z
Y′ + Y″	Y′	Y″	$\|Y\| + \phi_Y$	$\|Y\|$	Φ_Y
M′ + M″	M′	M″	$\|M\| + \phi_M$	$\|M\|$	Φ_M
E′ + E″	E′	E″	$\|E\| + \phi_E$	$\|E\|$	ϕ_E

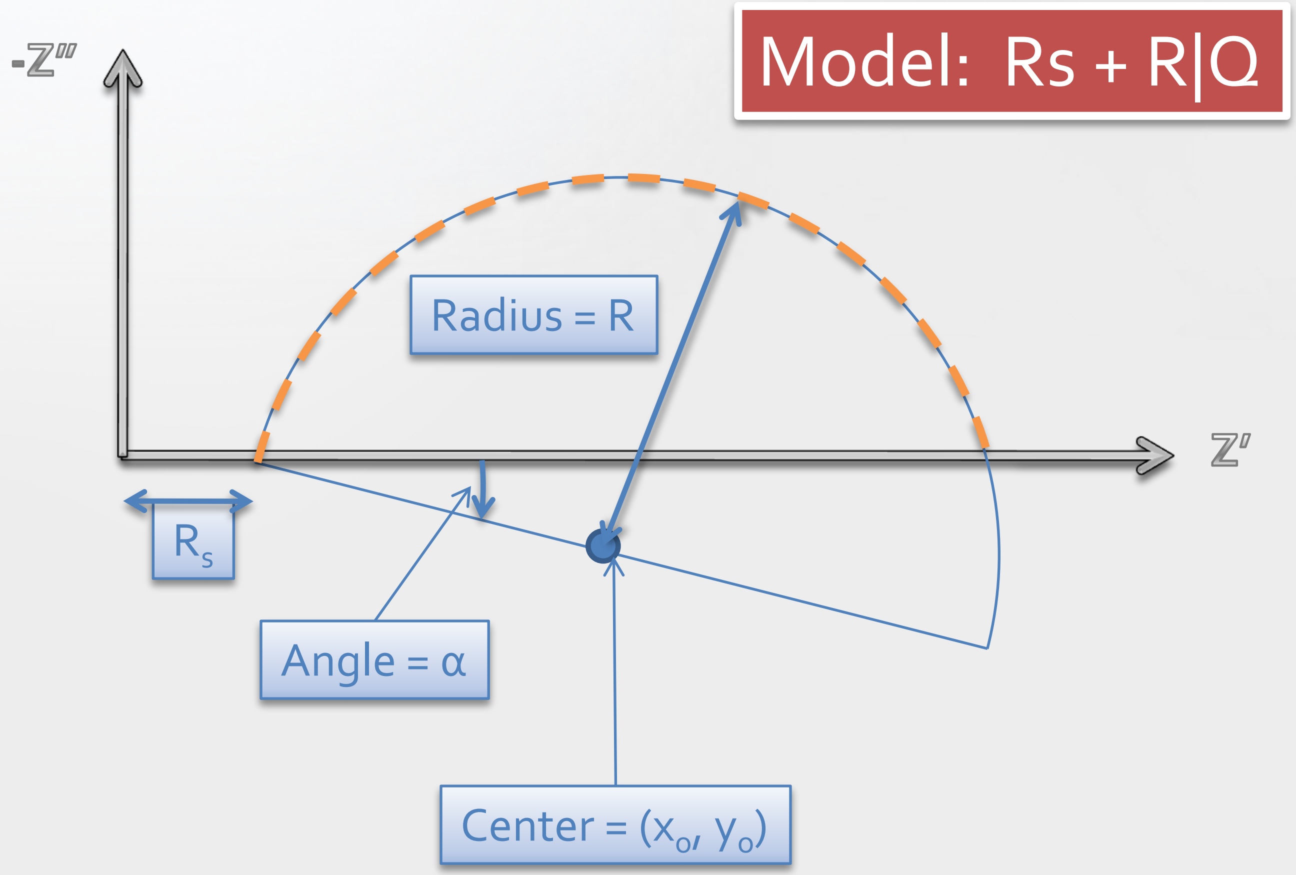
- 3 Weighting Functions

In case of Z′ + Z″		
Unity	$\sigma_i = 1$	for i =0 to 2N-1
Proportional to Data	$\sigma_i = Z'_i$	for i = 0 to N-1
	$\sigma_i = Z''_i$	for i = N to 2N-1
Modulus to Data	$\sigma_i = \|Z_i\| = \sqrt{Z'^2 + Z''^2}$	for i = 0 to 2N-1

Modeling of Data



Initial Guessing: Circular Fit

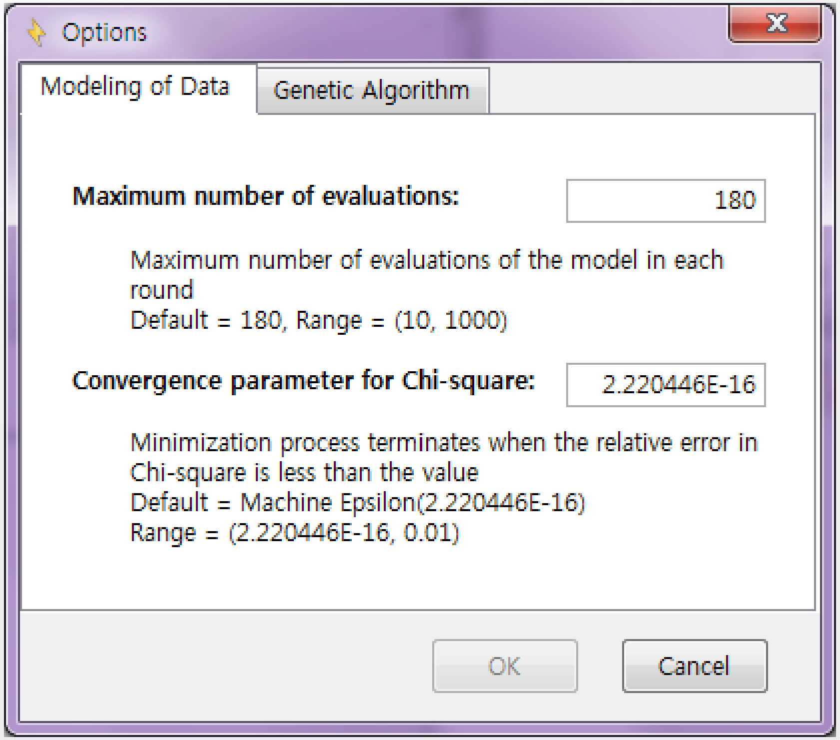


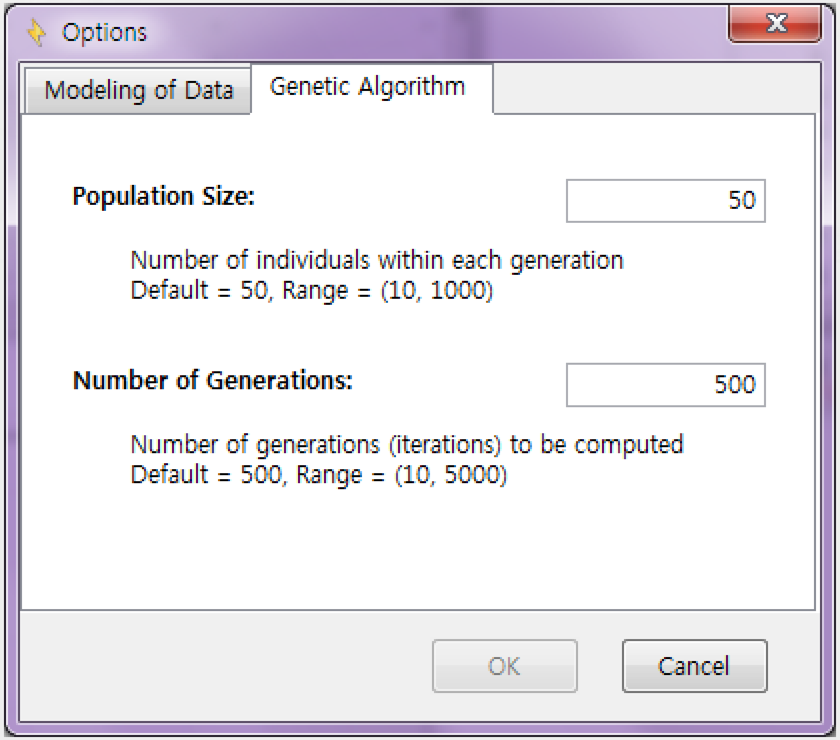
Initial Guessing: Genetic Algorithm

- A search heuristic that mimics the process of natural evolution
  - What's the best answer? It's survival of the fittest.

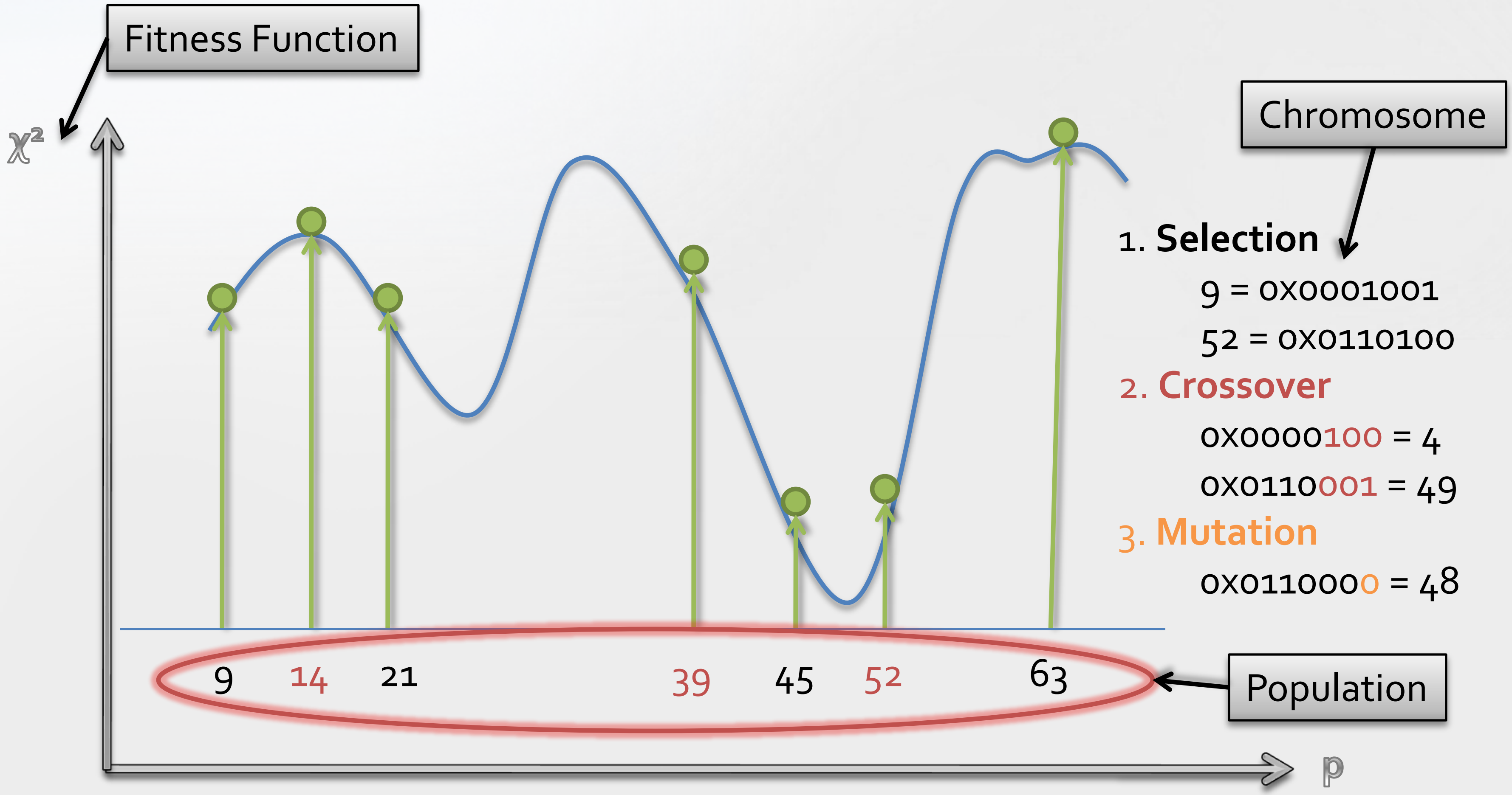
- Methodology
  - **Initialization**: Initial individuals are randomly generated to form initial population
  - **Selection**: During each successive generation, a proportion of the existing population is selected to breed a new generation. Individuals solutions are selected through a fitness-based process, where fitter solutions (as measured by a fitness function) are typically more likely to be selected.
  - **Reproduction**: **Crossover** and **Mutation**
  - **Termination**: This generational process is repeated until a termination condition has been reached.

Options

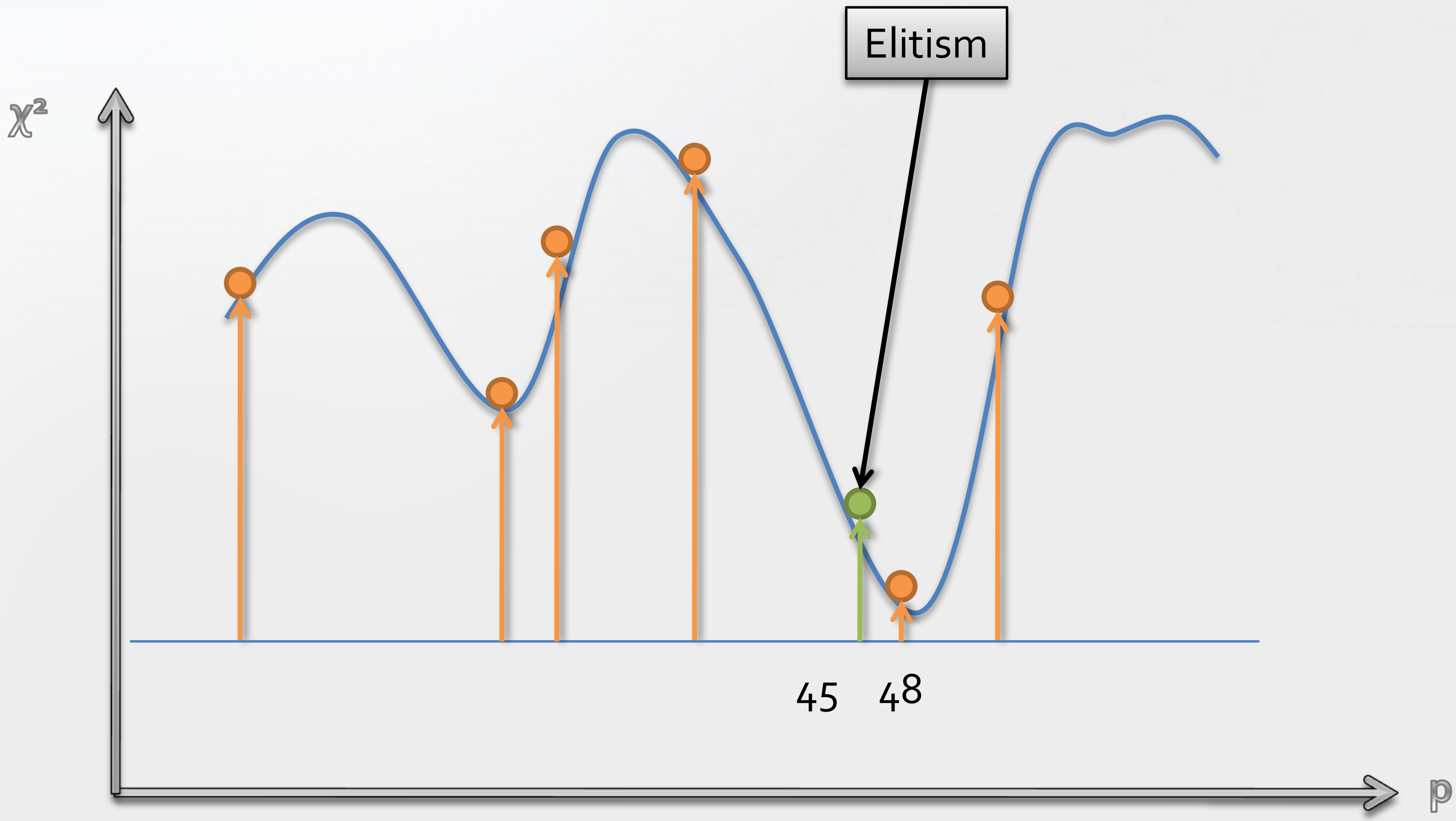

Options
Modeling of Data
Genetic Algorithm
Maximum number of evaluations:
180
Maximum number of evaluations of the model in each round
Default = 180, Range = (10, 1000)
Convergence parameter for Chi-square:
2.220446E-16
Minimization process terminates when the relative error in Chi-square is less than the value
Default = Machine Epsilon(2.220446E-16)
Range = (2.220446E-16, 0.01)
OK
Cancel


Options
Modeling of Data
Genetic Algorithm
Population Size:
50
Number of individuals within each generation
Default = 50, Range = (10, 1000)
Number of Generations:
500
Number of generations (iterations) to be computed
Default = 500, Range = (10, 5000)
OK
Cancel

Genetic Algorithm
1^{st} Generation



Genetic Algorithm
2^{nd} Generation



4. Presentation

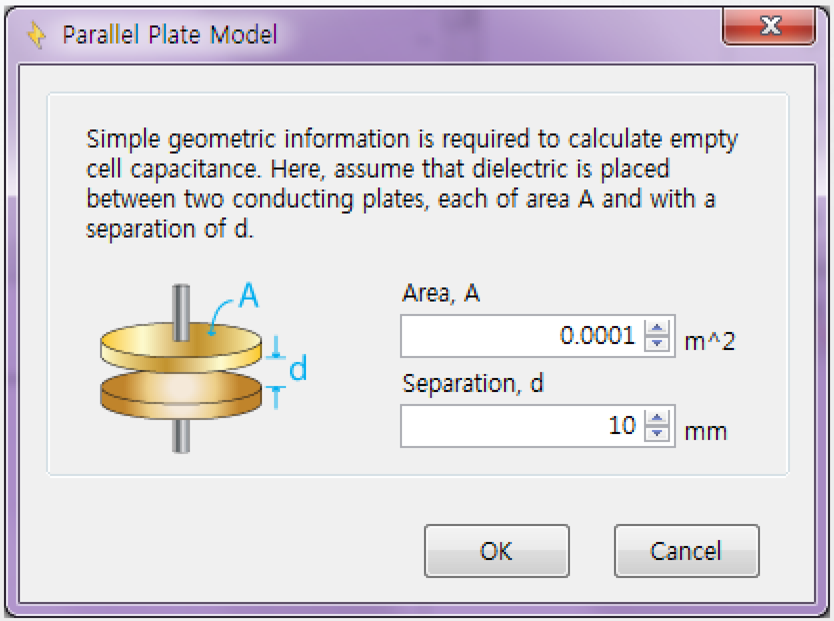
- Immittance
  - Impedance(Z), Admittance(Y), Modulus(M), and Dielectric Constant(E)

	Z Z′ + jZ″	**Y** Y′ + jY″	**M** M′ + jM″	**E** E′ - jE″
Z	Z	Y^{-1}	$\mu^{-1}M$	$\mu^{-1}E^{-1}$
Y	Z^{-1}	Y	μM^{-1}	μE
M	μZ	μY^{-1}	M	E^{-1}
E	$\mu^{-1}Z^{-1}$	$\mu^{-1}Y$	M^{-1}	E

* $\mu \equiv j\omega C_c$, where C_c is the capacitance of the empty cell
* C_c can be expressed as $\varepsilon_o A/d$ in simple parallel plate model

- Nyquist(Cole-Cole), Bode, Black-Nichols, 3D Curve, 3D Surface, and Parameter Plot

Parallel Plate Model



$$C = \varepsilon \frac{A}{d} = \varepsilon_r \varepsilon_o \frac{A}{d} = \varepsilon_r C_c$$

$$Z = \frac{1}{j\omega C}$$

$$\therefore \varepsilon_r = \frac{1}{j\omega C_c Z} = \frac{1}{\mu Z}$$