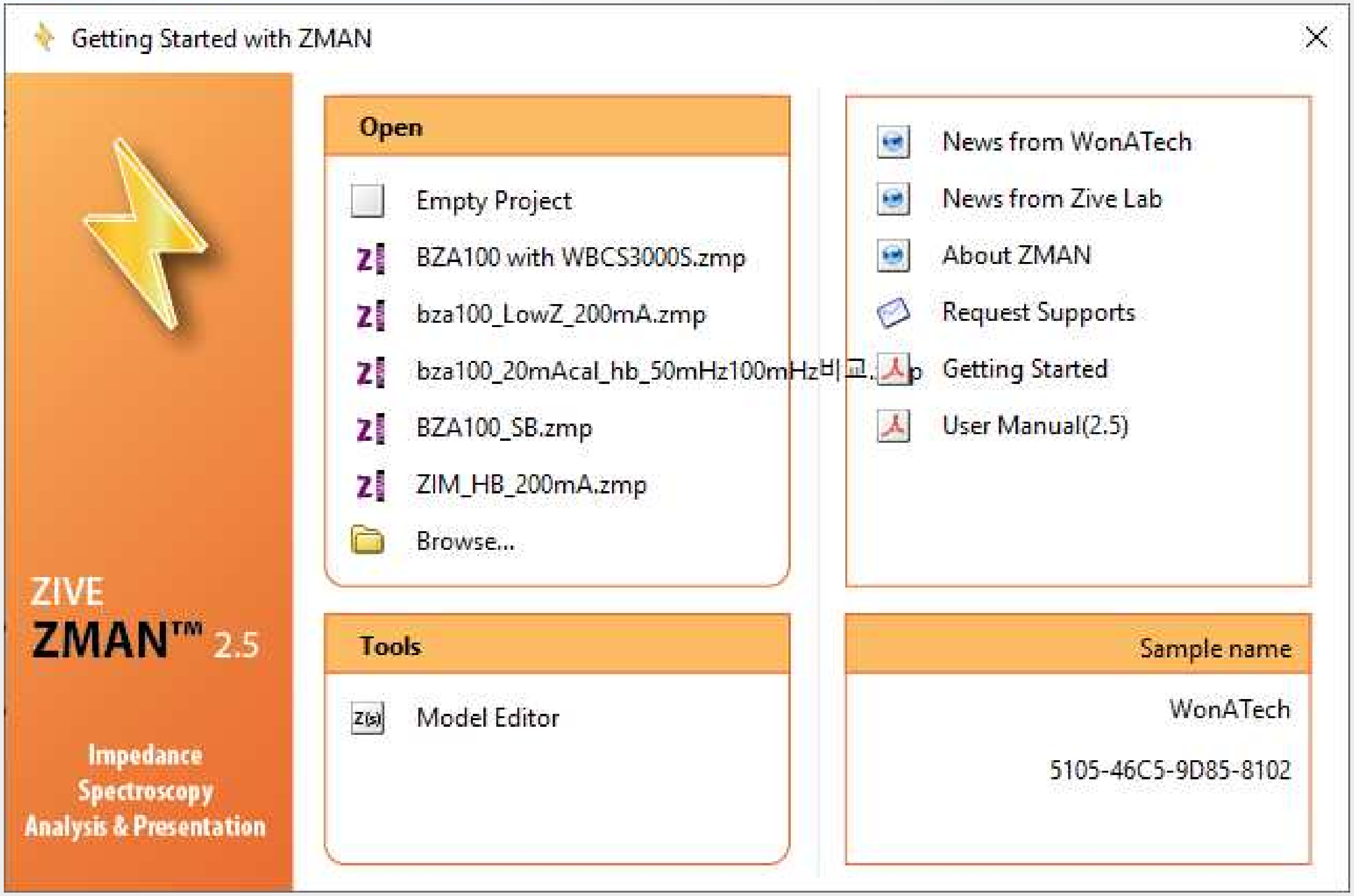
Getting Started with ZMAN

May 2022

ZIVE LAB

WonATech
Designing the Solutions for Electrochemistry
Potentiostat/Galvanostat| Battery test system | Impedance Analyser | Fuel cell test system
T. +82-2-578-6516 F. 82-2-576-2635 email: sales@wonatech.com
wonatech.com | zivelab.com | electrochemistry.co.kr | qrins.com



Getting Started with ZMAN
ZIVE
ZMAN™ 2.5
Impedance
Spectroscopy
Analysis & Presentation
Open
Empty Project
BZA100 with WBCS3000S.zmp
bza100_LowZ_200mA.zmp
bza100_20mAcal_hb_50mHz100mHz비교..p
BZA100_SB.zmp
ZIM_HB_200mA.zmp
Browse...
Tools
Model Editor
News from WonATech
News from Zive Lab
About ZMAN
Request Supports
Getting Started
User Manual(2.5)
Sample name
WonATech
5105-46C5-9D85-8102

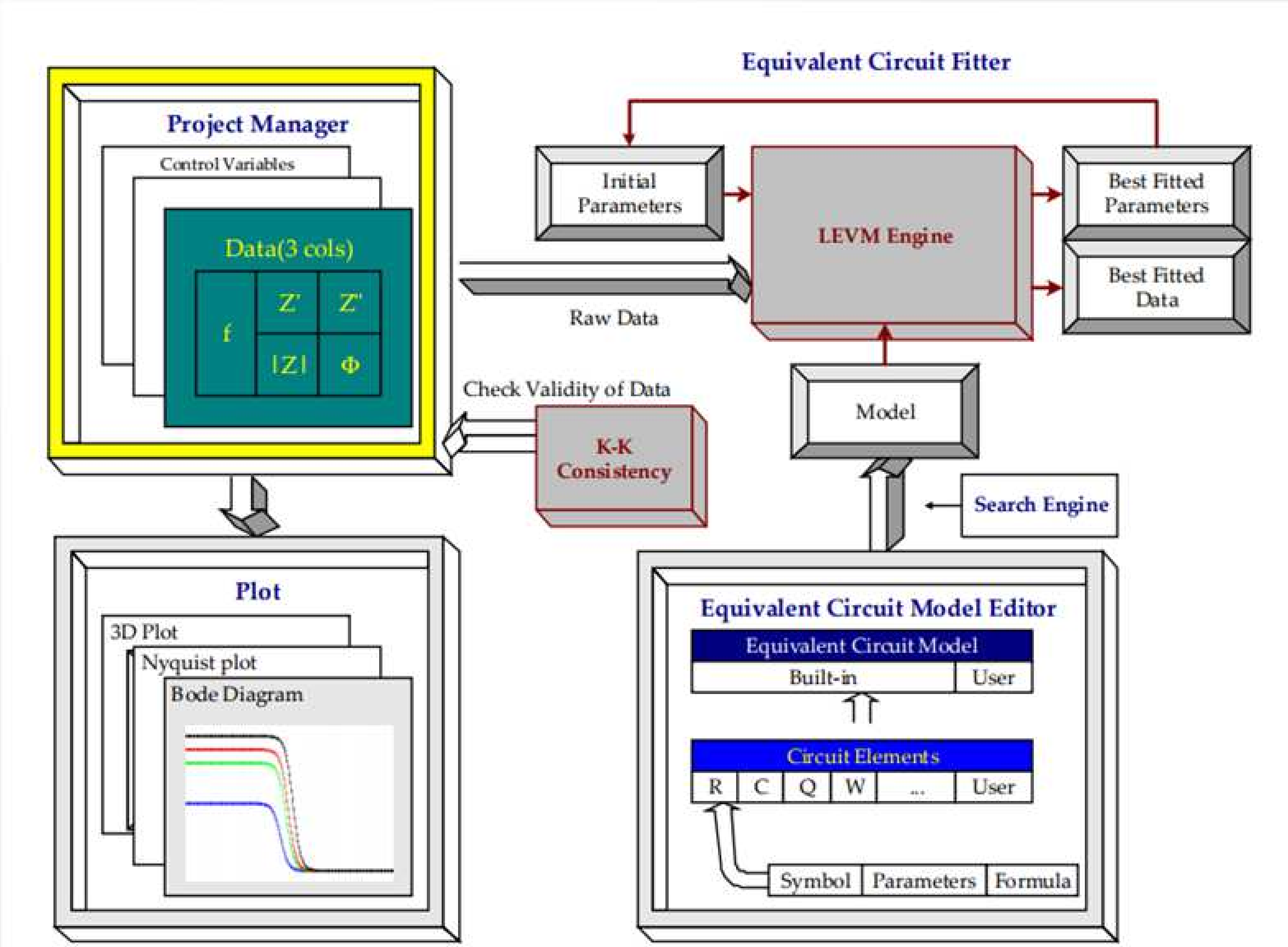
ZIVE LAB

What is ZMAN?

- Ans: Electrochemical 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

ZMAN Diagram



ZMAN
Installation and Activation

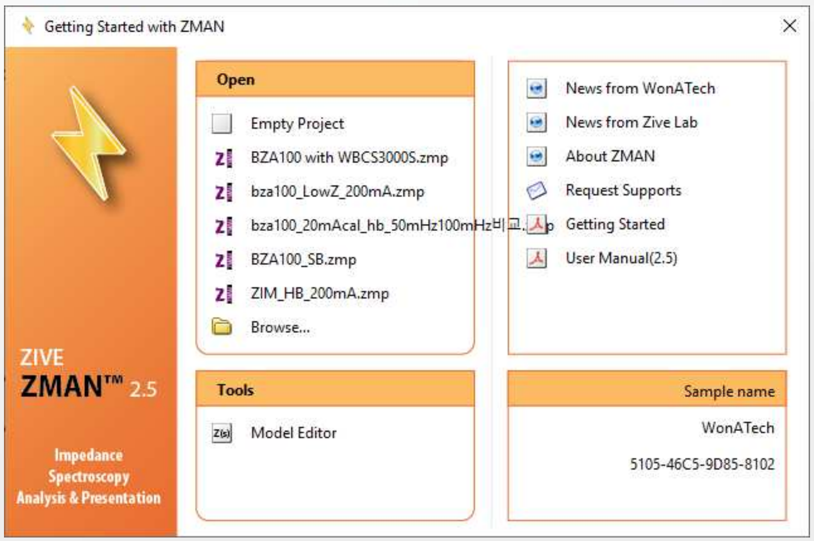
ZIVE LAB

Installation and Activation

1. Setup "LabVIEW Run-Time Engine 2010 SP1"
   - How to get? Install CD or NI website (www.ni.com)
   - http://joule.ni.com/nidu/cds/view/p/id/2292/lang/en
   - Only 32-bit RTE is working for ZMAN
2. Setup "ZMAN 2.5"
   - How to get? Install CD or ZIVE LAB website (www.zivelab.com)
   - Click "support" and "Software Download"
3. Activate ZMAN 2.5
   - Is it necessary? Once activated, you can open any ASCII files or registered 3rd parties data files.
   - How to activate? Click **Activate** button in **Getting Started Window** and email to us

ZIVE LAB

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 ZIVE LAB Web site, zivelab.com
d. Launch the ZMAN User Manual
e. Manage Model Editor

ZIVE LAB

ZMAN
Overall Procedure

ZIVE LAB

1. Selecting Data Files

- Available File Formats
  - WonATech Binary Files:
    - *.wdf(WEIS Series), *.sde, *.seo(ZIVE workstation series), *wis(Z#,zcon series),*.z# (BZA series)
    - No activation required
  - 3rd Party Binary Files:
    - *.ism(Zarner)
  - 3rd Party ASCII Files:
    - Gamry,Solartron),Bio-Logic, AutoLab, InPhaze, Palmsens, Orgalys, Ivium (Please check whether your data version is compatible or not before purchasing. Contact with sales representative)

  - 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

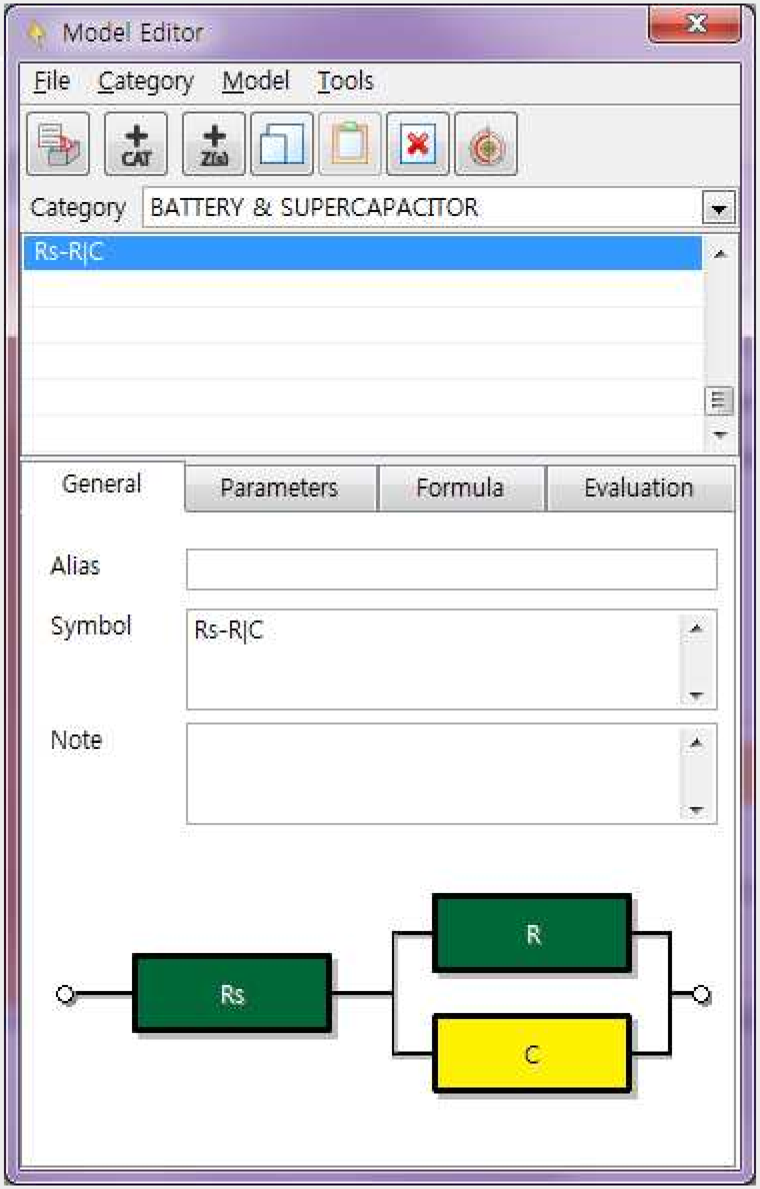
- abs(x)
- acos(x)
- acosh(x)
- acot(x)
- acoth(x)
- asin(x)
- asinh(x)
- atan(x)
- atan2(x,y)
- atanh(x)
- ceil(x)
- cos(x)
- cosh(x)
- cot(x)
- coth(x)
- csc(x)
- csch(x)
- deg(x)
- e(x)
- erf(x)
- erfc(x)
- exp(x)
- factr(x)
- floor(x)
- fract(x)
- gamma(x)
- gammai(a,x)
- getexp(x)
- getman(x)
- 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. Model Editor

- Elements
  - Built-in
  - User-Defined
- Models
- Category



Basic 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 $s = j\omega = 2\pi f$

ZIVE LAB

Basic 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 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

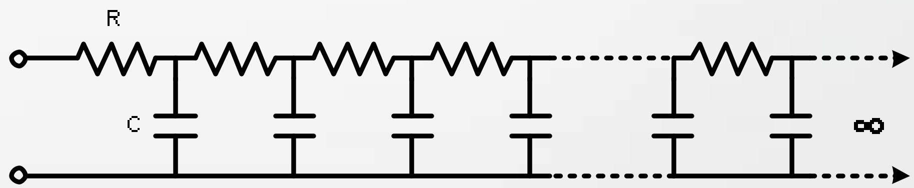
a. Impedance Spectroscopy: Theory, Experiment, and Applications, 2nd ed., Ed. E. Barsoukov, and J. R. Macdonald, John Wiley & Sons, Inc., Hoboken, New Jersey, 2005

b. $I_0(x)$ and $I_1(x)$ are Bessel-functions of the first kind, with 0 and 1 order correspondingly

Diffusion

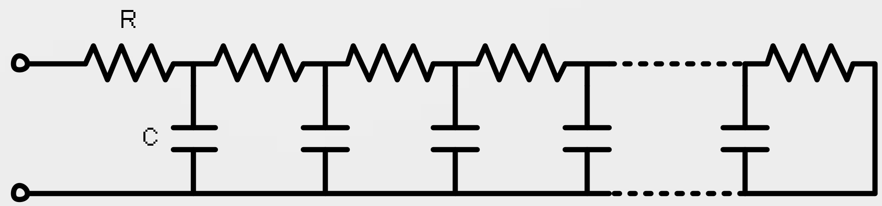
- Transmission Line Model

W: Warburg



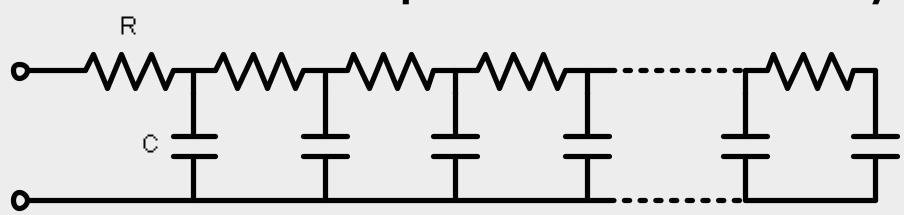
$$Z = \frac{\sigma}{\sqrt{\omega}}(1 - j)$$

O: Nernstian Impedance: Diffusion by Constant Concentration



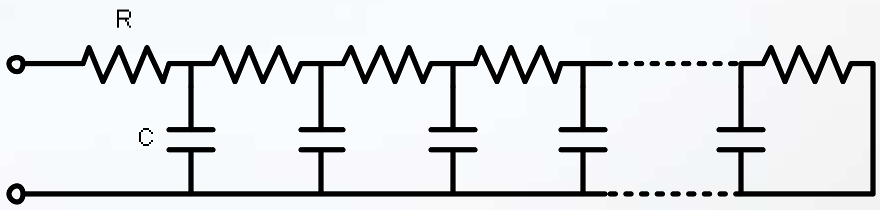
$$Z = \frac{\sigma}{\sqrt{\omega}}(1 - j)\tanh(\delta\sqrt{j\omega/D})$$

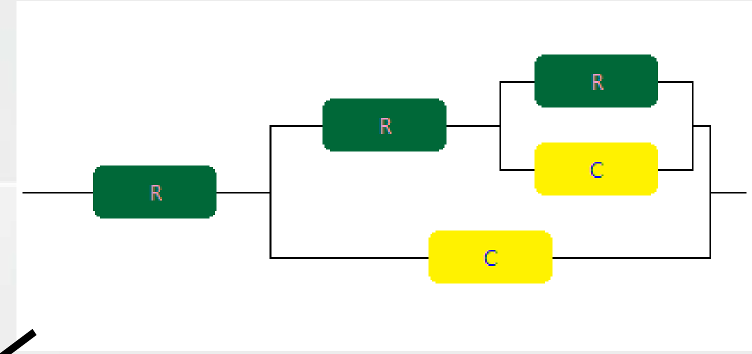
T: Finite Diffusion Impedance: Diffusion by Phase Boundary



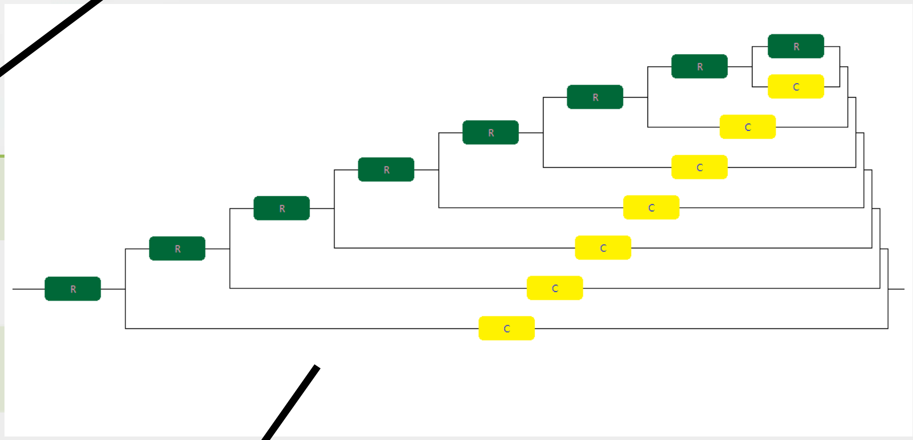
$$Z = \frac{\sigma}{\sqrt{\omega}}(1 - j)\coth(\delta\sqrt{j\omega/D})$$

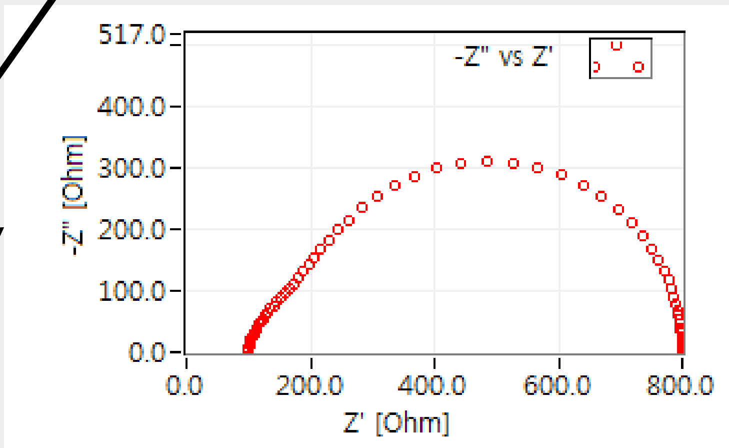
Transmission Line





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

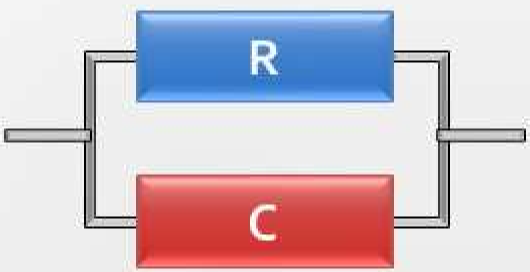




ZIVE LAB

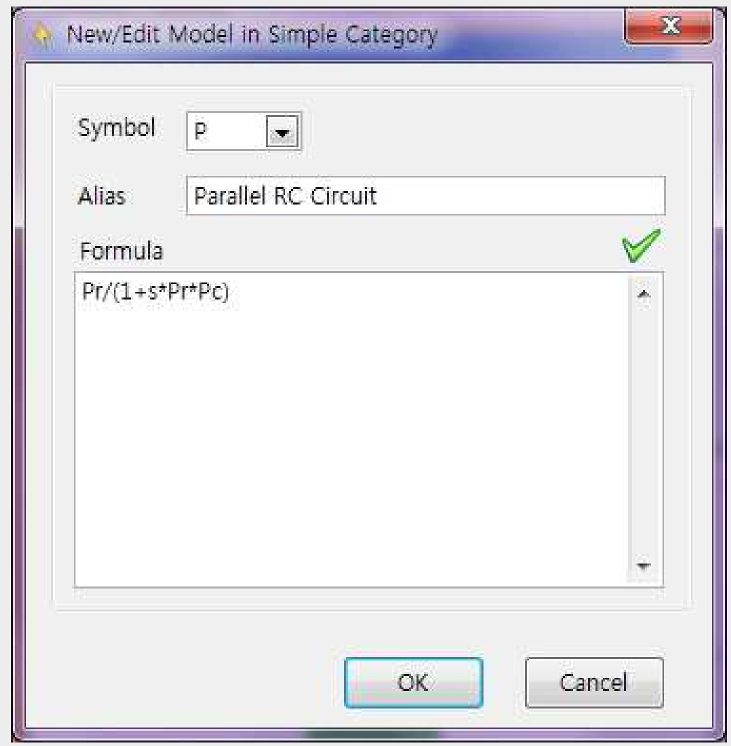
Simple Elements

	Description	Parameters	Formula	Note
P	Parallel RC Circuit R|C	Pr Pc	Pr/(1+s*Pr*Pc)	



$$\frac{1}{Z} = \frac{1}{R} + \frac{1}{1/_{j\omega C}}$$

$$\therefore Z = \frac{R}{1 + j\omega C}$$



Naming Convention - Element

Parameter naming convention for circuit element

ZMAN accepts only the following parameters:

A, AA, AB, AC, … AZ, Aa, Ab, Ac, … Az
B, BA, BB, BC, … BZ, Ba, Bb, Bc, … Bz
…
Z, ZA, ZB, ZC, … ZZ, Za, Zb, Zc, … Zz

- A parameter must consist of symbol and (or) an alphabetical character.
- A parameter name is case sensitive; i.e. AA and Aa are considered to be distinct parameters.

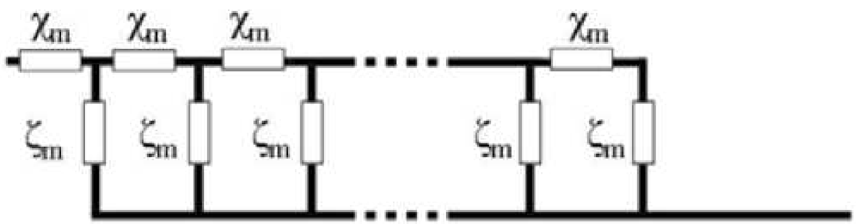
Naming Convention in a Model

Ex) Rs-Cc|(R1-Rct|Cdl)

Variables are distinguished by names. There are the following rules of naming variables:

- The first character should be a Symbol character(A to Z) and followed by alphabetical characters (capital and small letters), decimal digits, and underscore (_)
- A name is case sensitive; i.e. lowercase and uppercase letters are considered to be distinct characters
- There is no limit of name length; herewith all characters are significant

ex) How to add Bisquert open model



$$Z = \sqrt{\zeta_m \chi_m}\, \coth\left(L \sqrt{\frac{\chi_m}{\zeta_m}} \right) \quad \text{where} \quad \zeta_m = r_m \quad \text{and} \quad \chi_m = r_k \,||\, q_m$$

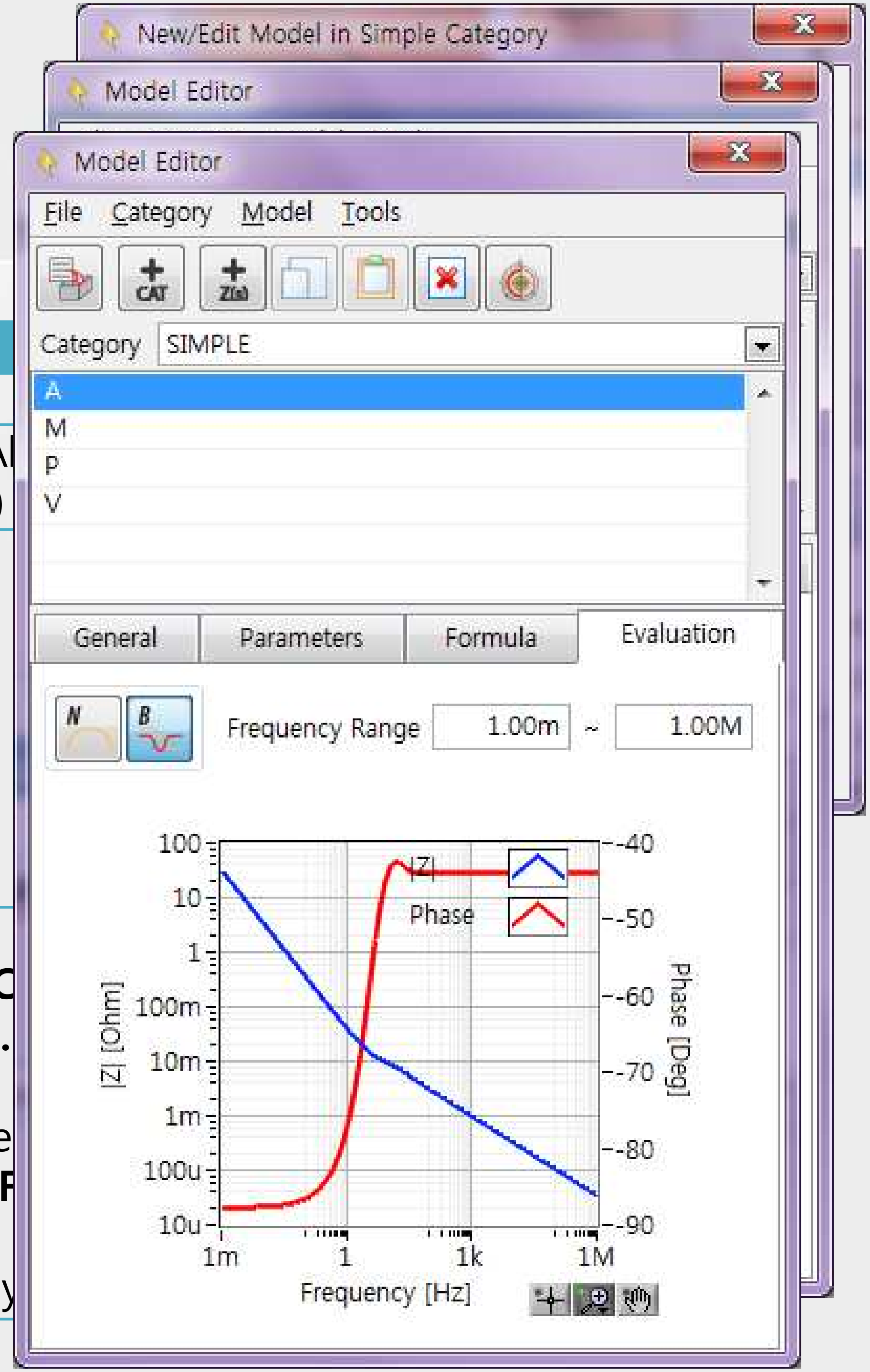
$$CPE,\ q_m = \frac{1}{Q_y s^{Q_a}} \quad \text{where } s = j\omega \text{ and } \quad j = \sqrt{-1}$$

So, $\chi_m = \dfrac{r_k}{1 + r_k Q_y s^{Q_a}}$

Then, $Z = \sqrt{\dfrac{r_m r_k}{1 + r_k Q_y s^{Q_a}}}\, \coth\left(L \sqrt{\dfrac{r_m}{r_k}\left(1 + r_k Q_y s^{Q_a}\right)} \right)$

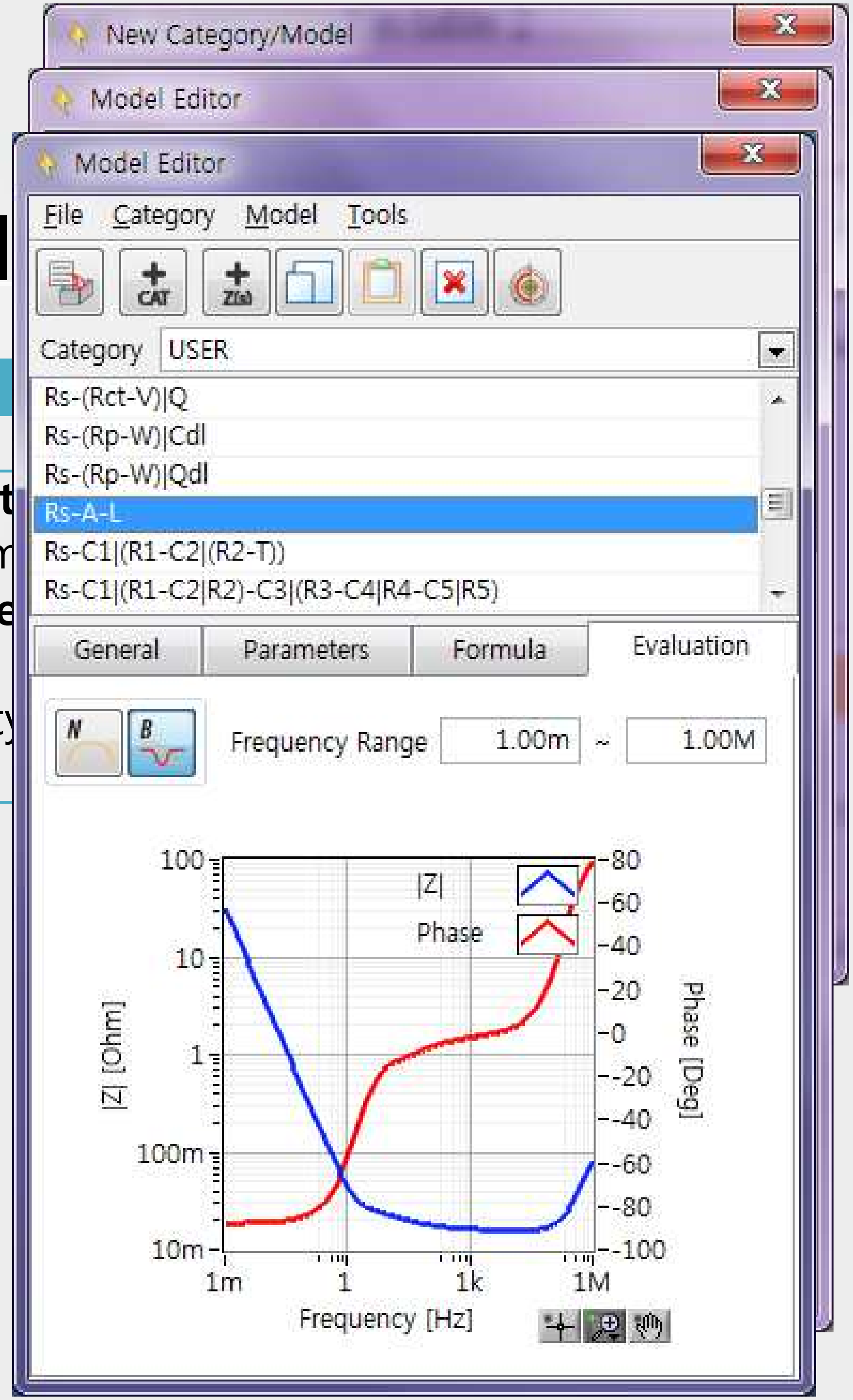
Step 1. Add “A” element in

Category	SIMPLE
Model	A
Formula	coth(AL * sqrt(Am / Ak * (1 + Al Ak / (1 + Ak * Ay * pow(s, Aa)))
Note	• $AL = L$ • $Am = r_m$ • $Ak = r_k$ • $Ay = Q_y$ • $Aa = Q_a$ • $s = j\omega$
Steps	(1) Open **Model Editor** dialog (2) Select **SIMPLE** item in the **C** (3) Select **Model > New/Edit…** (4) Select **A** as **Symbol** (5) Type “Bisquert Open” in the (6) Type above formula in the **F** (7) Click the **OK** button (8) Select **Parameter** tab and ty

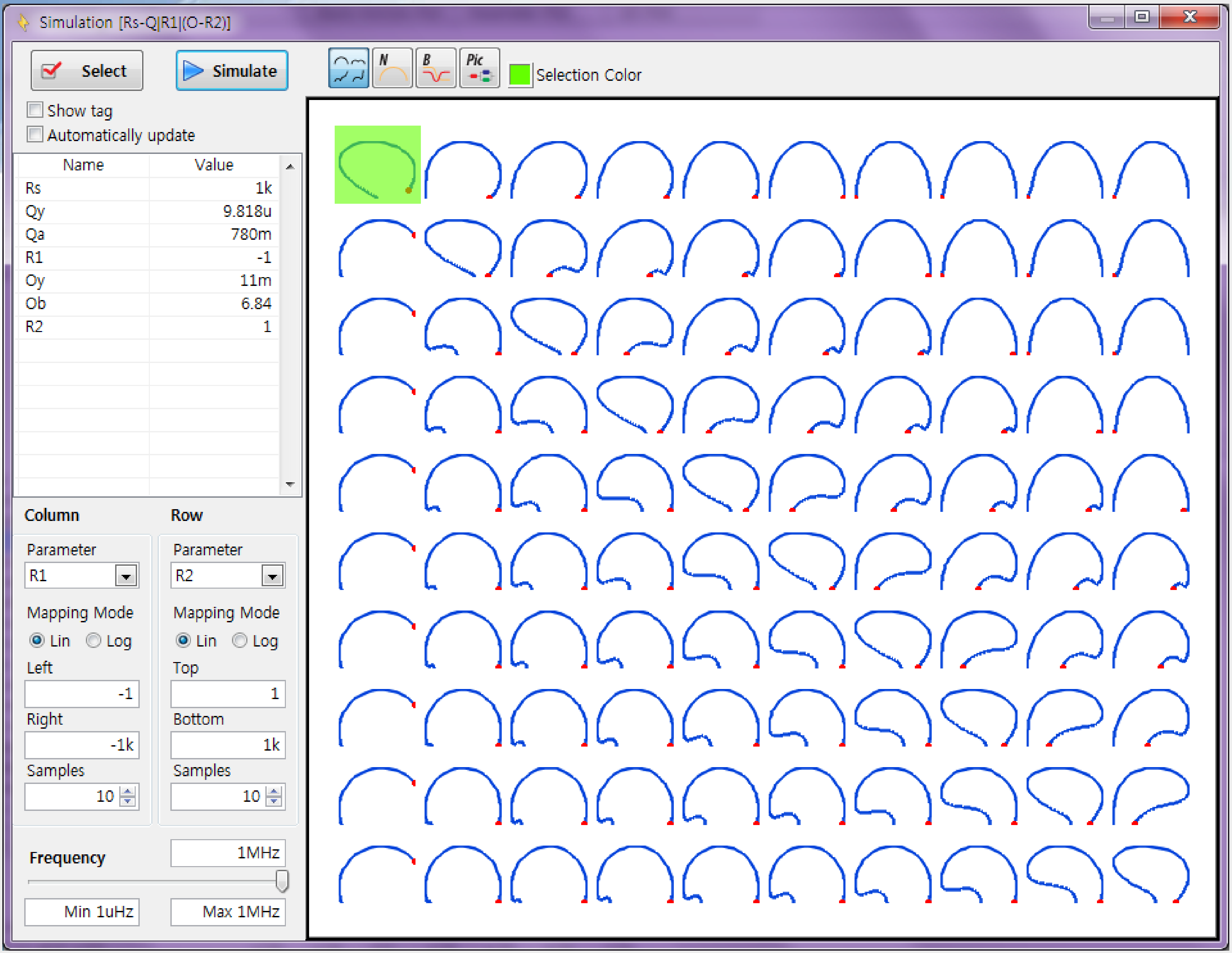


Step2. Add "Rs-A-L1" Model

Category	USER
Model	Rs-A-L1
Steps	(1) Select **USER** item in the **Cat** (2) Select **Model > New…** in m (3) Type "Rs-A-L1" in the **Mode** (4) Click the **OK** button (5) Select **Parameter** tab and ty



ZIVE LAB


Simulation [Rs-Q|R1|(O-R2)]
Select
Simulate
Selection Color
Show tag
Automatically update
Name
Value
Rs
1k
Qy
9.818u
Qa
780m
R1
-1
Oy
11m
Ob
6.84
R2
1
Column
Row
Parameter
R1
Parameter
R2
Mapping Mode
Lin
Log
Mapping Mode
Lin
Log
Left
-1
Top
1
Right
-1k
Bottom
1k
Samples
10
Samples
10
Frequency
1MHz
Min 1uHz
Max 1MHz

ZIVE LAB

4. Analysis Items

- **KK Consistency** for Validation
  - You can refine the data by ZHIT
- **Modeling:**
  - Initial Guessing: **Circular Fit**, Genetic Algorithm
  - **Model Searching**
- **Model Subtraction**
- **Model Editor:** Manage Library, **Model Simulation**

Validation of IS Data

- Kramers-Kronig Relation:

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

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

- Z-HIT:

$$\ln\left|Z(\omega_0)\right| \approx \text{const.} + \frac{2}{\pi}\int_{\omega_S}^{\omega_0} \varphi(\omega) d\ln\omega + \gamma \cdot \frac{d\varphi(\omega_O)}{d\ln\omega}$$

ZIVE LAB

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

ZIVE LAB

Modeling of Data

- 26 Data Sequence

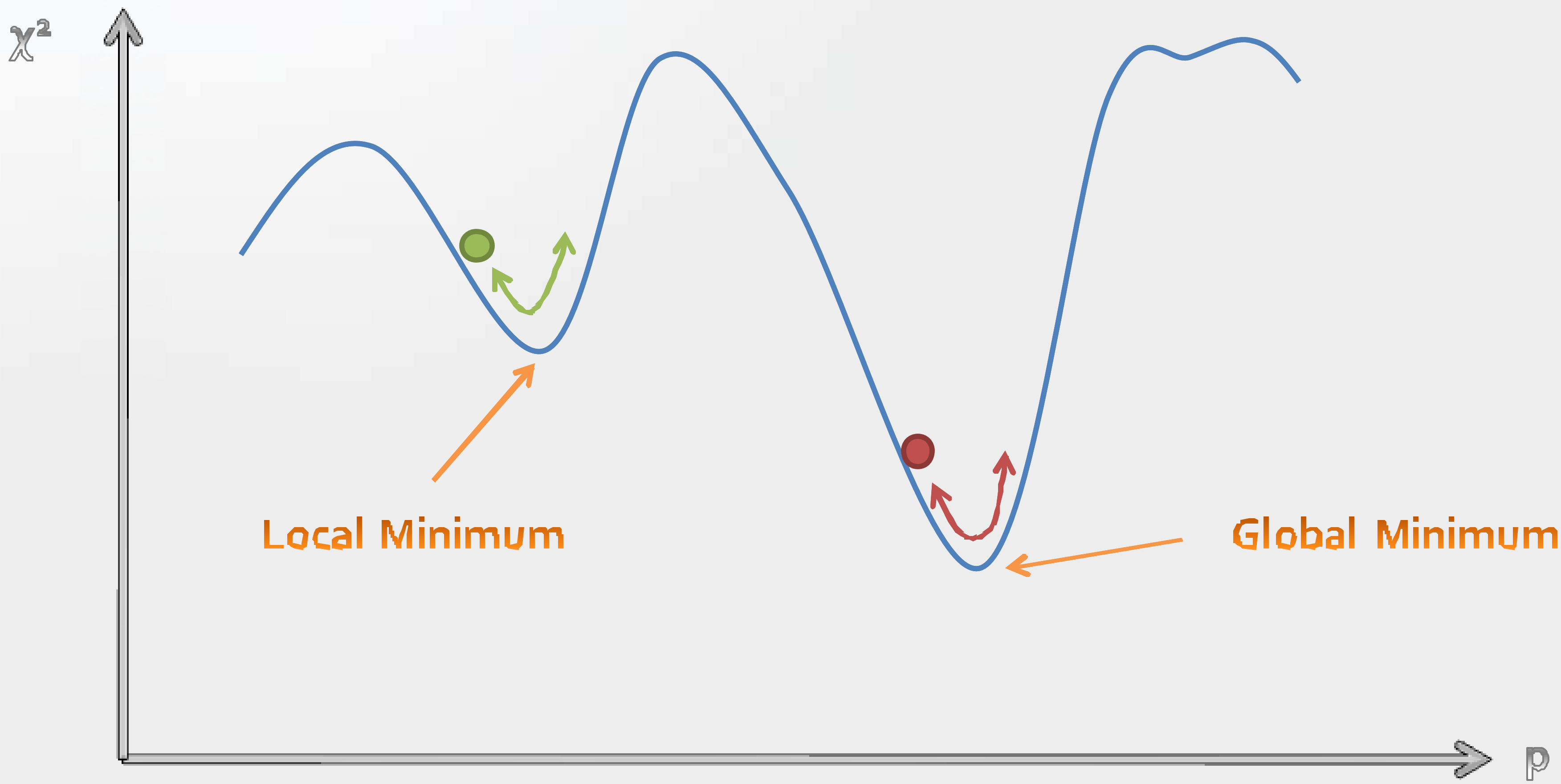
Z′ + Z″	Z′	Z″	$\|Z\| + \phi_Z$	$\|Z\|$	ϕ_Z
Y′ + Y″	Y′	Y″	$\|Y\| + \phi_Y$	$\|Y\|$	Φ_Y
M′ + M″	M′	M″	$\|M\| + \phi_M$	$\|M\|$	Φ_M
E′ + E″	E′	E″	$\|E\| + \phi_E$	$\|E\|$	ϕ_E

- 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

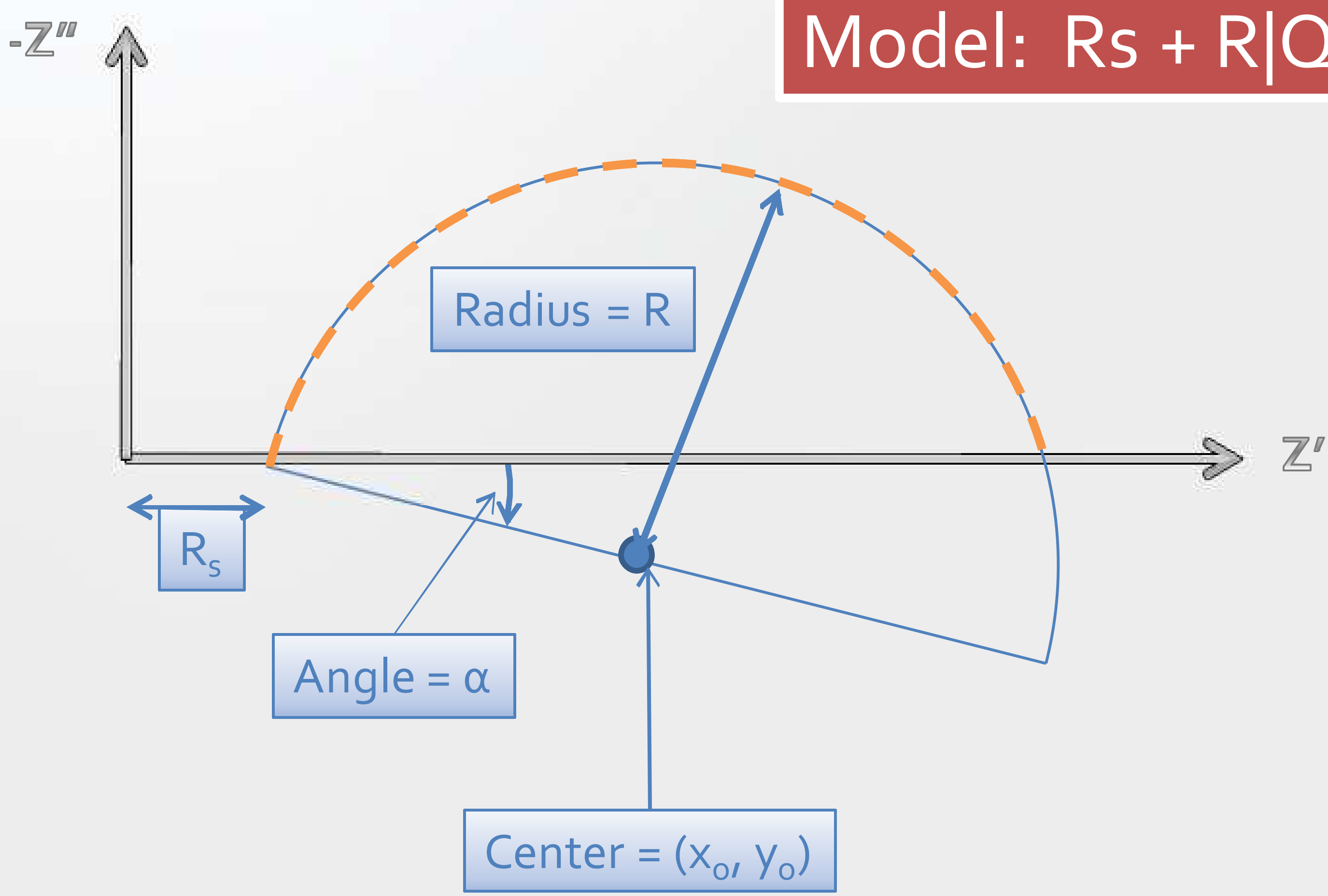
ZIVE LAB

Modeling of Data



Initial Guessing: Circular Fit

Model: Rs + R|Q



ZIVE LAB

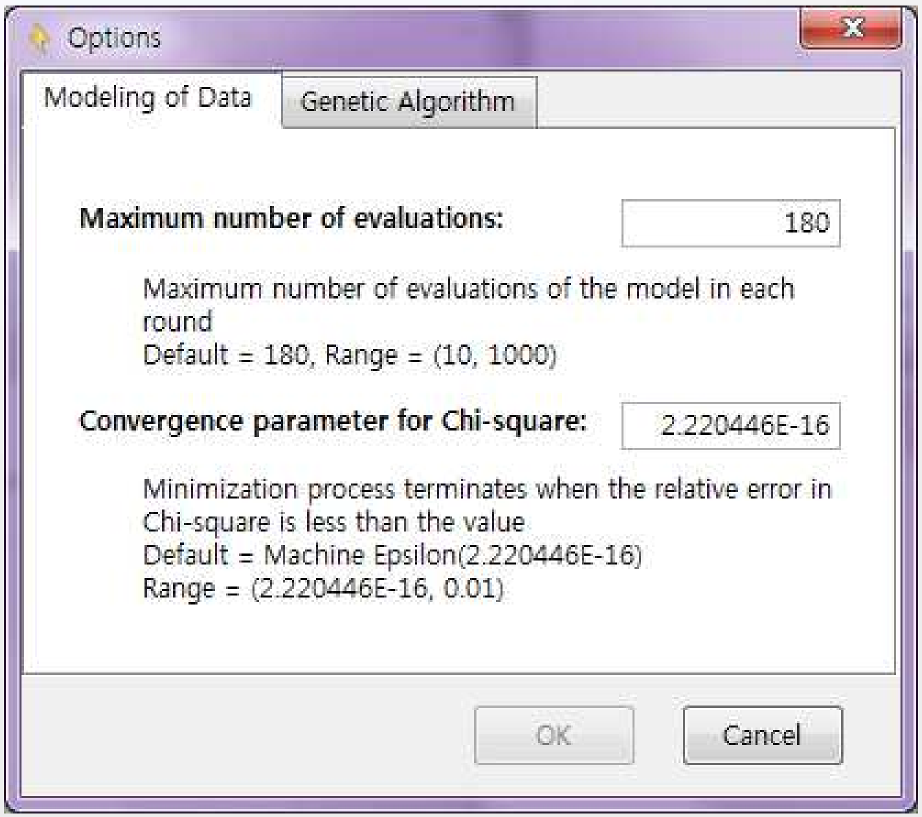
Initial Guessing: Genetic Algorithm

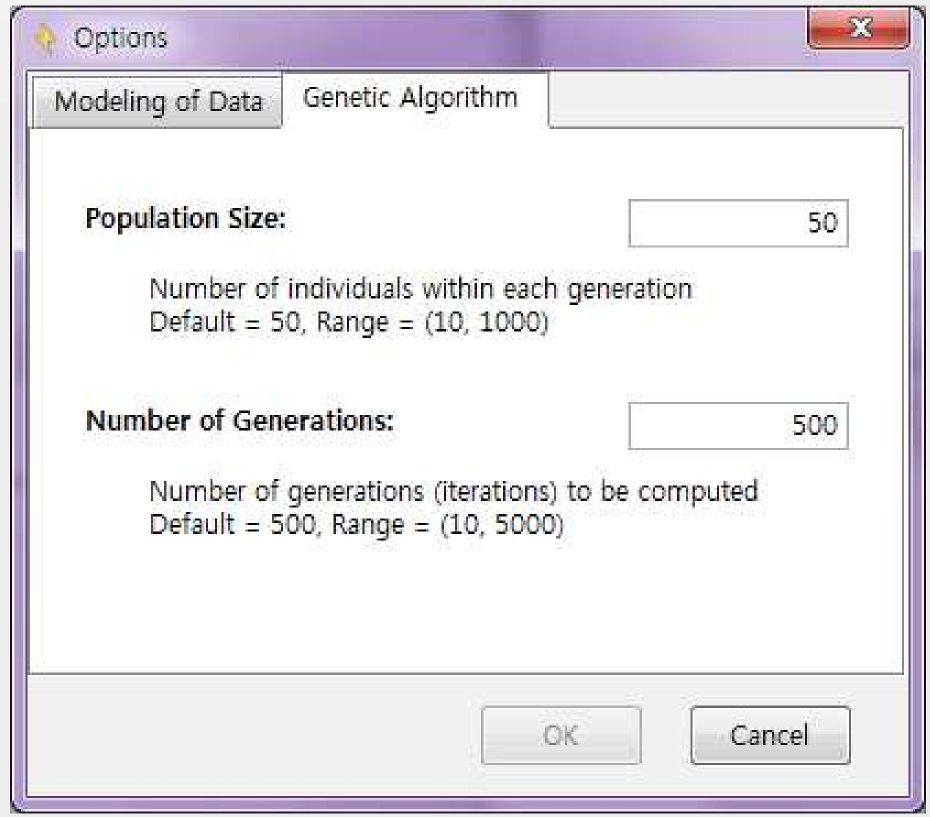
- A search heuristic that mimics the process of natural evolution
  - What’s the best answer? **It's survival of the fittest.**

- 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. Individual 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.

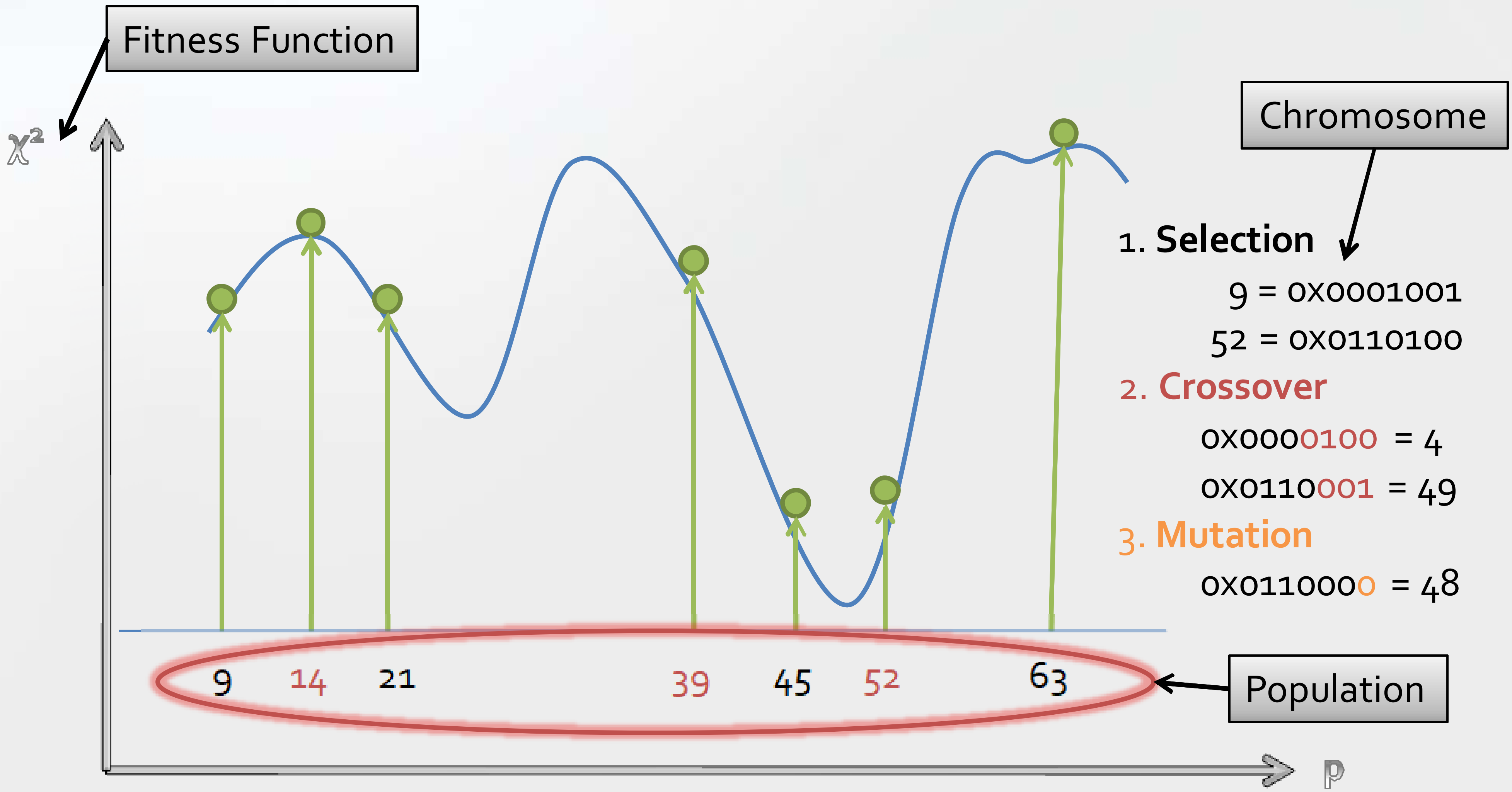
ZIVE LAB

Options

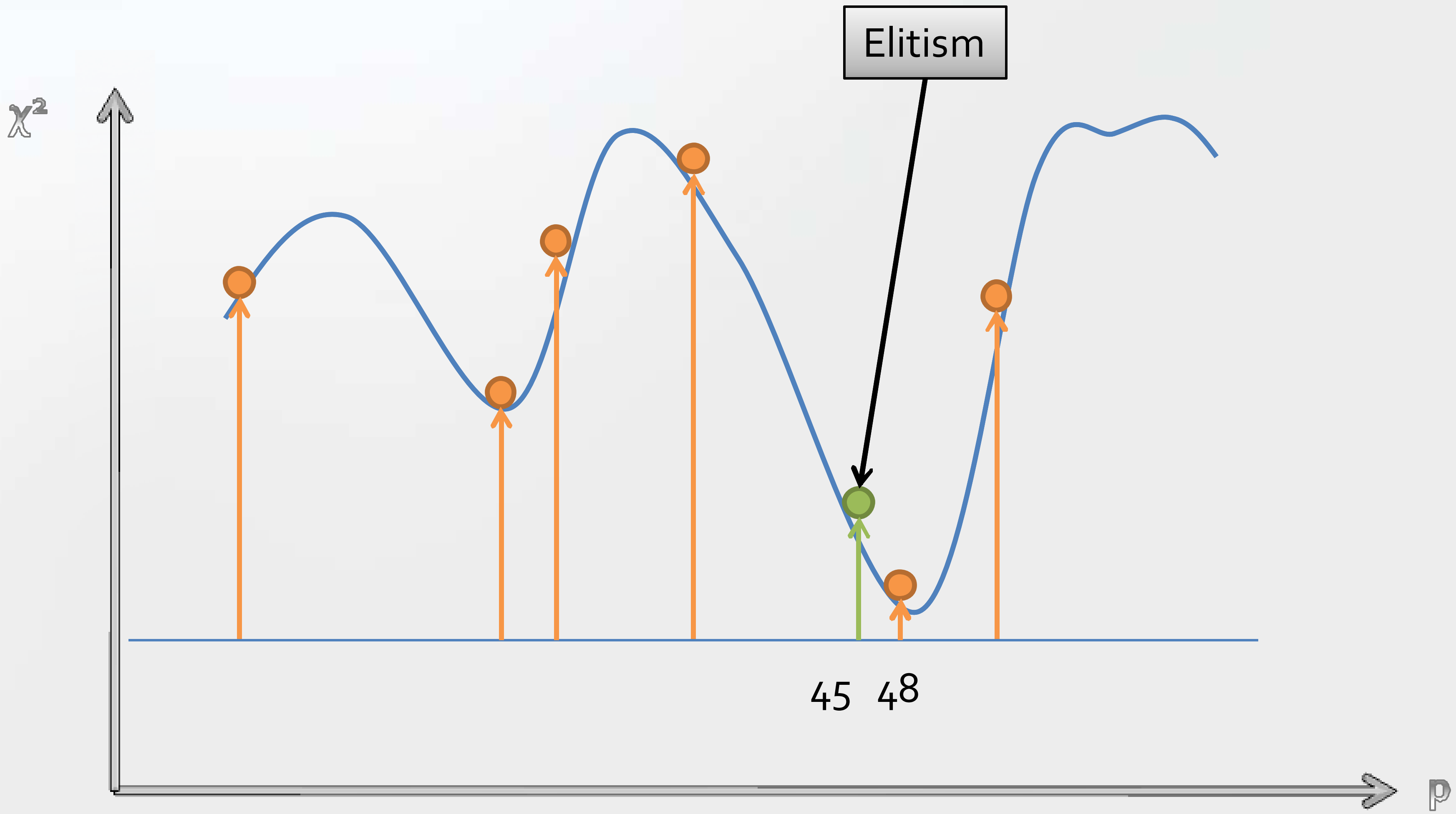

Options
Modeling of Data
Genetic Algorithm
Maximum number of evaluations:
180
Maximum number of evaluations of the model in each round
Default = 180, Range = (10, 1000)
Convergence parameter for Chi-square:
2.220446E-16
Minimization process terminates when the relative error in Chi-square is less than 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
1st Generation



Genetic Algorithm
2nd Generation



ZIVE LAB

5. 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

ZIVE LAB