第九章 交流阻抗谱技术

- **Introduction**
- **Basic elements in an electric circuit**
- **Nyquist and Bode plots**
- **Data analysis and software**
- **Examples**

What should you know?

- 阻抗谱的原理
- 如何看懂阻抗谱？
- 如何解析阻抗谱？（常用软件）
- 阻抗谱的常见错误

Introduction

Terminology:

- AC Impedance Spectroscopy (IS)
- Electrochemical Impedance Spectroscopy (EIS)
- Complex Impedance Spectroscopy (CIS)

References:

- J.R. MacDonald, Impedance Spectroscopy, Chapel Hill, North Carolina, 1987. (John-Wiley, 2005?)
- 史美伦，交流阻抗谱原理及应用，国防工业出版社，2001.
- 曹楚南, 张鉴清，电化学阻抗谱导论，科学出版社，2002.

Introduction

- **暂态与稳态: This is a transient technique, but one that requires a general steady state condition.**

- **可测性质: can be used for determining both:**

  Interfacial parameters (界面参数)

  a) reaction rates
  b) rate constants
  c) capacitance/charge storage abilities
  d) diffusion coefficients
  e) adsorption rate constants
  f) reaction mechanisms

And

Material parameters (材料参数)

a) conductivity
b) dielectric constants
c) bulk generation-recombination reaction rates
d) charge mobilities
e) film thickness
f) equilibrium conc. of charged species
g) presence of pores and cracks

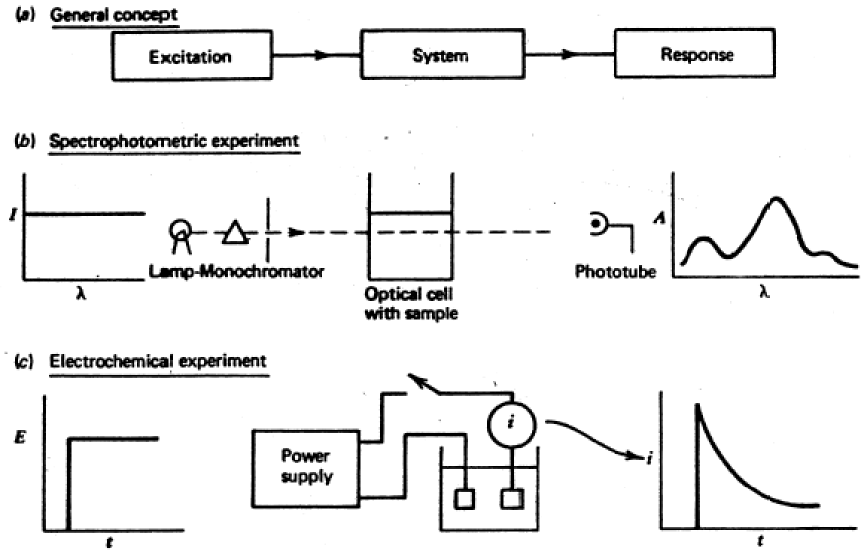
General concept

-- like other spectroscopy experiments, we apply an excitation to the system under study and observe its response (generally as a function of frequency)

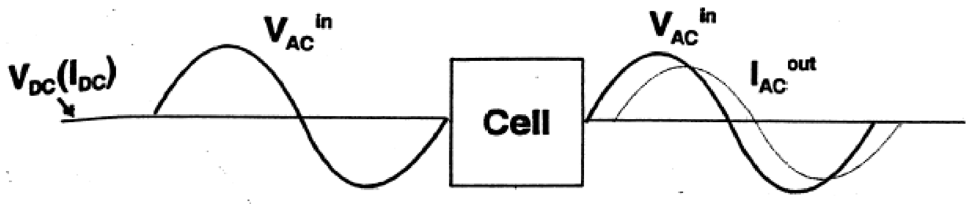
一般

光吸收

恒压测量



-- in EIS, we apply a potential perturbation (usually a Sine wave) and observe the current response, which is a sine wave at the same frequency, but with a different amplitude and phase than the potential signal.



Advantageous features of EIS

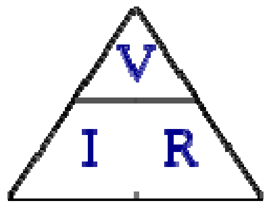
-- measurements are made under steady state conditions
-- all electrical parameters of the system can be determined in a single experiment
-- a simple measurement, easy to automate
-- characterize bulk and interfacial properties of all sorts of materials (conductors, semiconductors, ionic transport media, dielectrics (insulators))
-- can be used to help verify mechanistic models
-- works even in low conductivity electrolyte solutions
-- signal can be averaged over long periods to achieve high precision
-- non-destructive

Caution: Because it is easy to do, it is also easy to collect large amounts of meaningless data!（无效数据/错误数据）

Basis of EIS: Ohm's law

Ohm's law: current is approximately proportional to electric field for most materials.

$$I = \frac{V}{R} \quad \text{or} \quad V = IR \quad \text{or} \quad R = \frac{V}{I}$$

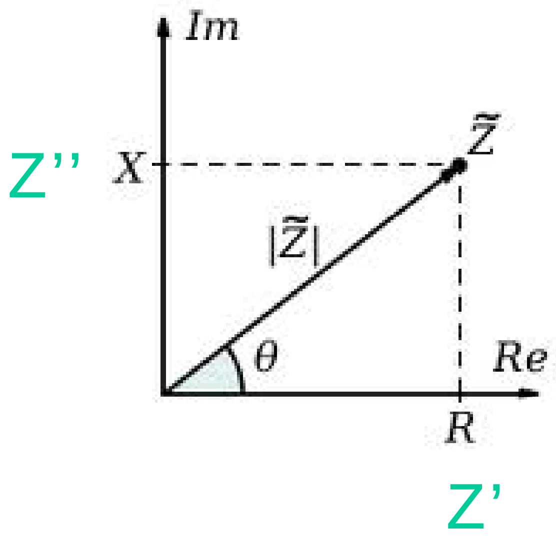


The complex generalization of resistance is impedance, usually denoted with Z.

$$V = I \cdot Z$$

$$Z = Z' + Z'' j$$

Real part (Z') — **Imaginary part** (Z'')



R: Resistance in AC

◆ Resistance circuit

- Applied electric energy is consumed as heat

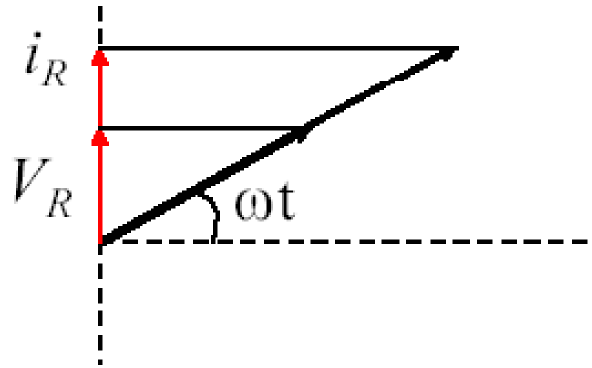
  $P=VI=I^2R=V^2/R$

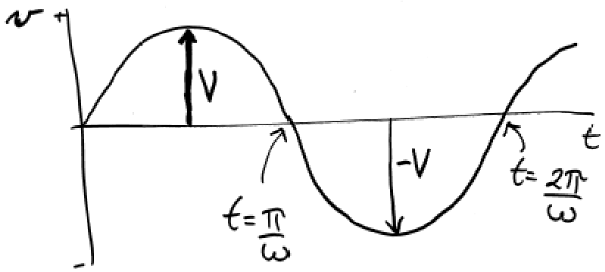
- V=IR (Ohm's Law)
- the identical phase between resistance and applied voltage

$$V_R = V_{RM}\sin\omega t$$

$$i_R = \frac{V_R}{R} = \left[\frac{V_{RM}}{R}\right]\sin\omega t$$

$$= i_{RM}\sin\omega t$$





R: Resistance in AC

欧拉（**Euler**）公式：

$$e^{ix} = \cos(x) + i\sin(x)$$

（另一个Euler公式：凸多面体F+V=E+2）

$$V = V_0(\cos(\omega t) + j\sin(\omega t)) = V_0 e^{j\omega t}$$

$$I = \frac{V_0}{R} e^{j\omega t}$$

$\therefore$ **Impedance:**

$$Z_R = \frac{V}{I} = R(\cos(0) + j\sin(0)) = R$$

R: Resistance in AC

$$
\begin{aligned}
e^{ix} &= 1 + ix + \frac{(ix)^2}{2!} + \frac{(ix)^3}{3!} + \frac{(ix)^4}{4!} + \frac{(ix)^5}{5!} + \frac{(ix)^6}{6!} + \frac{(ix)^7}{7!} + \frac{(ix)^8}{8!} + \cdots \\
&= 1 + ix - \frac{x^2}{2!} - \frac{ix^3}{3!} + \frac{x^4}{4!} + \frac{ix^5}{5!} - \frac{x^6}{6!} - \frac{ix^7}{7!} + \frac{x^8}{8!} + \cdots \\
&= \left(1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \frac{x^8}{8!} - \cdots\right) + i\left(x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots\right) \\
&= \cos x + i \sin x \ .
\end{aligned}
$$

C: Capacitance in AC

- Capacitance
  - Applied electric energy is stored as electrostatic energy
  - One half cycle → store the charge
    The next on half cycle → release the charge
  - the current leads voltage by 90°

$$V_C = V_{CM} \sin \omega t$$

$$q_C = CV_C = CV_{CM} \sin \omega t$$

$$i_C = \frac{dq_C}{dt} = \omega C V_{CM} \cos \omega t$$

$$X_C = \frac{1}{\omega C}$$

$$\cos \omega t = \sin(\omega t + 90^o)$$

$$i_C = \frac{V_{CM}}{X_C} \sin(\omega t + 90^o)$$

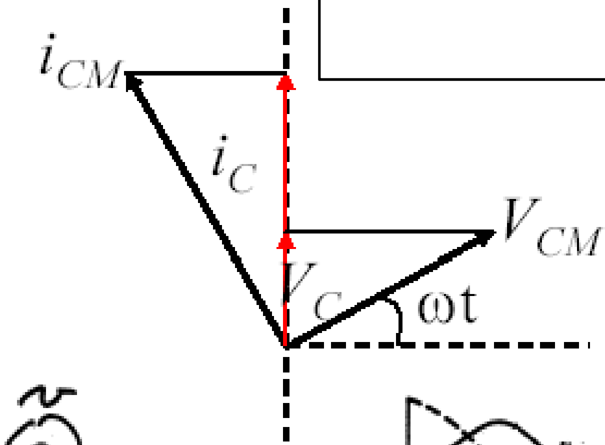
$$= i_{CM} \sin(\omega t + 90^o)$$

$V = V_0 e^{j\omega t}$

$Q = CV = CV_0 e^{j\omega t}$

$I = dQ/dt = j\omega CV_0 e^{j\omega t}$

$Z = V/I = 1/(j\omega C)$



L: Inductance in AC

$$e = -L\frac{di}{dt}$$

$$\frac{di_L}{dt} = \frac{V_L}{L} = \frac{V_{LM}}{L}\sin\omega t$$

$$i_L = \int\left(\frac{di}{dt}\right)dt$$

$$= \frac{V_{LM}}{\omega L}\int \sin\omega t d(\omega t)$$

$$= -\frac{V_{LM}}{\omega L}\cos\omega t$$

$$X_L = \omega L$$

$$-\cos\omega t = \sin(\omega t - 90^o)$$

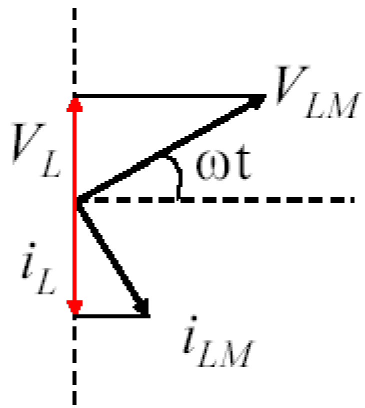
$$i_L = \frac{V_{LM}}{X_L}\sin(\omega t - 90^o)$$

$$= i_{LM}\sin(\omega t - 90^o)$$

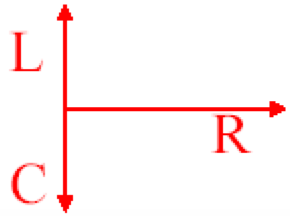
$I = I_0\, e^{j\omega t}$

$V = L\, dI/dt = LI_0 j\omega\, e^{j\omega t}$

$Z = V/I = j\omega L$



Complex impedance (impedance and admittance)



CIRCUIT	IMPEDANCE		ADMITTANCE	
	REAL	IMAGINARY	REAL	IMAGINARY
R	R	0	$\frac{1}{R}$	0
L	0	wL	0	$-\frac{1}{wL}$
C	0	$-\frac{1}{wC}$	0	wC

RC parallel circuit

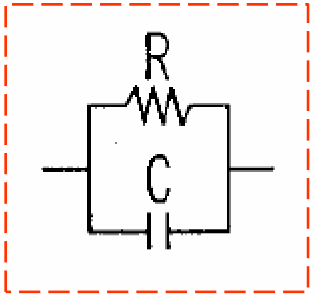
$$Y = \frac{1}{R} + j\omega C$$

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

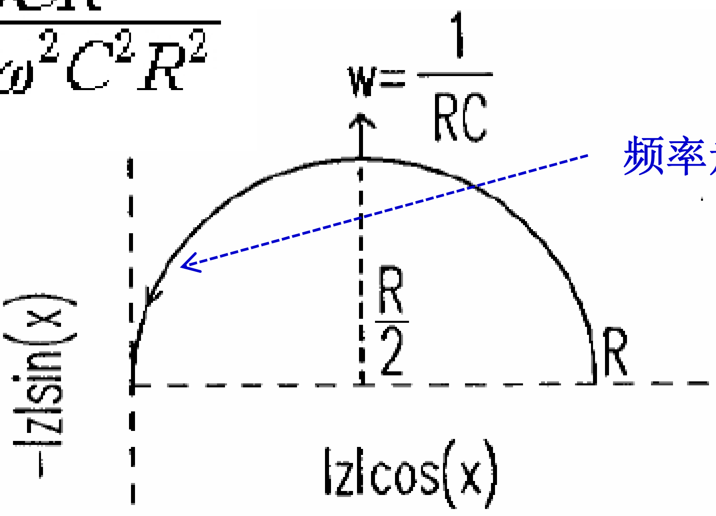
$$Z = \frac{R}{1+\omega^2 C^2 R^2} - j\frac{\omega C R^2}{1+\omega^2 C^2 R^2}$$

$$Z' = \frac{R}{1+\omega^2 C^2 R^2}$$

$$Z'' = -\frac{\omega C R^2}{1+\omega^2 C^2 R^2}$$



(a)



(b)

$$\tan(\theta) = (-Z'')/Z' = \omega CR$$

半圆：$$(Z' - \frac{R}{2})^2 + Z''^2 = (\frac{R}{2})^2$$

Nyquist plot

1) **Nyquist plot: -Z” vs. Z’**

2) **Characteristic frequency: $\omega_c = 1/(RC)$**

（maximum point）

or time constant: $\tau = RC$

3) **Frequency change direction**

4) **Components: semicircles + straight lines**

RL parallel circuit

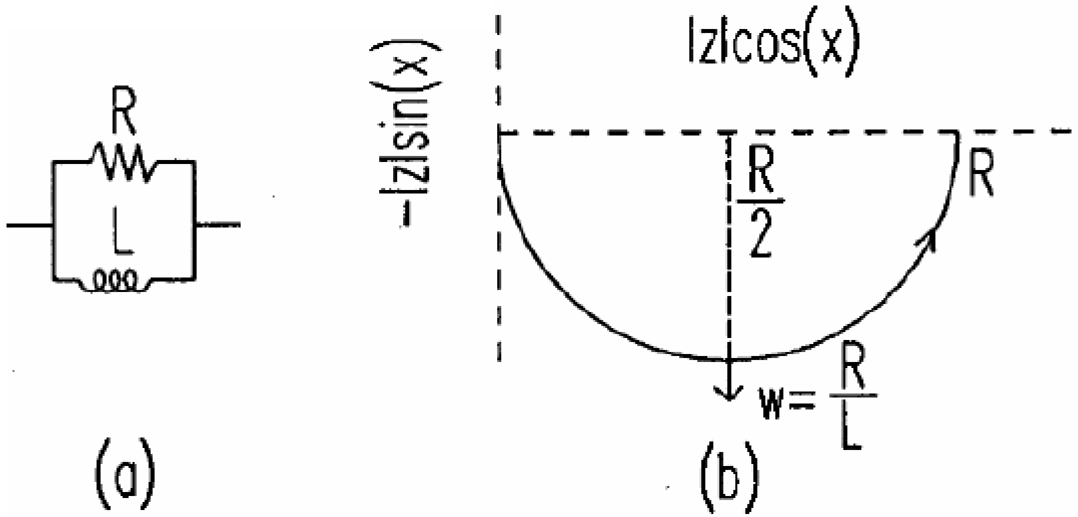
$$Y = \frac{1}{R} - \frac{1}{\omega L} j$$

$$Z = \frac{1}{\frac{1}{R} - \frac{1}{\omega L} j}$$

$$Z = \frac{R\omega^2 L^2}{\omega^2 L^2 + R^2} + j\frac{R^2 \omega L}{\omega^2 L^2 + R^2}$$

$$Z' = \frac{R\omega^2 L^2}{\omega^2 L^2 + R^2}$$

$$Z'' = -\frac{\omega L R^2}{\omega^2 L^2 + R^2}$$



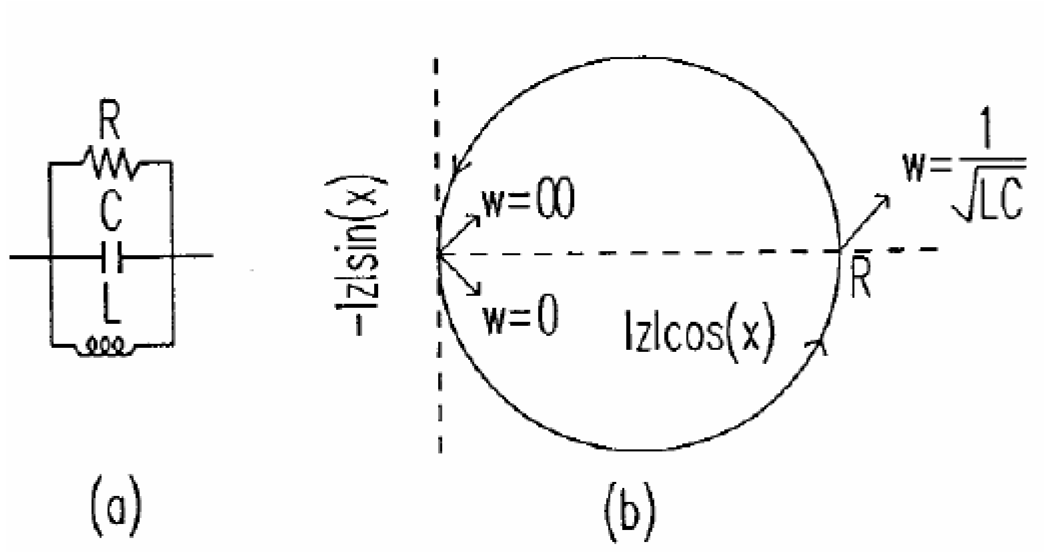
$$\left(Z' - \frac{R}{2}\right)^2 + Z''^2 = \left(\frac{R}{2}\right)^2$$

RLC parallel circuit

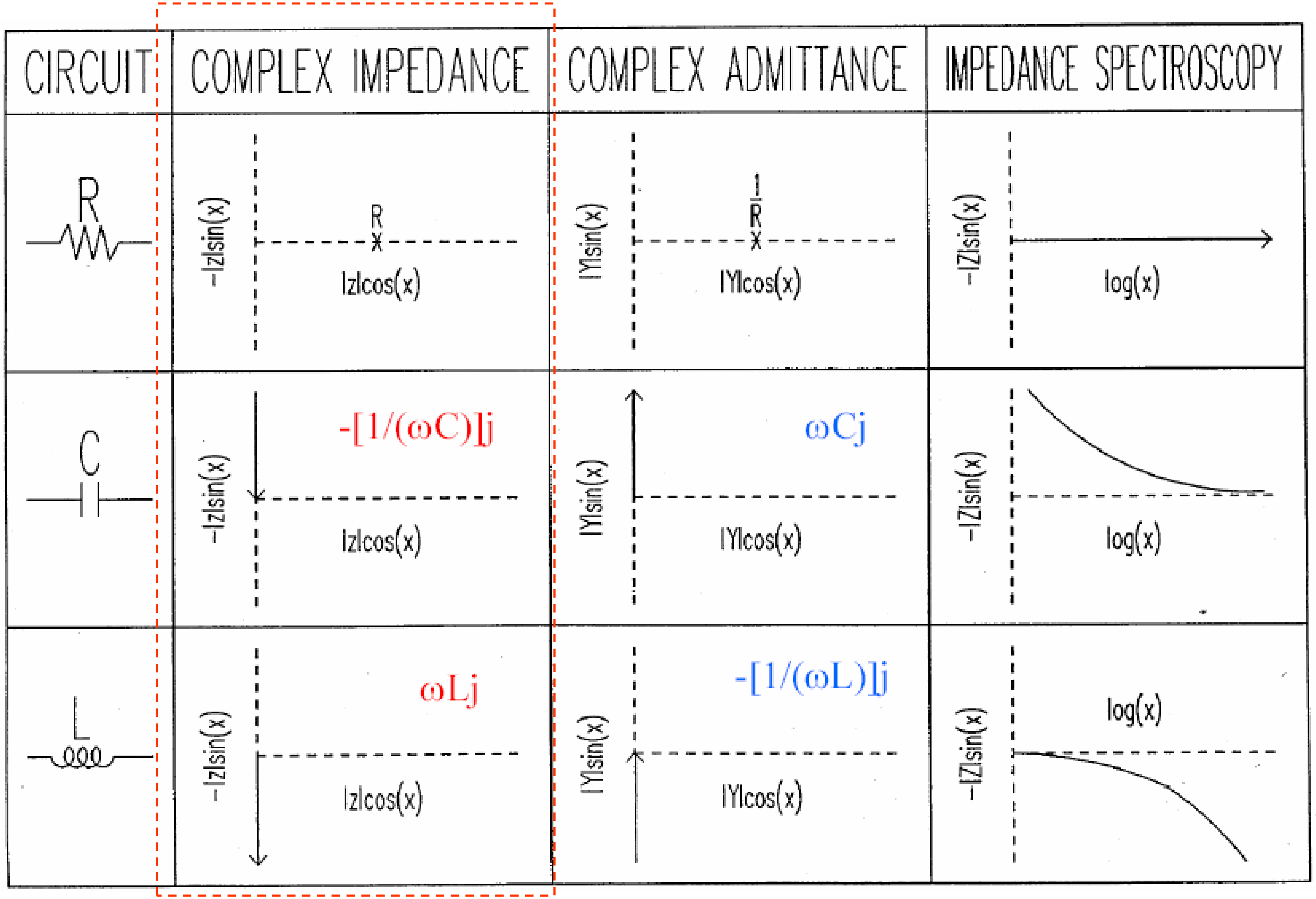
$$Y = \frac{1}{R} + \left[\omega C - \frac{1}{\omega L}\right] j$$

$$Z = \frac{1}{\frac{1}{R} + \left[\omega C - \frac{1}{\omega L}\right] j}$$

$$Z = \frac{R\omega^2 L^2}{\omega^2 L^2 + (R\omega^2 LC - R)^2} - j\frac{R\omega L(R\omega^2 LC - R)}{\omega^2 L^2 + (R\omega^2 LC - R)^2}$$

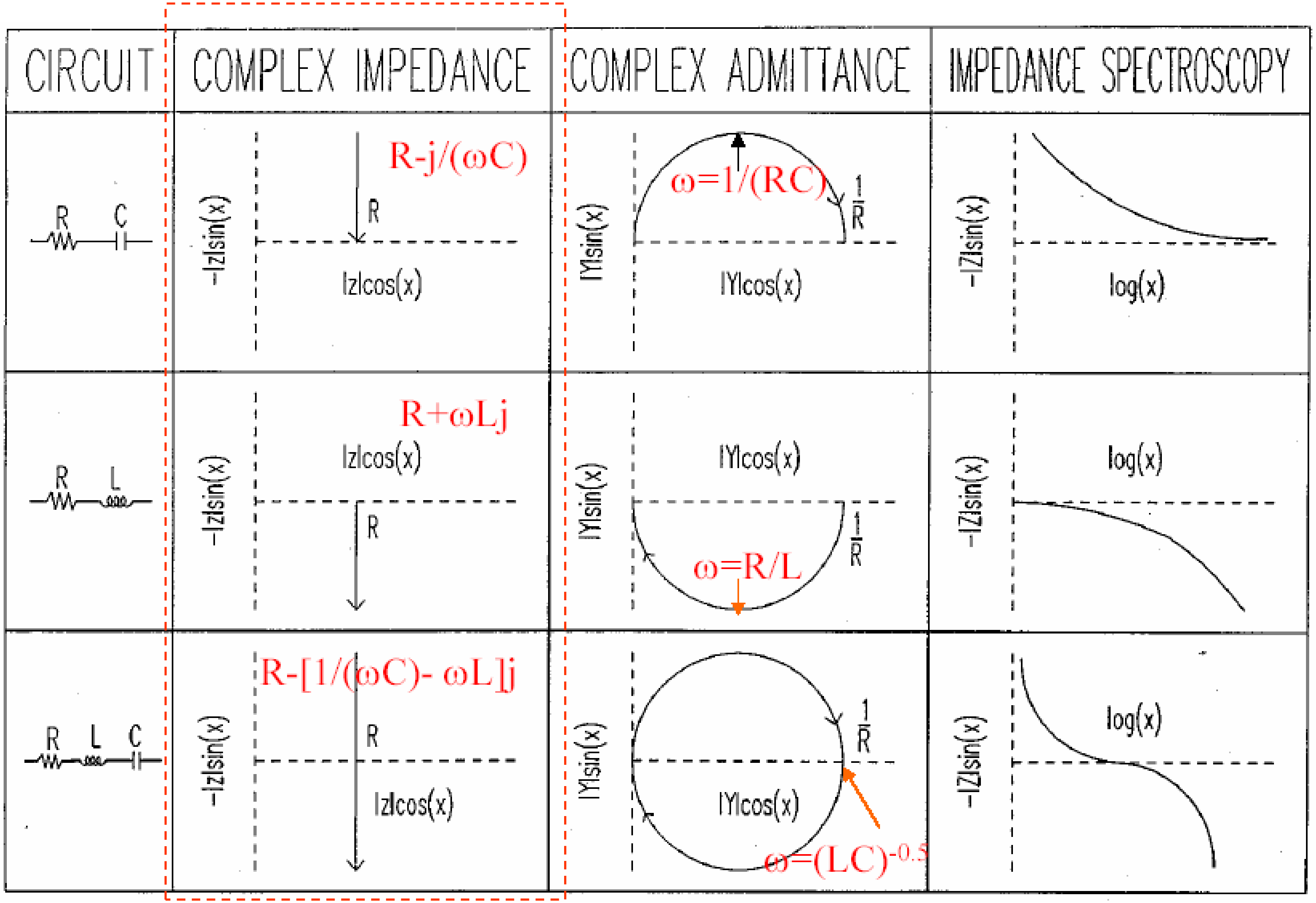


R, L, C

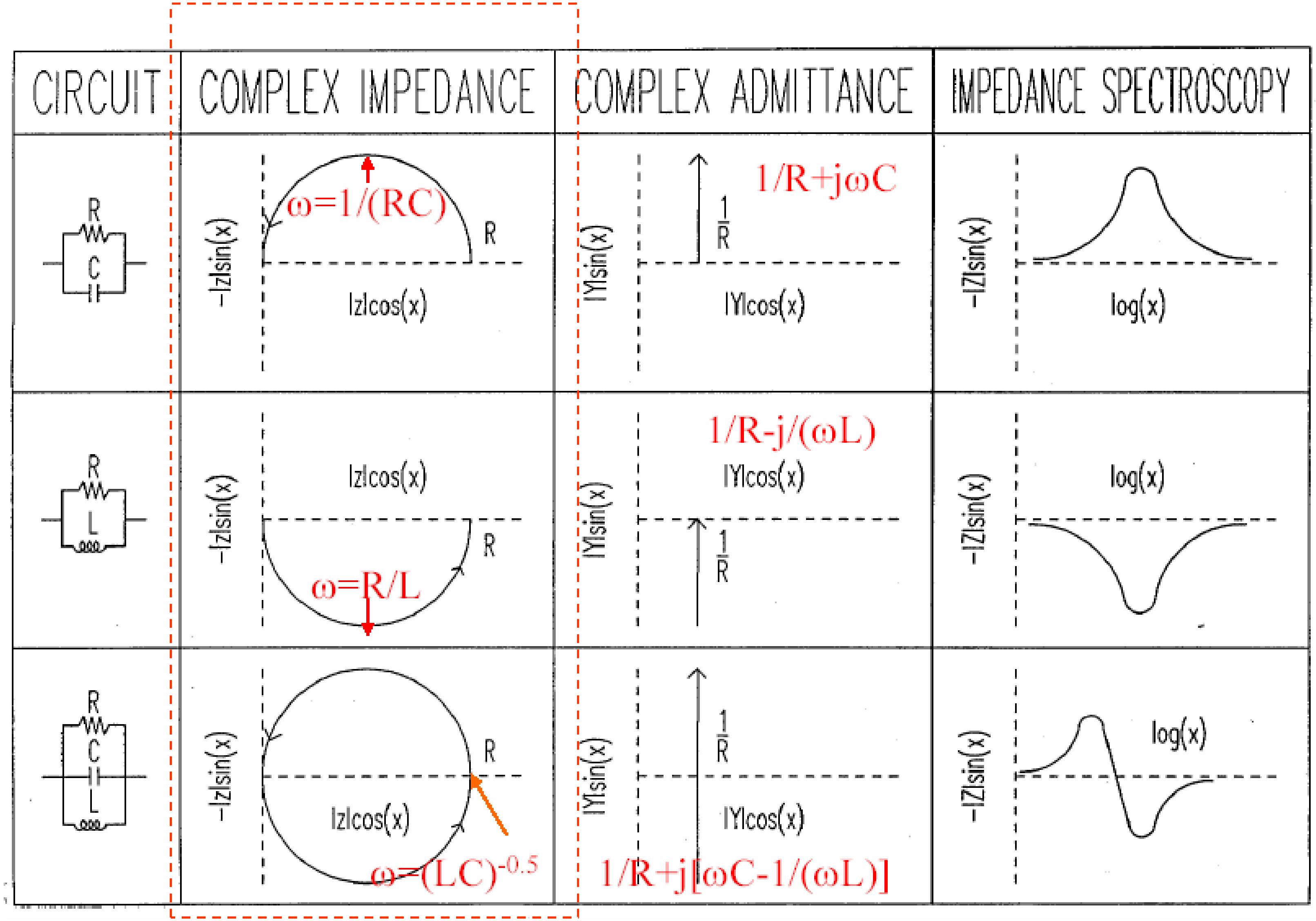


CIRCUIT
COMPLEX IMPEDANCE
COMPLEX ADMITTANCE
IMPEDANCE SPECTROSCOPY
R
-|z|sin(x)
R
|z|cos(x)
|Y|sin(x)
1/R
|Y|cos(x)
-|Z|sin(x)
log(x)
C
-|z|sin(x)
-[1/(ωC)]j
|z|cos(x)
|Y|sin(x)
ωCj
|Y|cos(x)
-|Z|sin(x)
log(x)
L
-|z|sin(x)
ωLj
|z|cos(x)
|Y|sin(x)
-[1/(ωL)]j
|Y|cos(x)
-|Z|sin(x)
log(x)

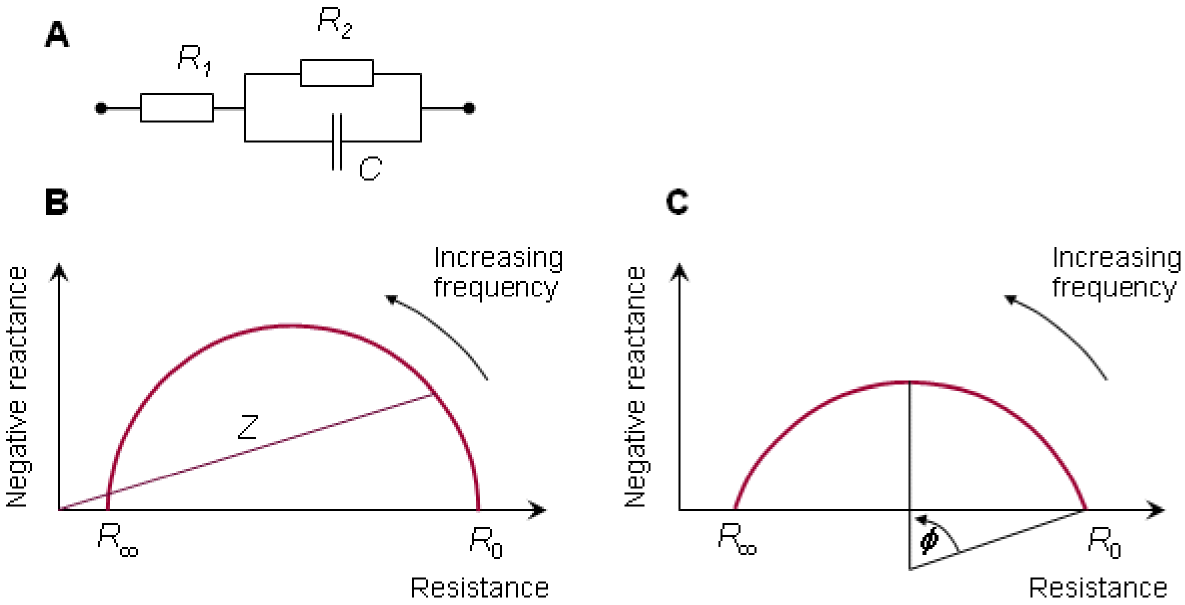
RC serial, RL serial, RLC serial



RC parallel, RL parallel, RLC parallel



R(RC) circuit: RC parallel in series with R



$$Z_f = R_\infty + \frac{R_0 - R_\infty}{1 + j\omega\tau} = R_\infty + \frac{R_0 - R_\infty}{1 + \omega^2\tau^2} - j\omega\tau\frac{R_0 - R_\infty}{1 + \omega^2\tau^2}$$

where Z_f = impedance (as a function of frequency f)

R_0 = resistance at $f = 0$

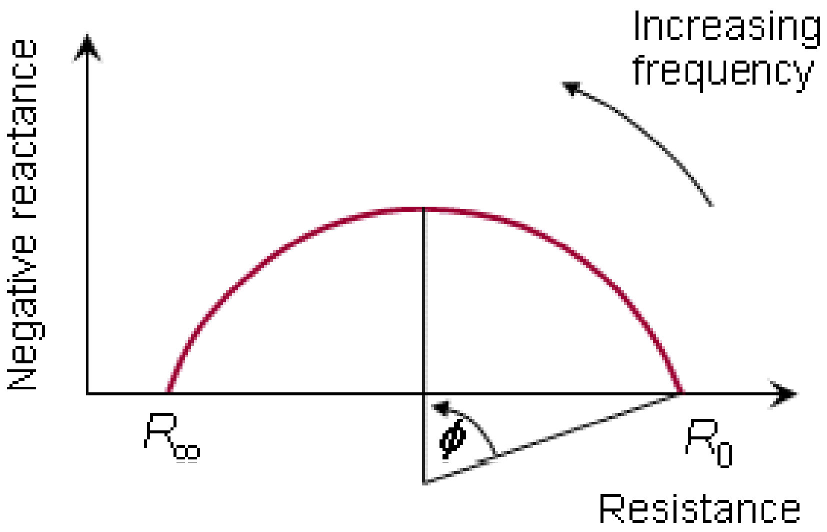
R_∞ = resistance at f = ∞

τ = time constant (R_2C)

$(R_0 = R_1 + R_2)$

$$\left(R_e - \frac{R_0 + R_\infty}{2}\right)^2 + \mathrm{Im}^2 = \left(\frac{R_0 - R_\infty}{2}\right)^2$$

Depressed semicircle



$$Z_f = R_\infty + \frac{R_0 - R_\infty}{1 + j\omega\tau^{(1-\alpha)}}$$

where $\phi = (1 - \alpha)\pi/2$

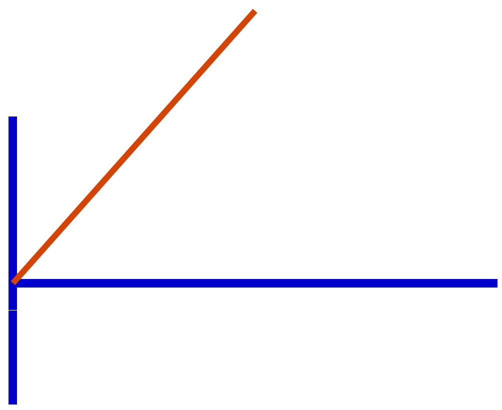
Constant phase angle element

Q: CPE (constant phase angle element)

$$Z = \frac{1}{T(j\omega)^p} \quad (|p| \leqq 1)$$

Phase angle = -p (π/2)

$$p = \begin{cases} 0 & \textbf{resistance} \\ 1 & \textbf{capacitor} \\ -1 & \textbf{inductor} \\ 0.5 & \textbf{Warburg impedance} \end{cases}$$

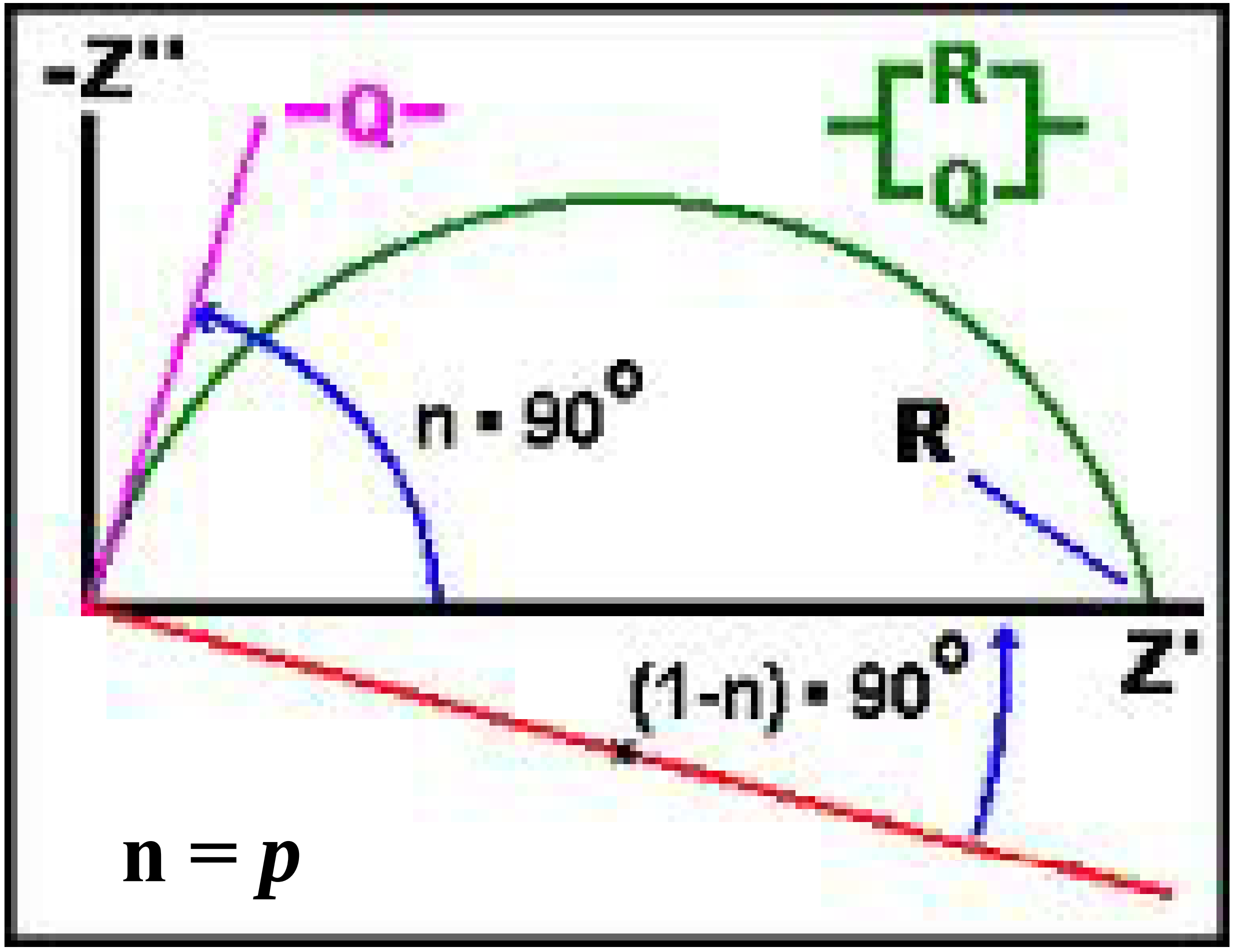


From RC to RQ parallel circuit

Q: CPE (constant phase angle element)

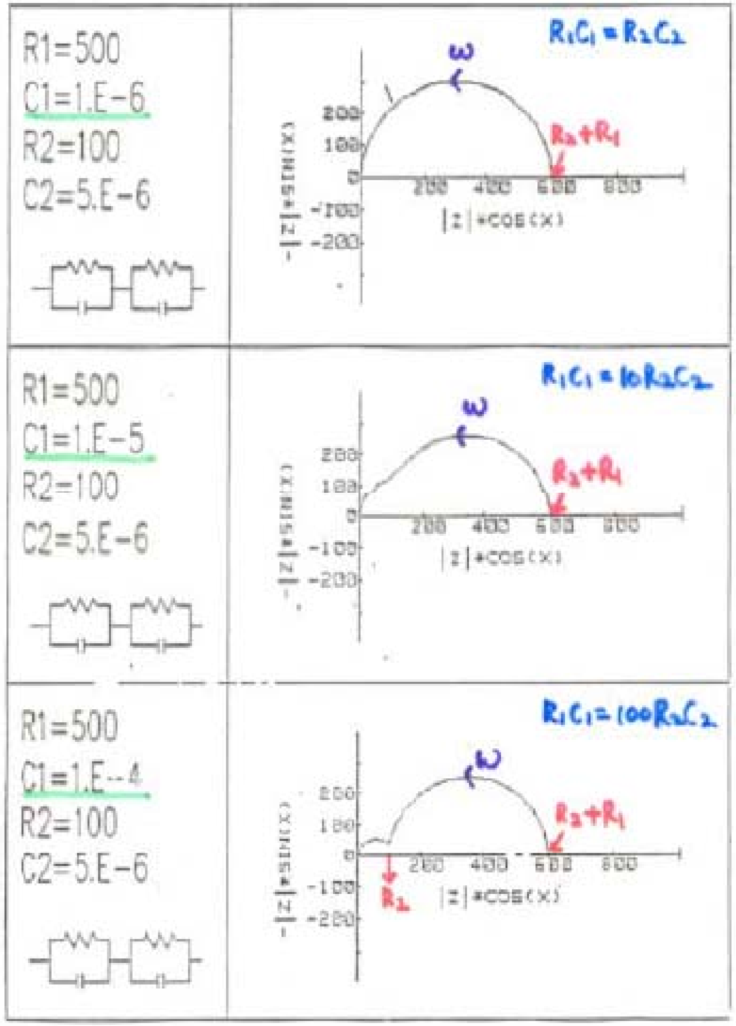
$$Z = \frac{1}{T(j\omega)^p}$$

$$0.5 < p < 1$$



$n = p$

RC-RC circuit: (RC)(RC)



τ = RC: relaxation time constant (unit: sec)

$$Z = \frac{R}{1+\omega^2C^2R^2} - \frac{\omega C R^2}{1+\omega^2C^2R^2} j$$

$$Z_1+Z_2 = \left(\frac{R_1}{1+(\omega\tau_1)^2} + \frac{R_2}{1+(\omega\tau_2)^2}\right) - \left(\frac{\omega R_1 \tau_1}{1+(\omega\tau_1)^2} + \frac{\omega R_2 \tau_2}{1+(\omega\tau_2)^2}\right) j$$

if $\tau_1 = 5\times10^{-2}$, $R_1 = 500$
$\tau_2 = 5\times10^{-4}$, $R_2 = 100$

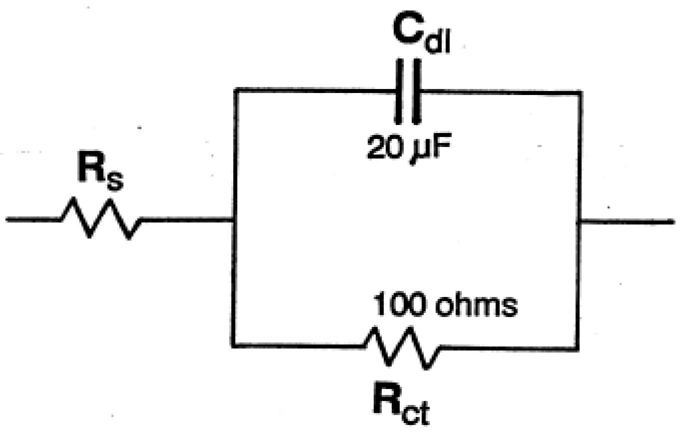
at $\omega = 10^{-2}$: $\omega\tau_1 = 5\times10^{-4}$, $\omega\tau_2 = 5\times10^{-6}$ $\rightarrow$ $Z_{real} \doteq 500 + 100 = 600$

at $\omega = 10^{2}$: $\omega\tau_1 = 5$, $\omega\tau_2 = 5\times10^{-2}$ $\rightarrow$ $Z_{real} = \frac{500}{1+25} + \frac{100}{1} \doteq 120$

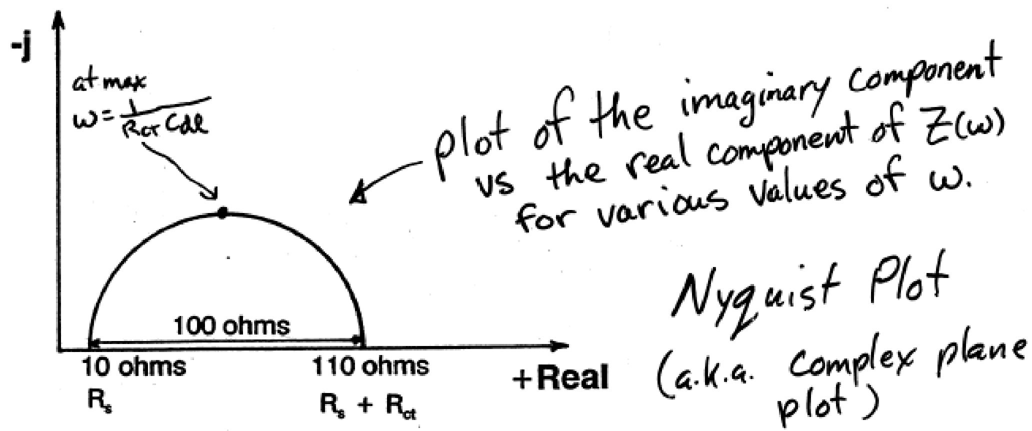
at $\omega = 10^{4}$: $\omega\tau_1 = 500$, $\omega\tau_2 = 5$ $\rightarrow$ $Z_{real} = \frac{500}{1+250000} + \frac{100}{1+25} \doteq 4$

A typical electrode-solution interface in a cell

-- We have a capacitance due to charging/discharging the electrical double layer
-- In parallel with the double layer we have a faradaic reaction proceding at some potential-dependent rate. This is equivalent to a resistance (remember linear polarization ΔE/ΔI = Rct).
-- Finally, in series with those, there is the ever-present solution resistance Rs



$$\left(Z_{Re} - R_s - \frac{R_{ct}}{2}\right)^2 + Z_{Im}^2 = \left(\frac{R_{ct}}{2}\right)^2$$



Nyquist plot: Electrode-solution interface in a cell

$$Z = \underbrace{R_S + \frac{R_{CT}}{1+\omega^2 C_{dl}^2 R_{CT}^2}}_{\text{real part}} - j\underbrace{\left(\frac{\omega C_{dl} R_{CT}^2}{1+\omega^2 C_{dl}^2 R_{CT}^2}\right)}_{\text{imaginary part.}}$$

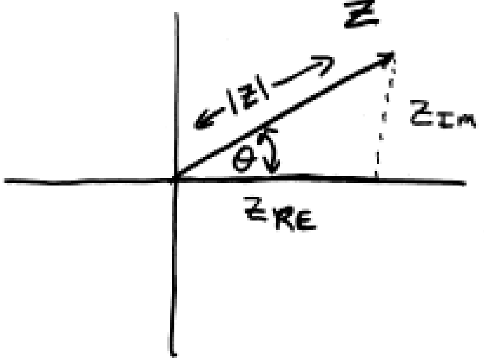
- the plot traces a semicircle with diameter R_{CT}, centred on the real axis at $Z_{RE} = R_S + \frac{R_{CT}}{2}$
- the Nyquist plot makes it easy to determine R_{CT}.
- R_S simply translates the semicircle along the real axis, so it doesn't really interfere with the measureme

but

- disadvantages of this type of plot are:
  - → ω information is lost
  - → plot looks the same for any value of C

Bode plots: Electrode-solution interface in a cell

- to highlight other features we may want to plot other parameters



using Pythagorus:

$$Z^2 = Z_{RE}^2 + Z_{Im}^2$$

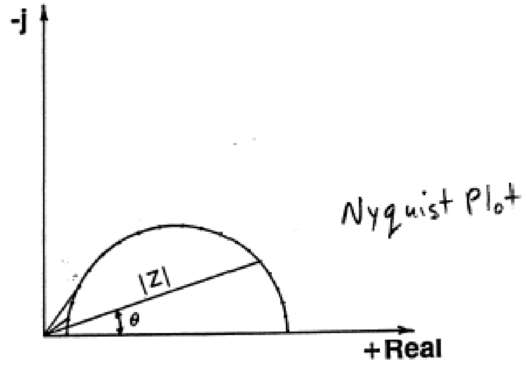
$$|Z| = \sqrt{Z_{RE}^2 + Z_{Im}^2}$$

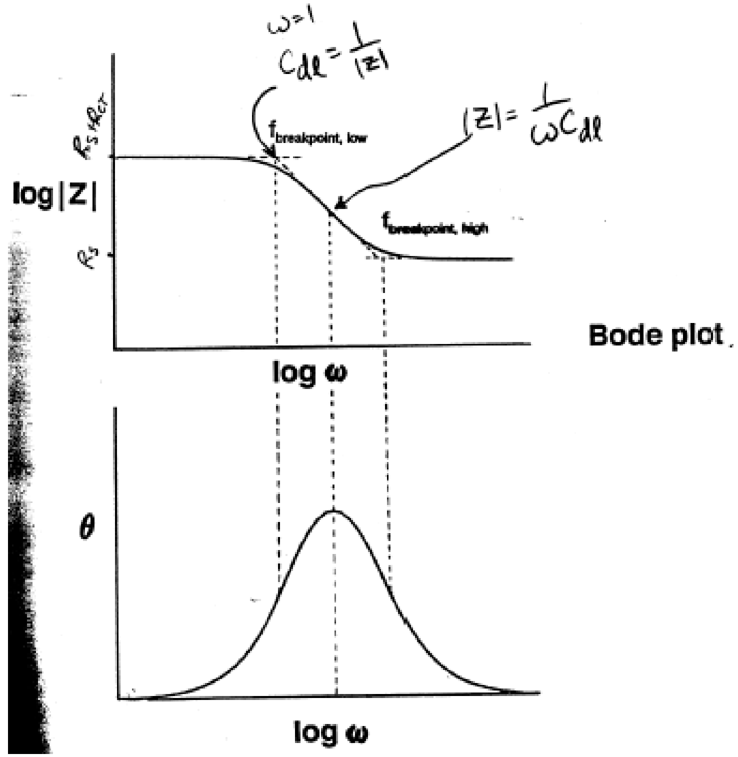
and

$$\frac{Z_{Im}}{Z_{RE}} = \tan\theta$$

$$\theta = \arctan\left(\frac{Z_{Im}}{Z_{RE}}\right)$$

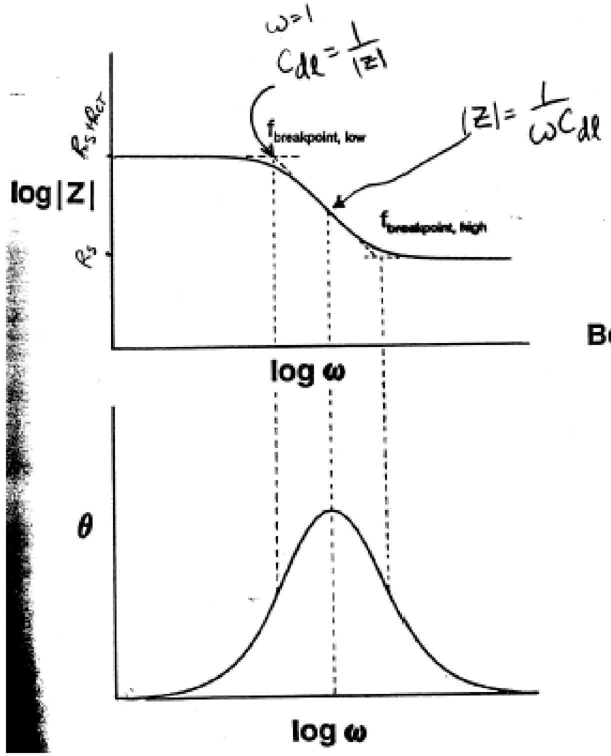
- plots of log|Z| and θ vs. log ω are called Bode plots





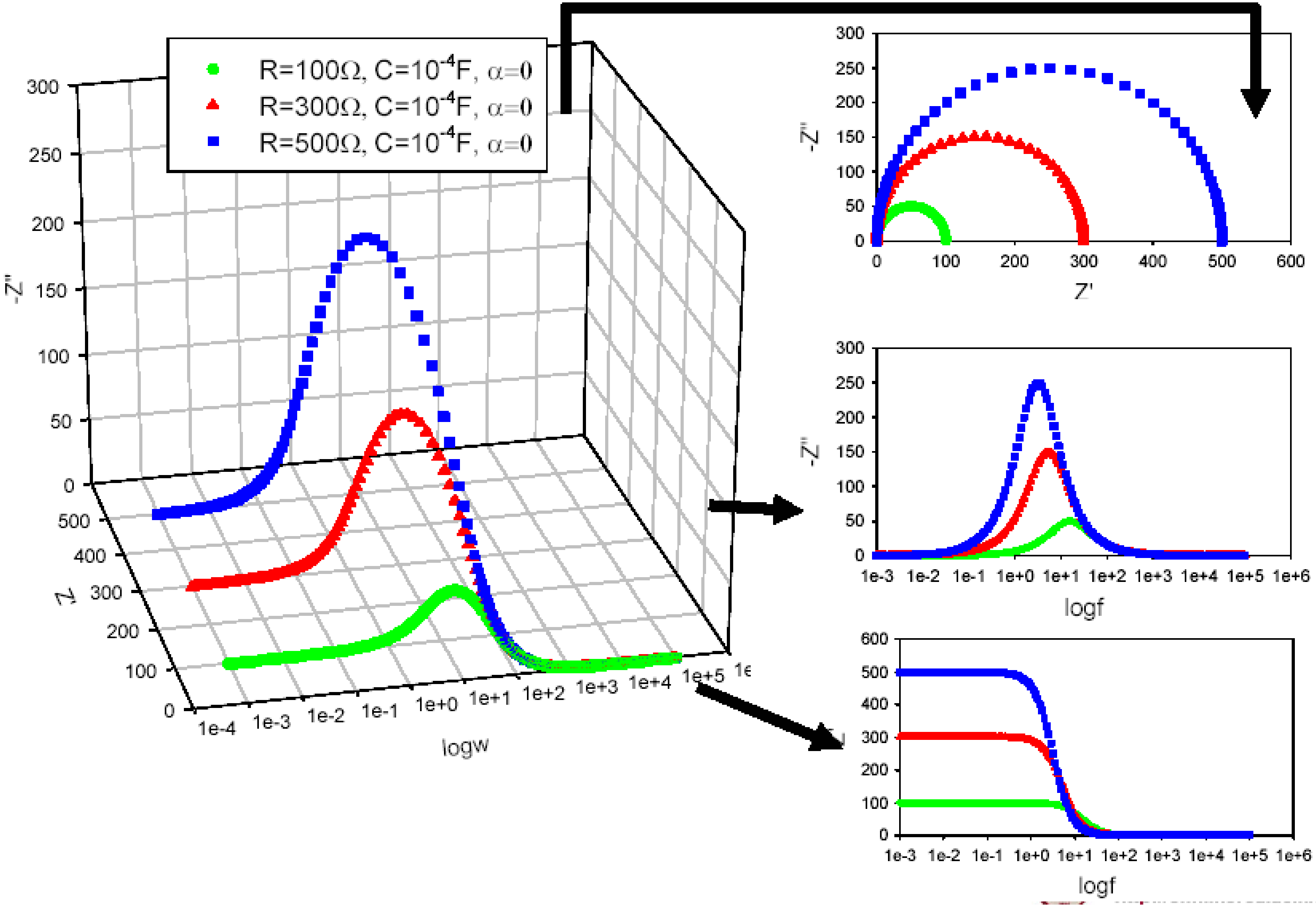
Advantages of Bode plots

- advantages of Bode plot
  - → can get R values from plateaus of the magnitude plot
  - → can get C from the values of |z| and ω in linear sloping region
  - → ω information is not lost.
- there are many other plotting possibilities using derivative parameters. these may highlight specific features and minimize others. It depends on the application which plots will be the most useful. The most common are Nyquist and Bode plots.

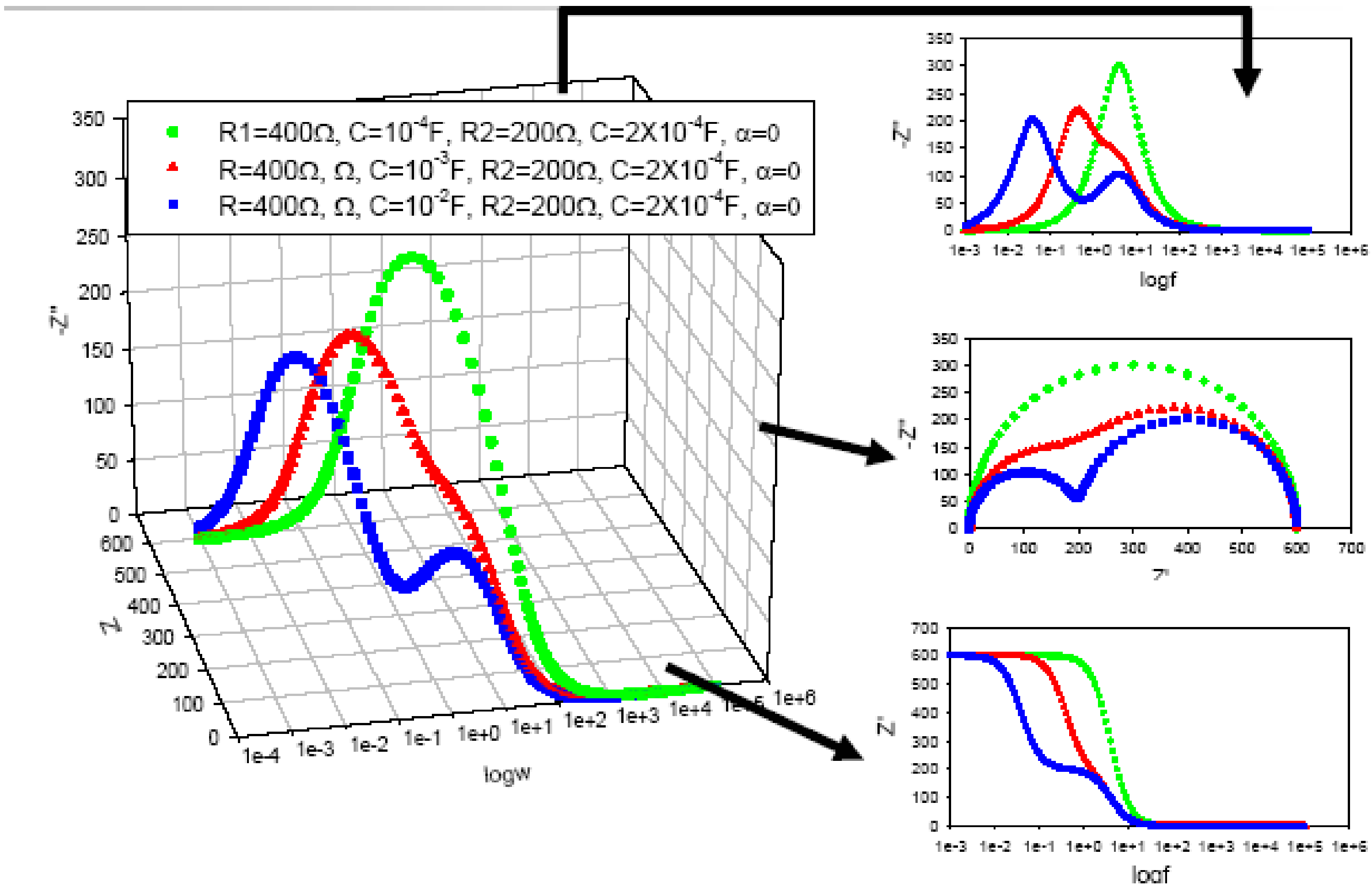


Bode plot

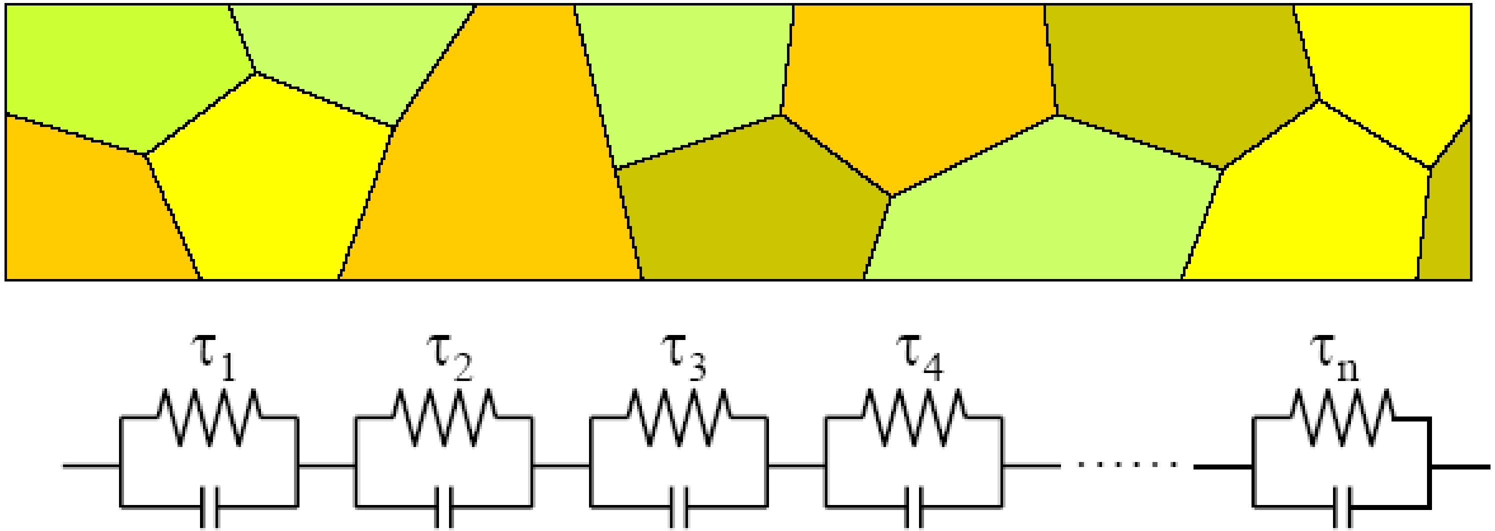
3-D impedance: resistance variation



3-D impedance: R&C variation

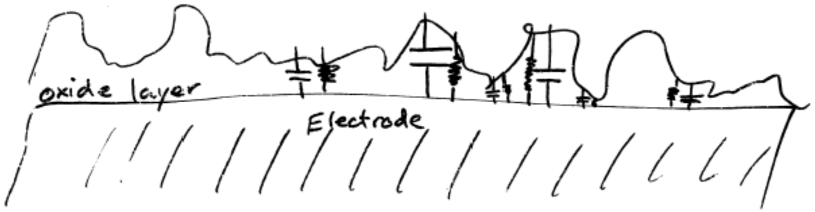


An origin for the depressed semicircles: 1. polycrystal

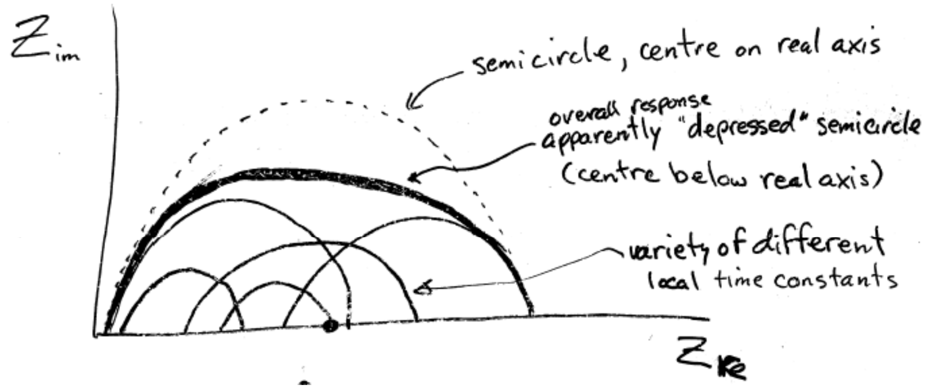


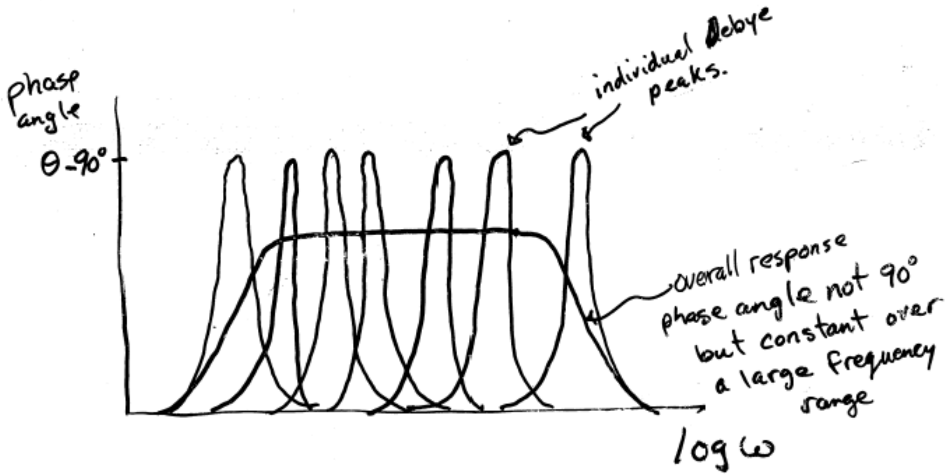
if $\tau_1 = \tau_2 = \bullet\bullet\bullet\bullet = \tau_n \rightarrow$ one RC parallel circuit(α=0)
The wider gaussian distribution in τ
- The more depression

An origin of depressed semicircles: 2. rough surface



different R and C at different spots on surface

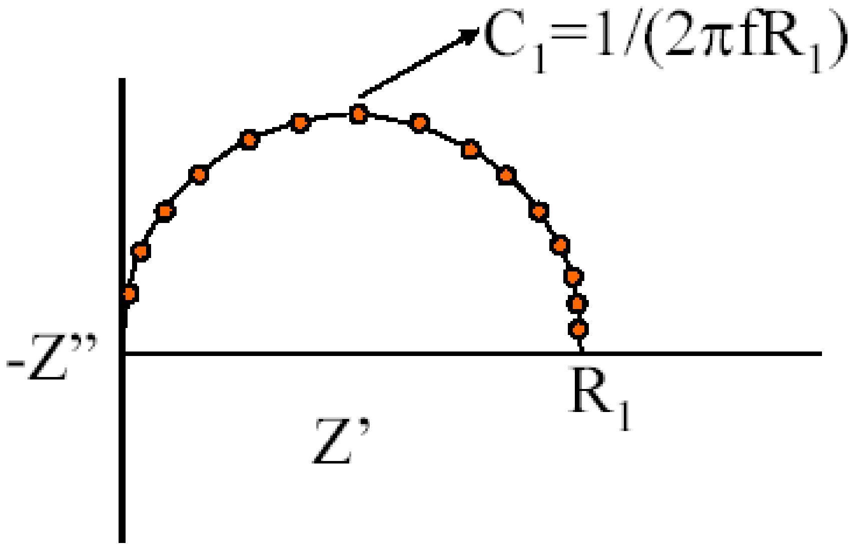


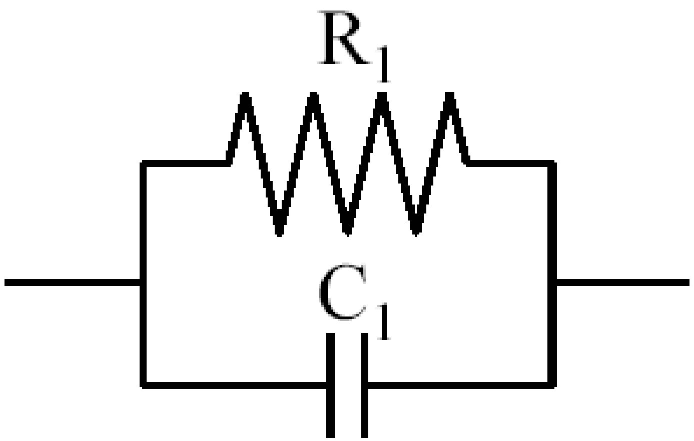


Data analysis

1. A portion of the experimental data set is selected using an appropriate criterion
2. From these selected experimental points approximated values of the parameters are calculated by simple method or Complex Nonlinear Least Square(CNLS) method.
3. Compare with theoretical values
4. The difference between these two points is calculated
5. The same procedure is applied till minimum dissimilarity is obtained.

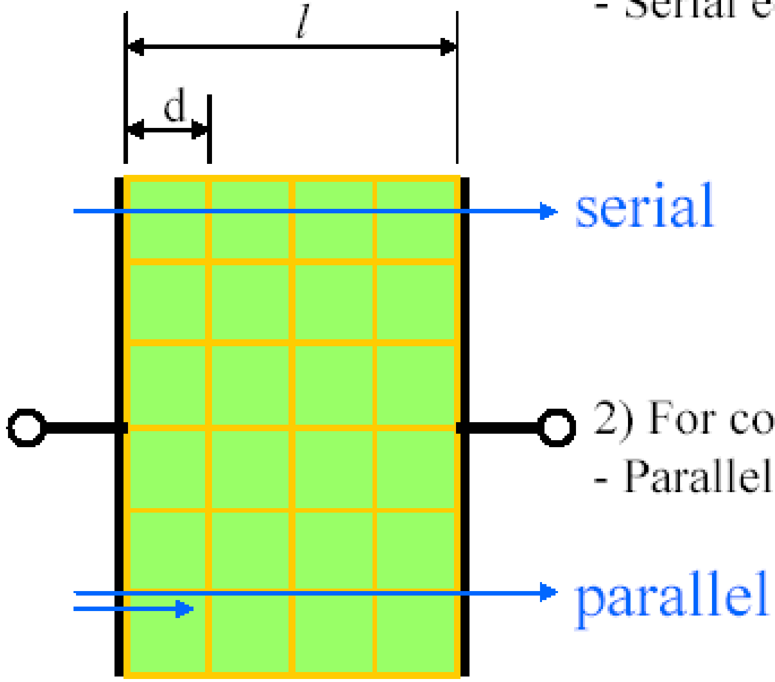
First term approximation of capacitance





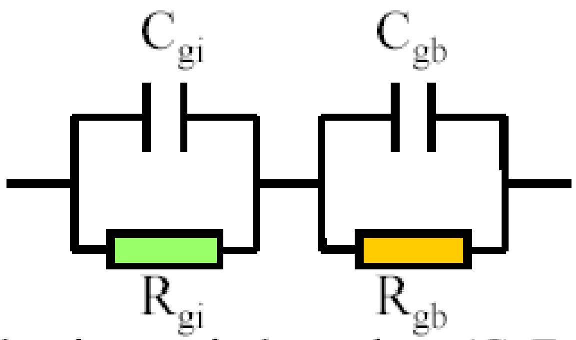
1. The top point is usually unavailable
 - using data point near the top point
2. No consideration for the depression of semicircle
 - rough estimation of capacitance

Define equivalent circuit



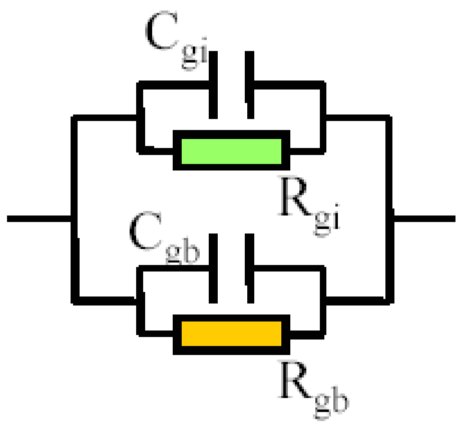
1) For resistive grain boundary (PTC thermistor, YSZ, …)

- Serial equivalent circuit $\rho_{gb}^{sp} = \rho_{gb}\,(d/\delta_{gb})$



2) For conductive grain boundary (CaF_2, AgCl…)

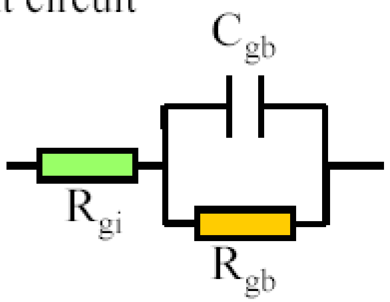
- Parallel equivalent circuit



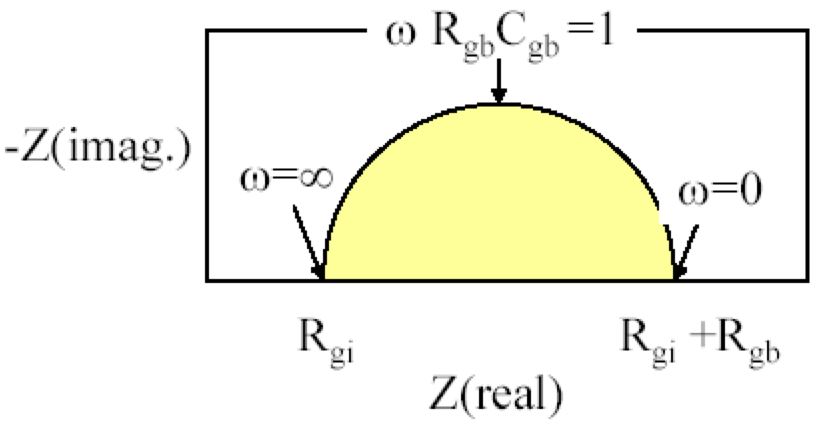
$$C = \frac{\varepsilon A}{d}$$

Impedance Spectroscopy: Application 1 (PTCR Thermistor)

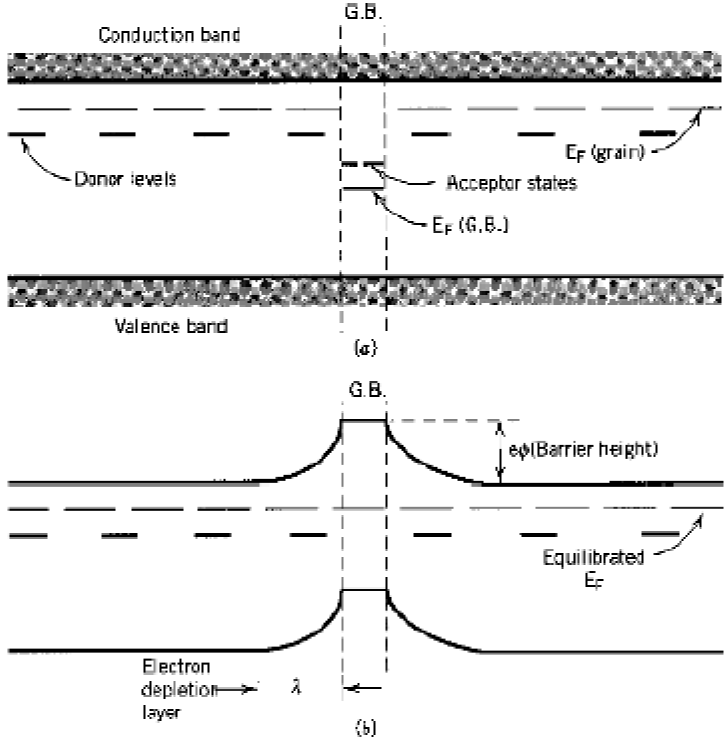
1) Equivalent circuit



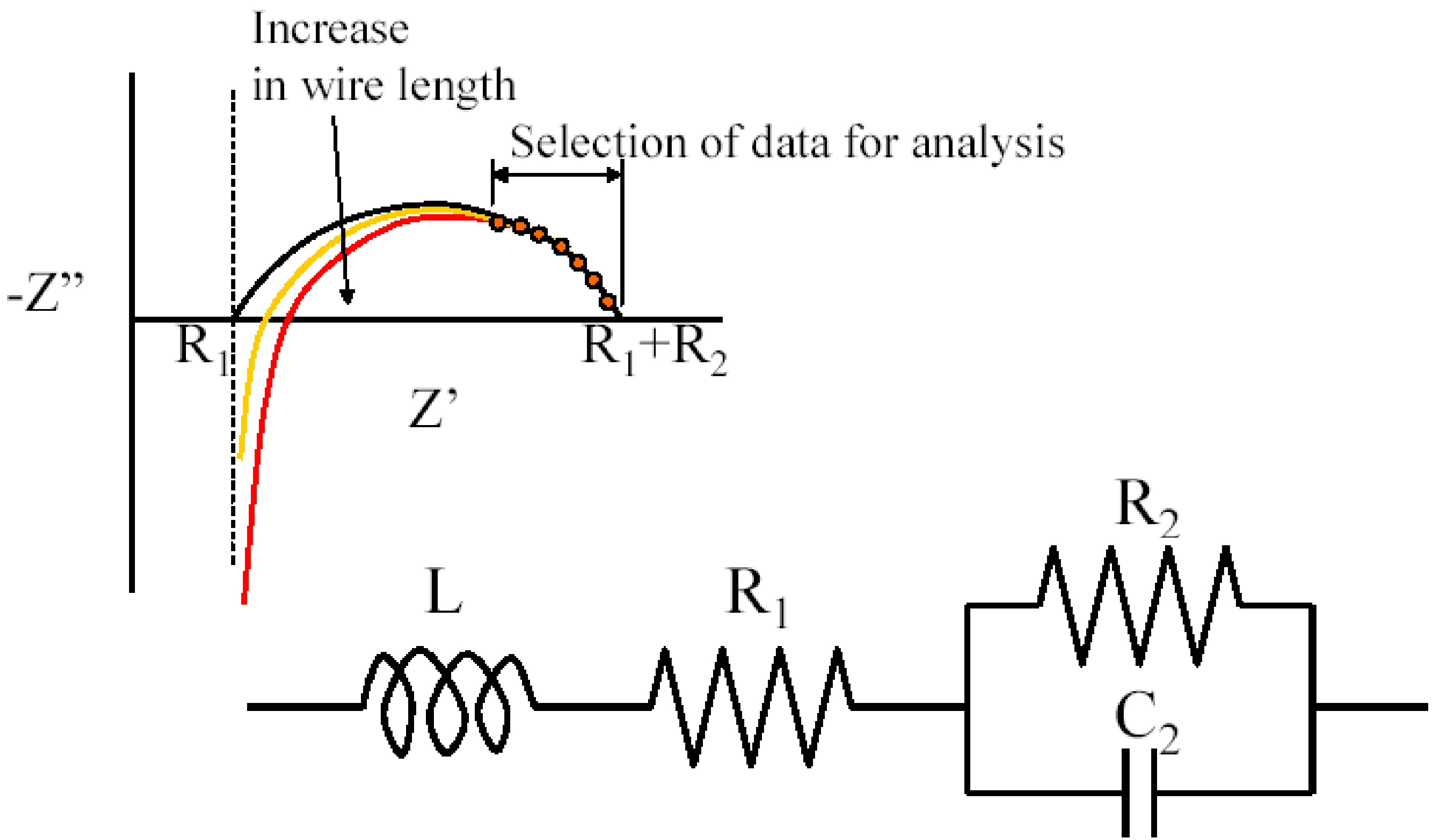
2) Impedance spectrum



- Donor doped $BaTiO_3$
- Oxidative Cooling
- formation of G.B. electrical barrier via fast G.B. diffusion



Note: Error from the inductance of lead wire



Instrumentation for EIS

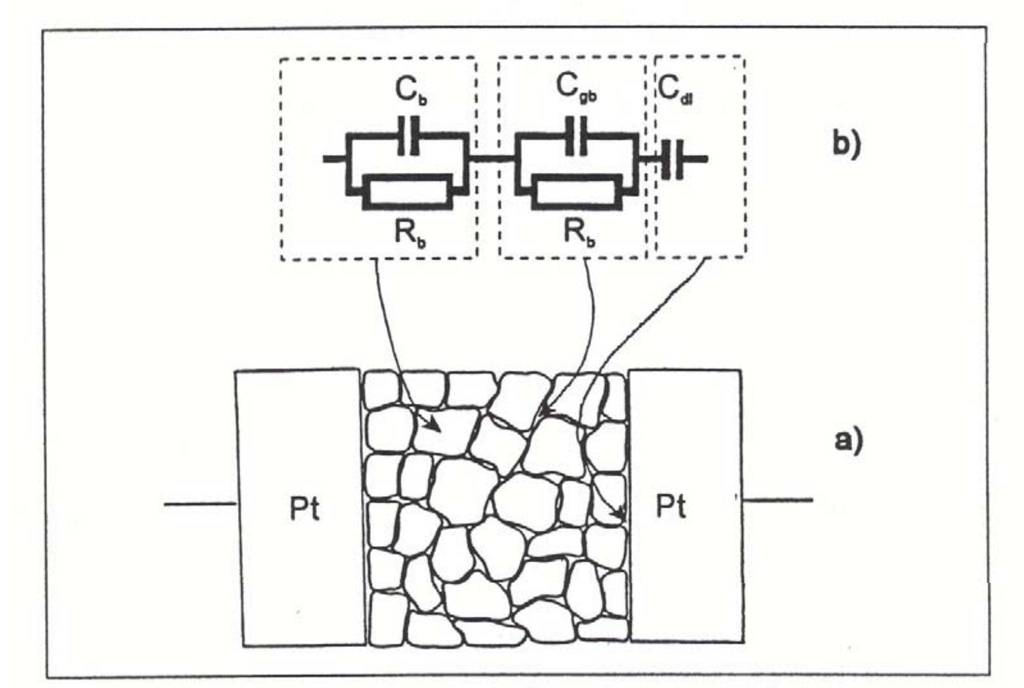
Solartron

CHI Electrochemical workstation

Impedance spectroscopy (basic aspects)

Purpose: Exploring the electrical behavior of a microcrystalline solid sample as function of an alternating current (ac) with a variable frequency.

(note: difference between ac-/dc- and ionic/electronic conduction !!!)



three basically different regions for the exchange interactions between current and sample:

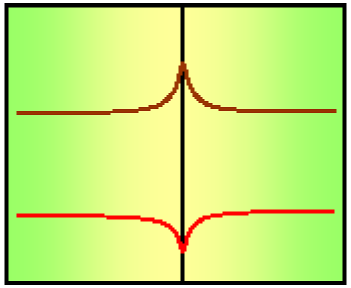
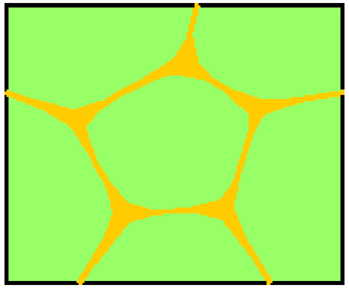
a) inside the grains („bulk“)

b) at grain boundaries

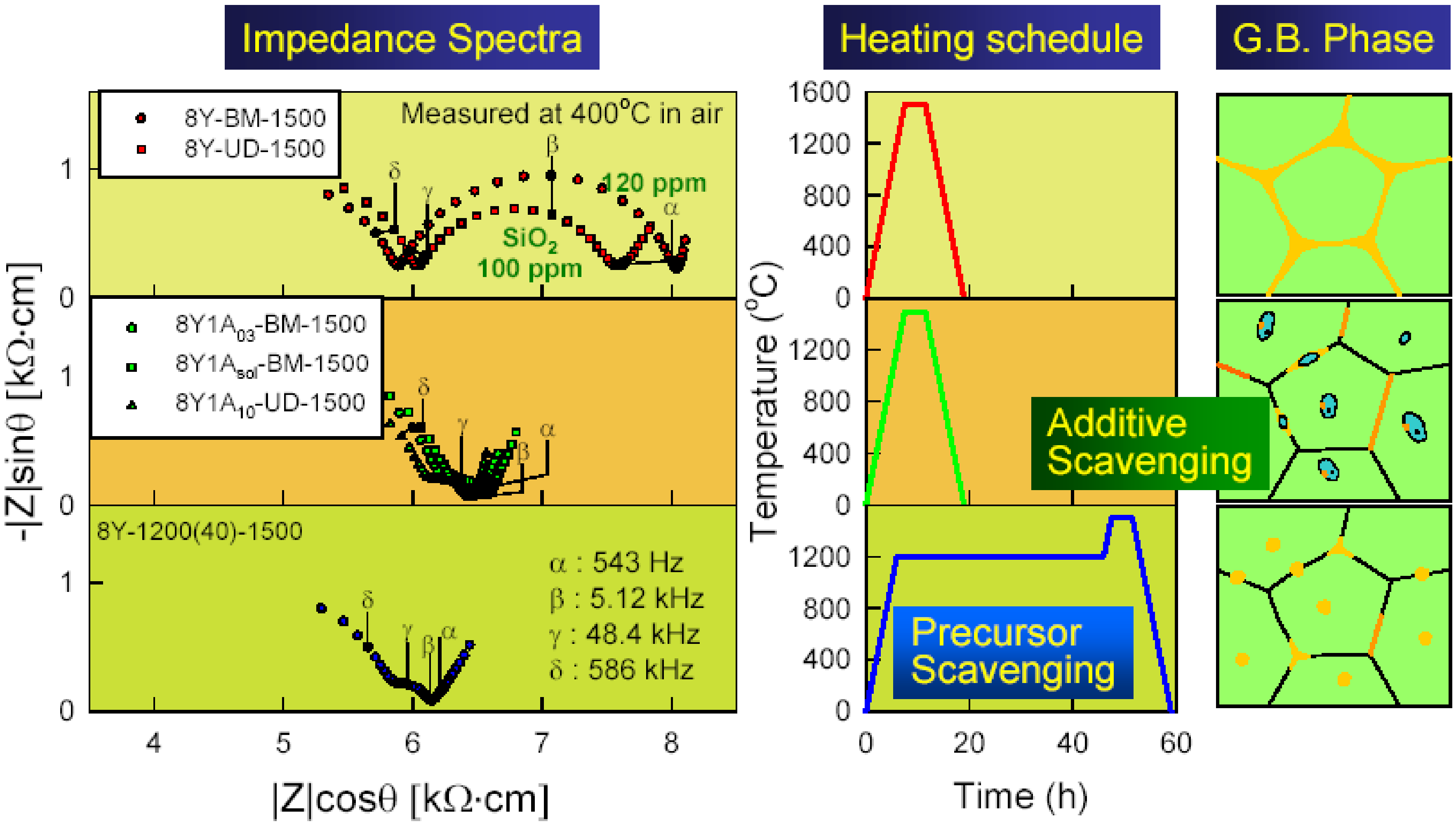
c) surface of the electrodes

the electrical behavior is simulated by a suitable combination of RC circuits: R = resistivity, C = capacity

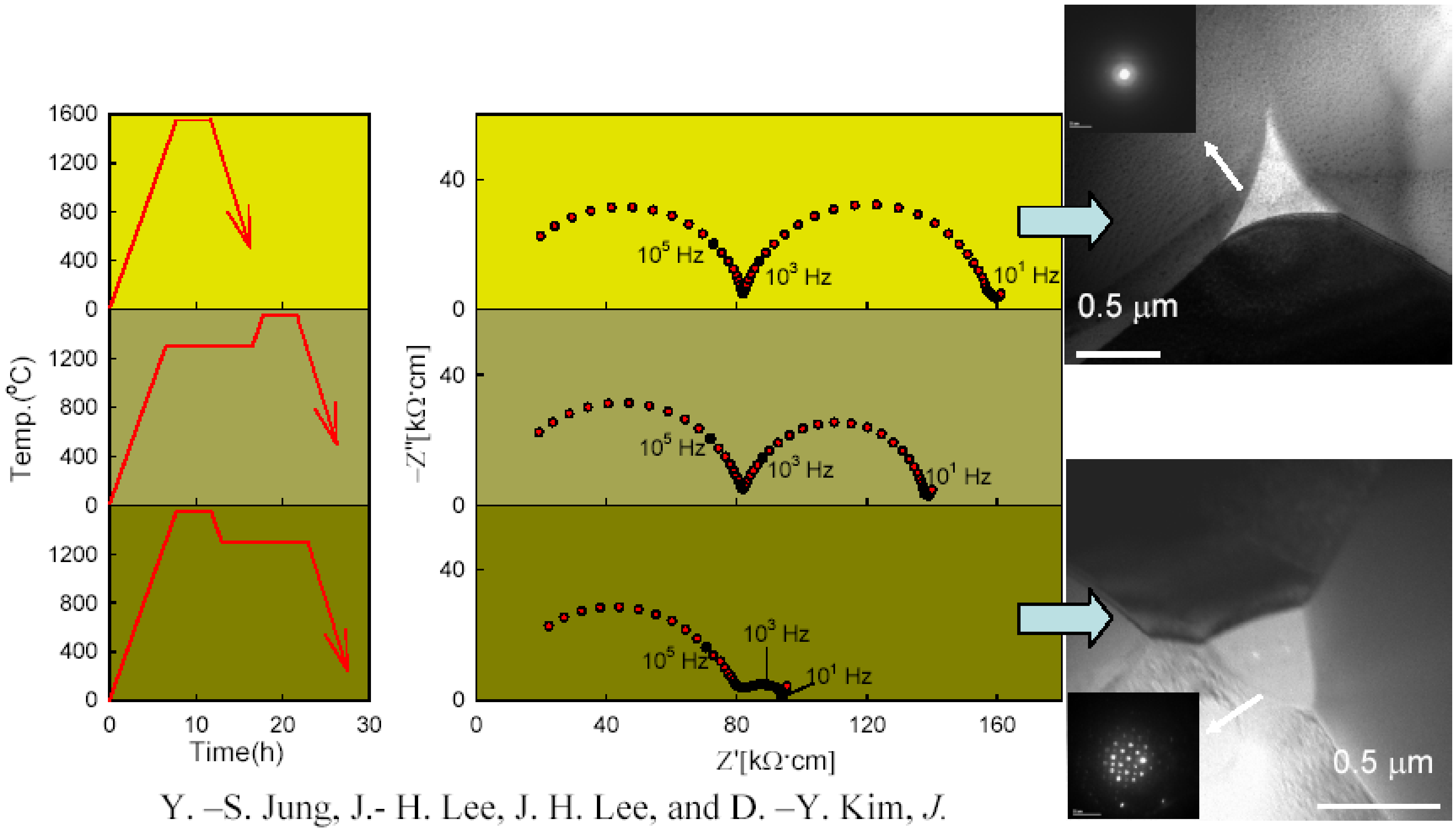
Origin of Grain Boundary Resistance in Stabilized Zirconia

	Space charge layer	Siliceous film
Model		
Origin	Solute segregation near G.B. by different formation energies of point defect $[Vo^{\bullet\bullet}]_{gb} < [Vo^{\bullet\bullet}]_{gi}$	Background silica impurity trace amount (several hundreds ppm in weight) plays role of blocking
Materials	Highly pure material	Relatively impure material

Improvement of R_{gb} by scaveging siliceous G.B. phase



Post-Sintering Heat Treatment: 15CSZ sintered at 1550°C



Y. –S. Jung, J.- H. Lee, J. H. Lee, and D. –Y. Kim, *J. Electrochem. Soc.*, **150,** J49 **(2003)**

Impedance data analysis: Z-view

CPE = Constant Phase Element

$$Z = 1 / [T(j\omega)^p]$$

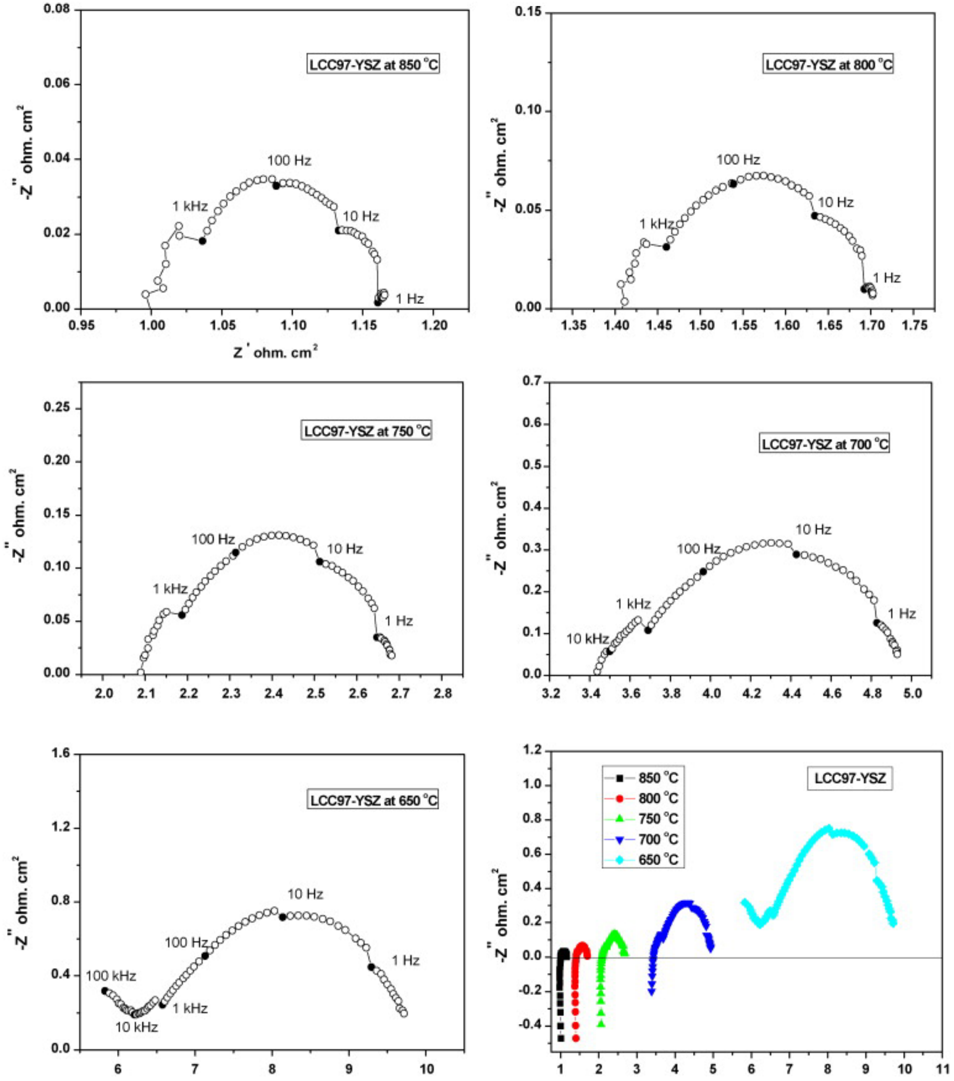
p = 1 $Z = 1/(j\omega T)$ → 电容 $C = T$ $\theta = 90^o$

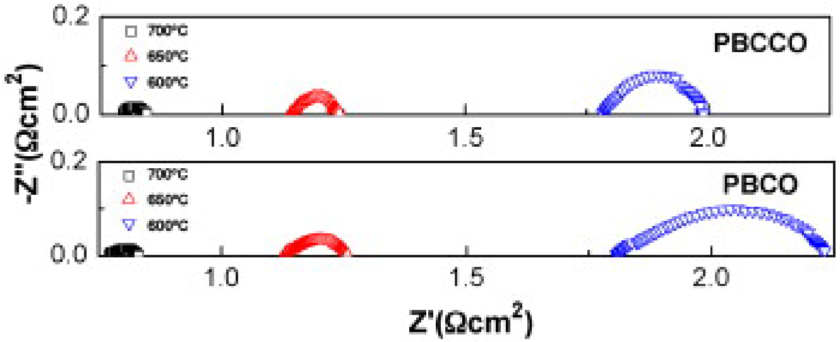
p = -1 $Z = j\omega/T$ → 电感 $L = 1/T$ $\theta = -90^o$

p = 0 $Z = 1/T$ → 电阻 $R = 1/T$ $\theta = 0^o$

p = 0.5 $Z = 1 / [T(j\omega)^{0.5}]$ → **Warburg阻抗** $\theta = 45^o$

Examples

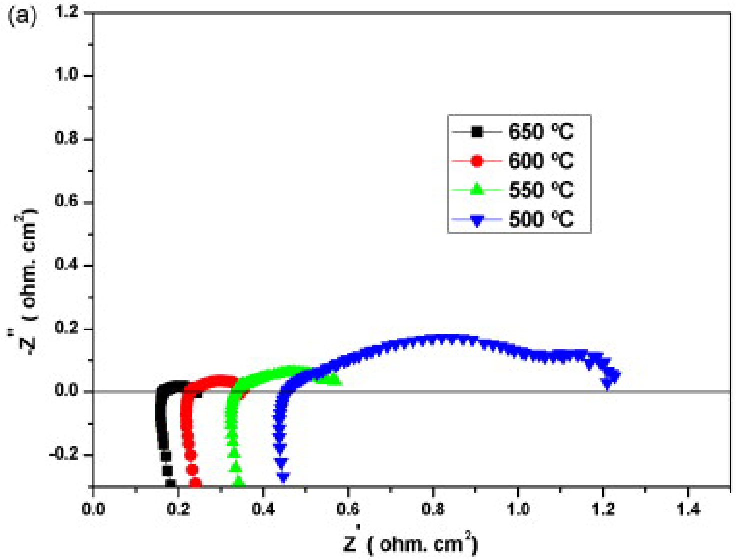


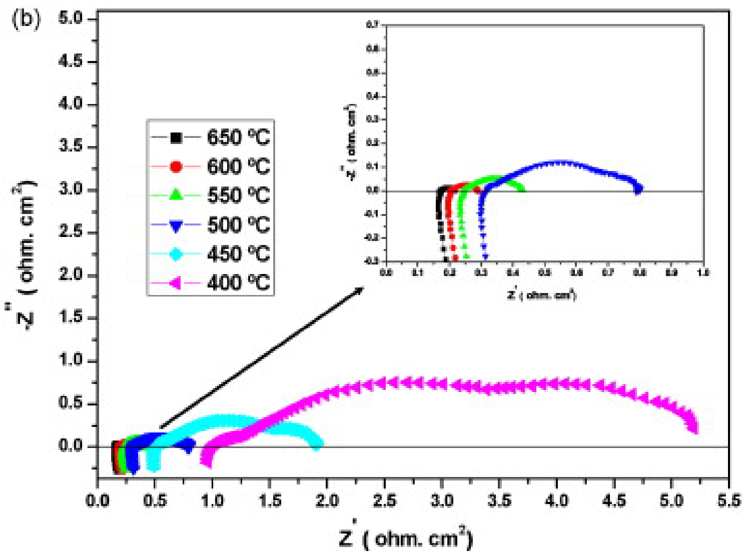


J. Power Sources 195 (2010) 453.

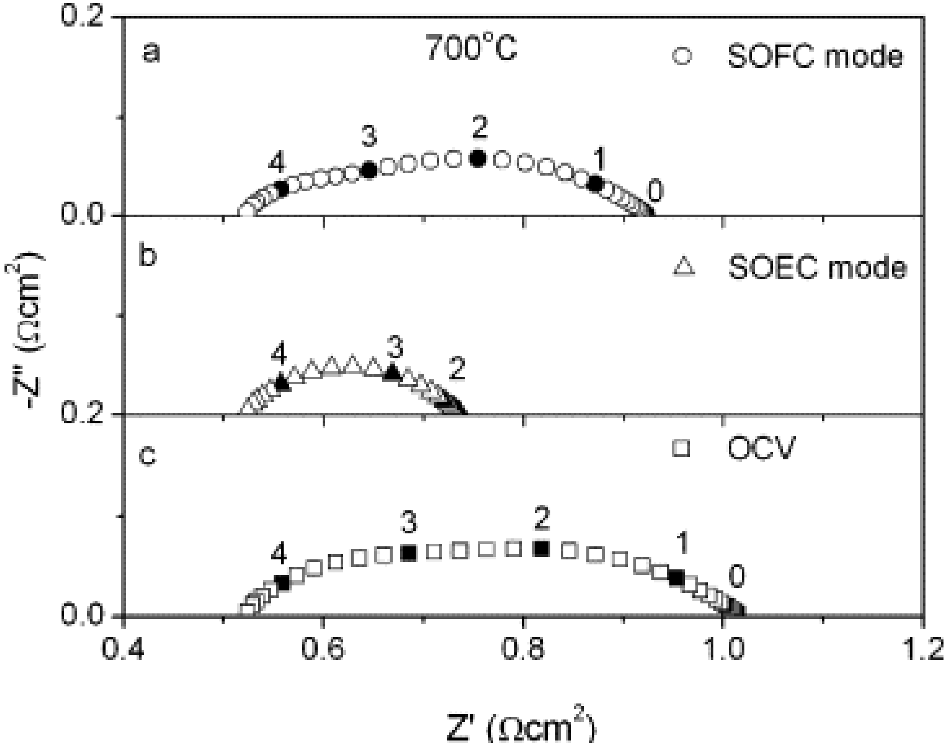
J. Alloy & Compd. 490 (2010) 214-222.

Examples



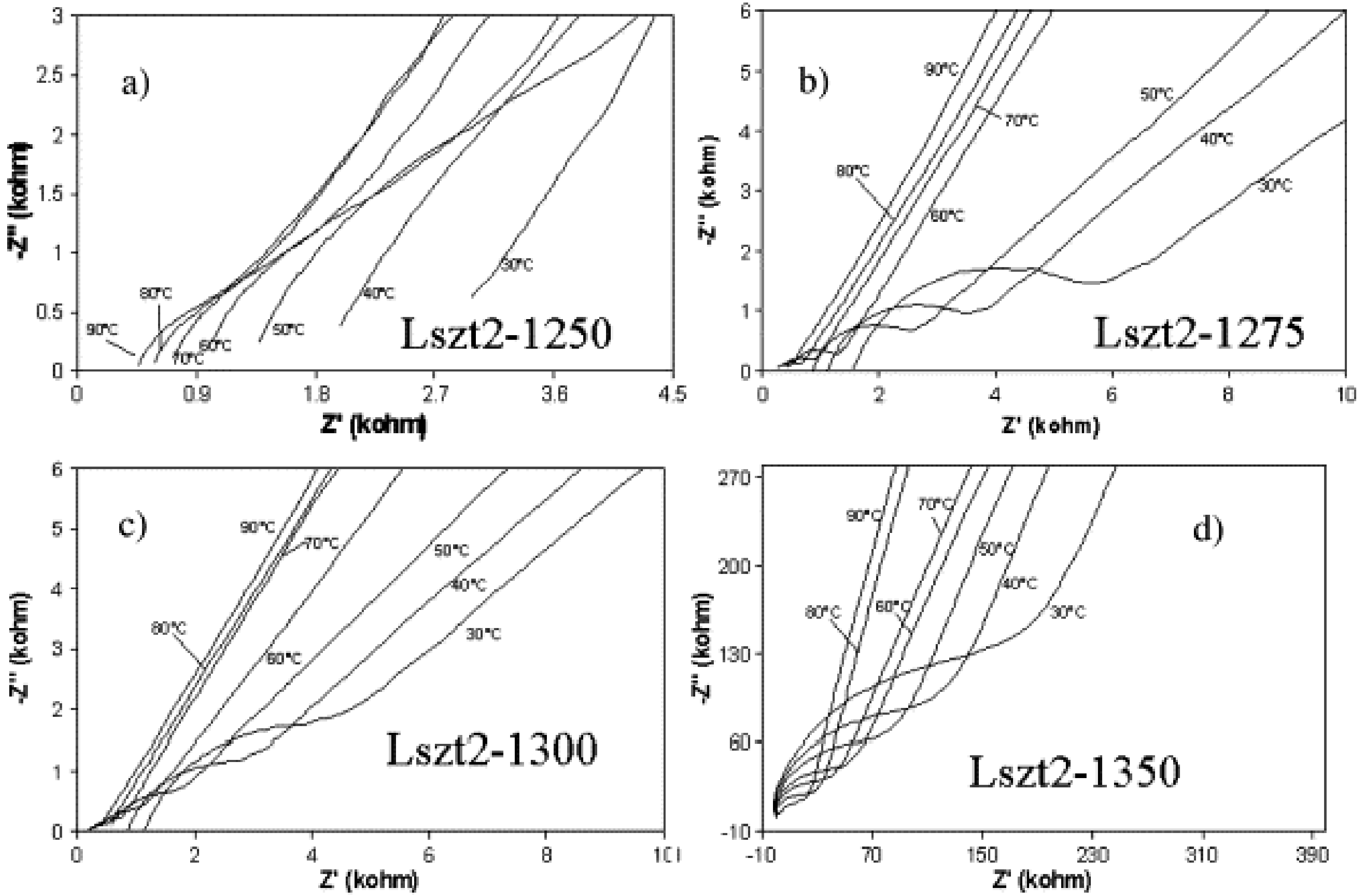


J. Power Sources 195 (2010) 1624.



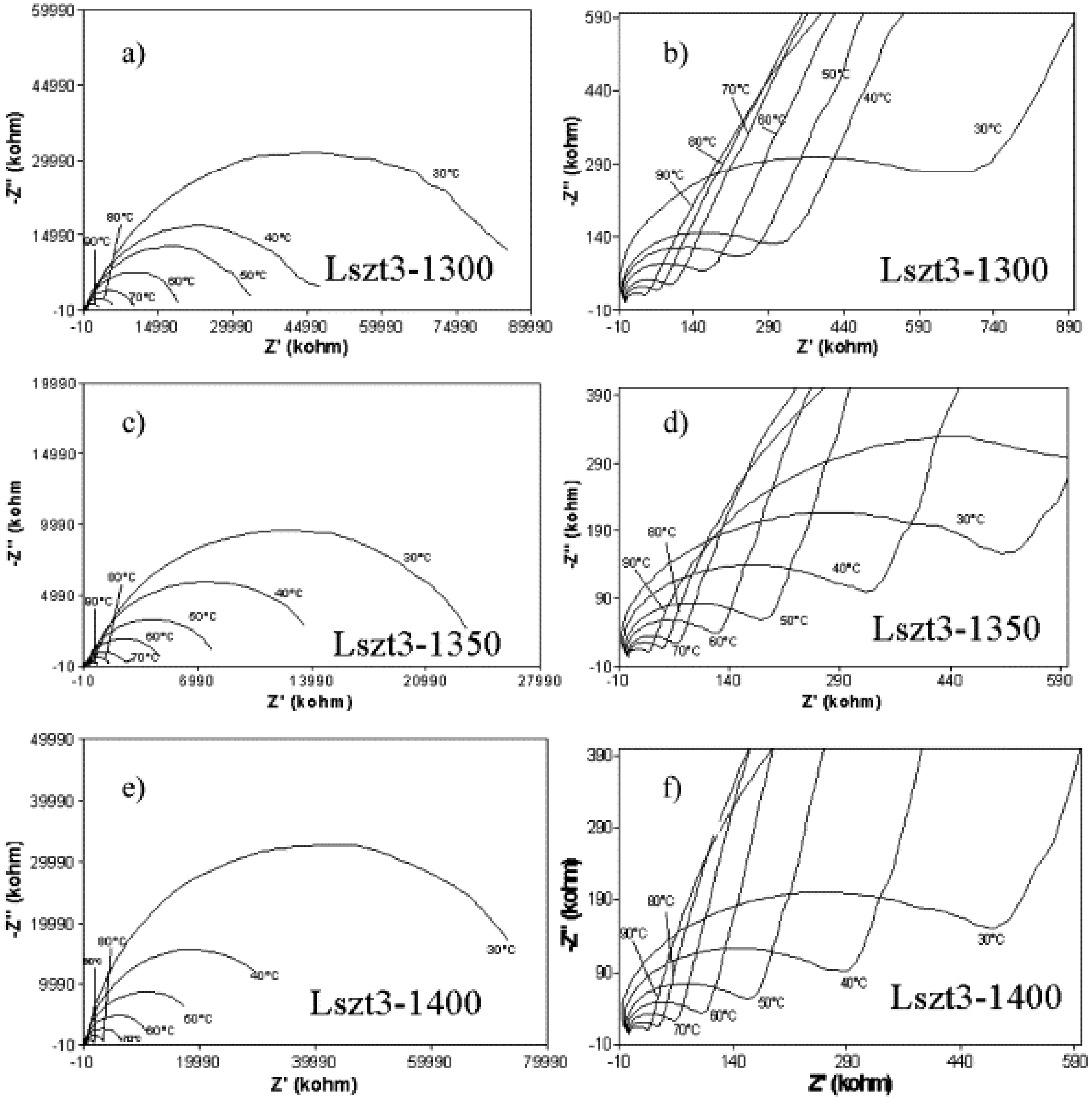
J. Power Sources 195 (2010) 3359.

Examples



Solid State Ionics 167 (2004) 263.

Examples



Solid State Ionics 167 (2004) 263.

Examples

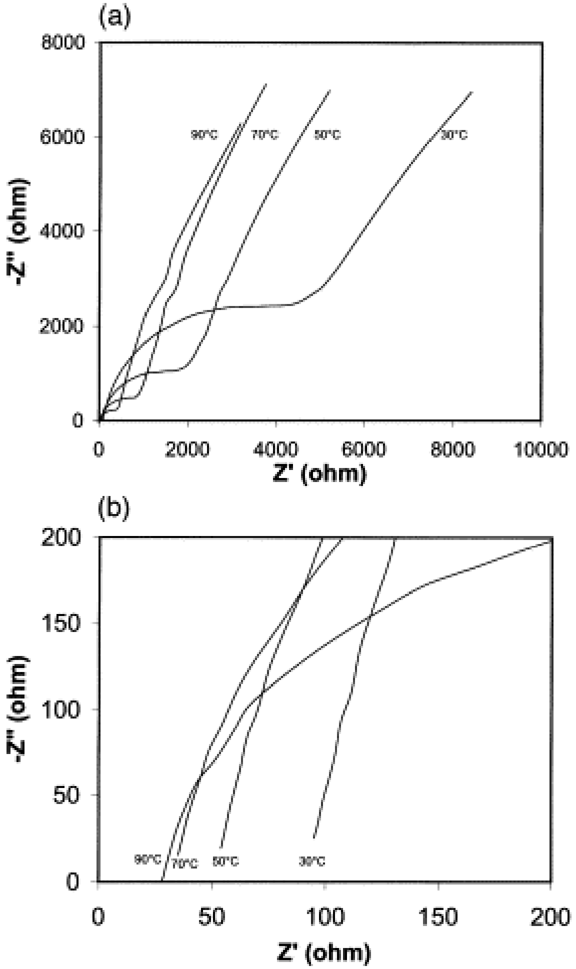
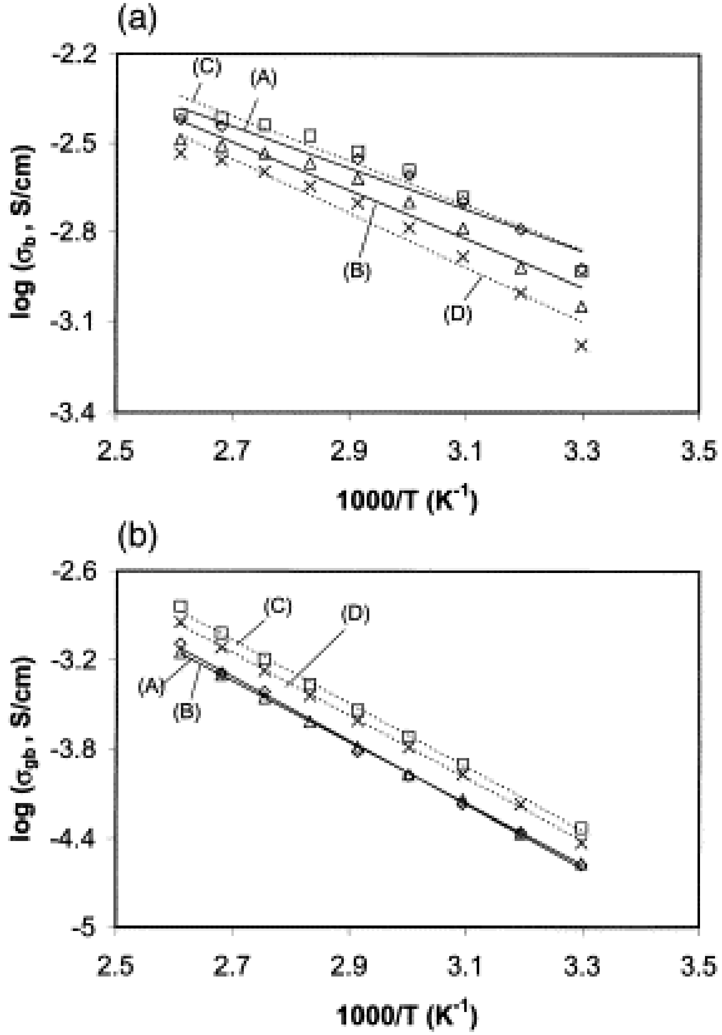


Fig. 1. AC impedance spectra of a $La_{0.55}Li_{0.35}TiO_3$ pellet at different temperatures after it had been calcined at 1100 ºC and sintered at 1200 ºC: (a) full spectra and (b) high-frequency part.



Solid State Ionics 144 (2001) 51.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

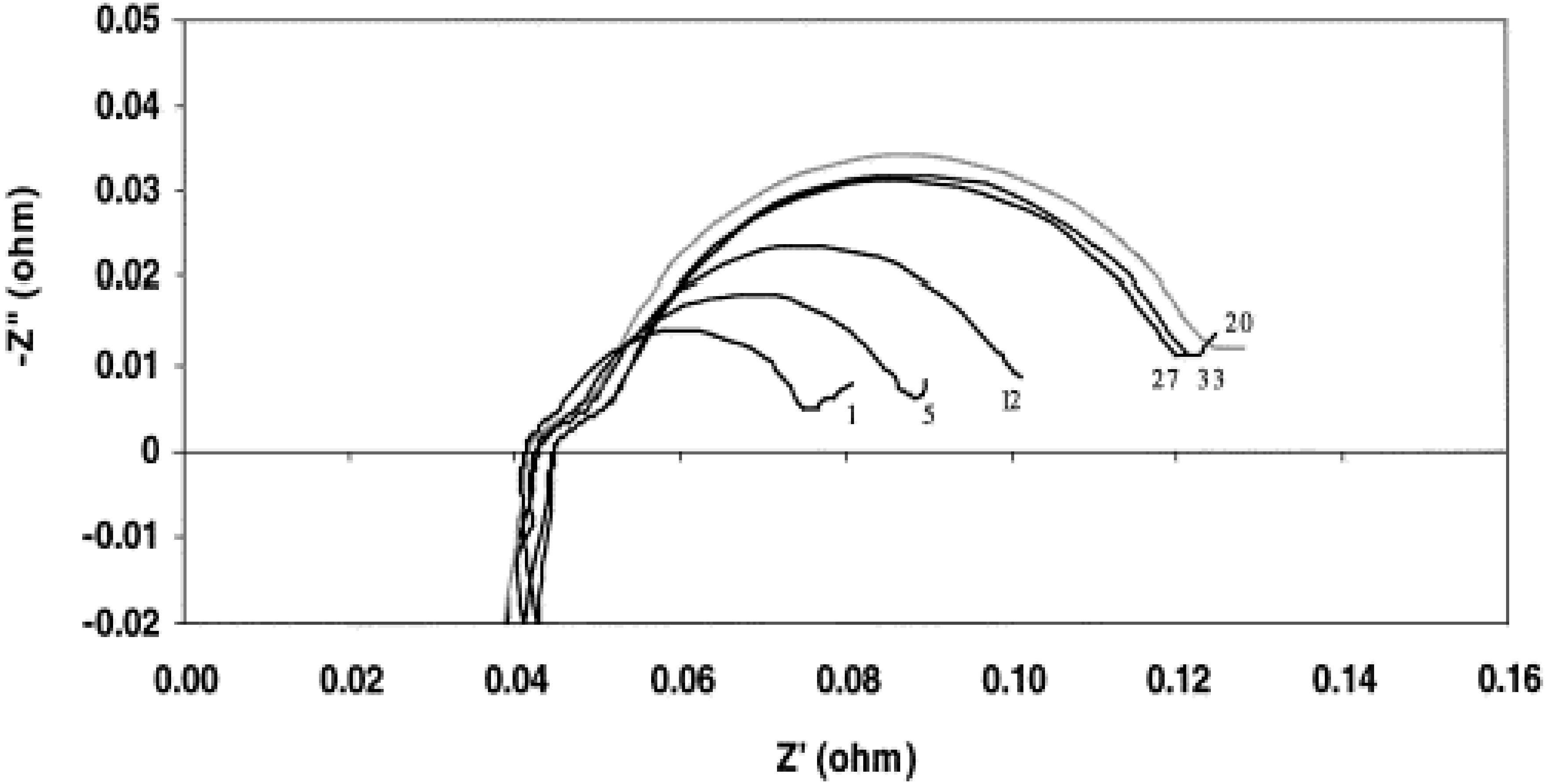


Fig. 1. An ac impedance spectra of an Argonne 18650 lithium-ion cell as a function of storage time. Numbers on the spectrum indicate days of storage.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

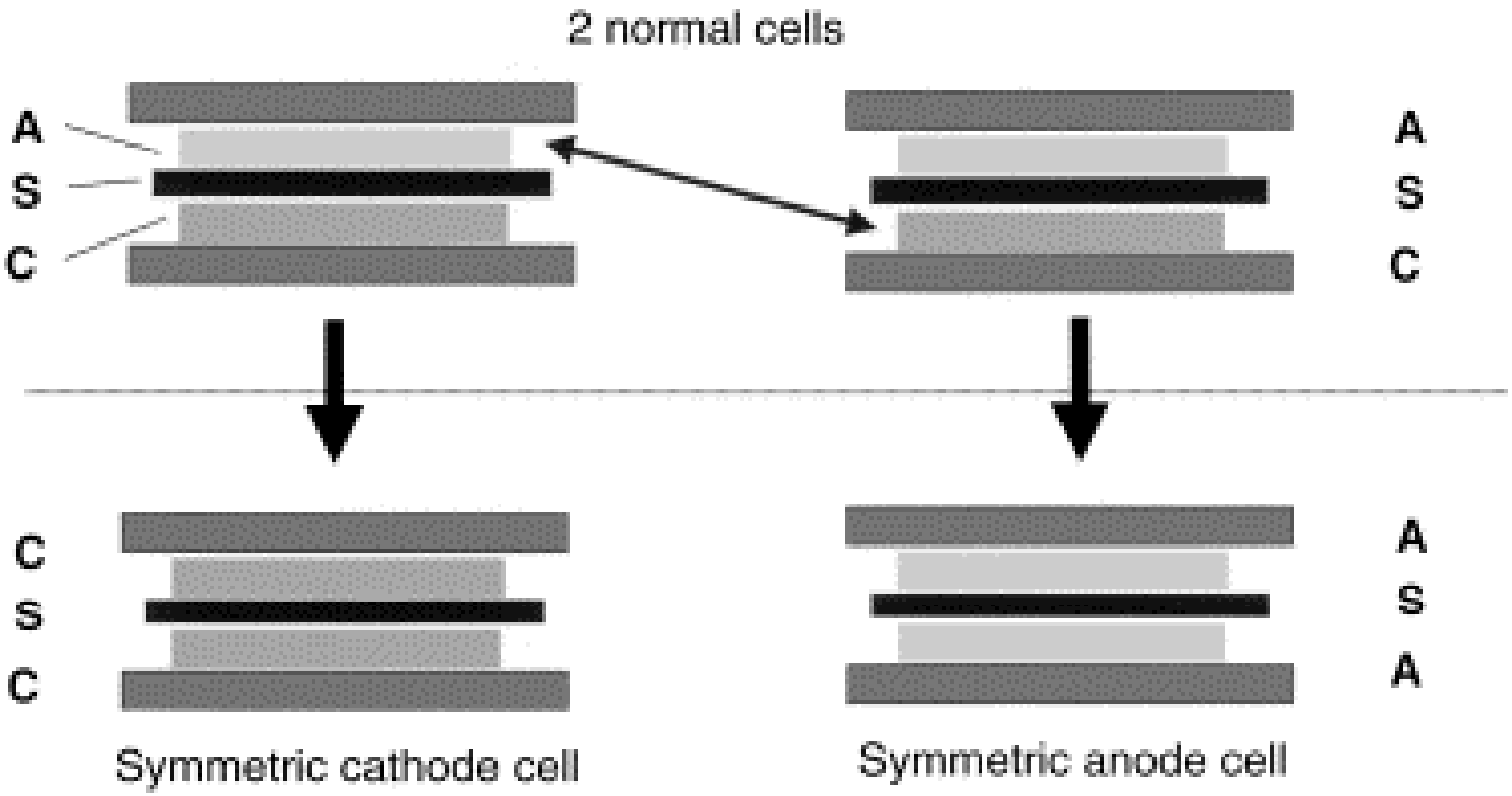


Fig. 2. Scheme of symmetric cell approach. A, S, and C stand for anode, separator, and cathode, respectively.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

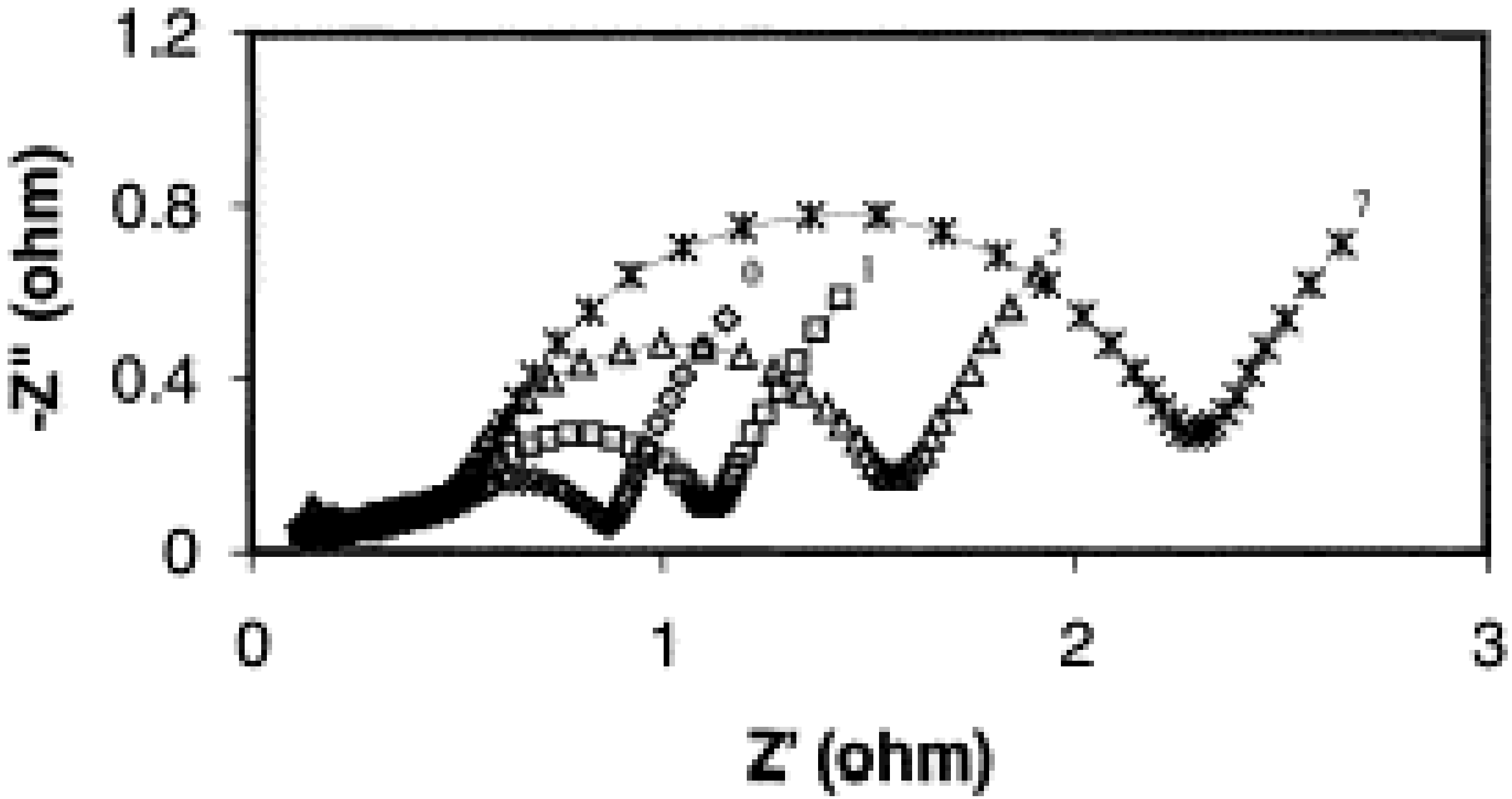


Fig. 3. An ac impedance spectra of a laboratory-scale lithium-ion cell during storage. Numbers on the spectrum indicate days of storage. The electrode area was 20.3 cm2; the electrolyte solvent was EC:DEC.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

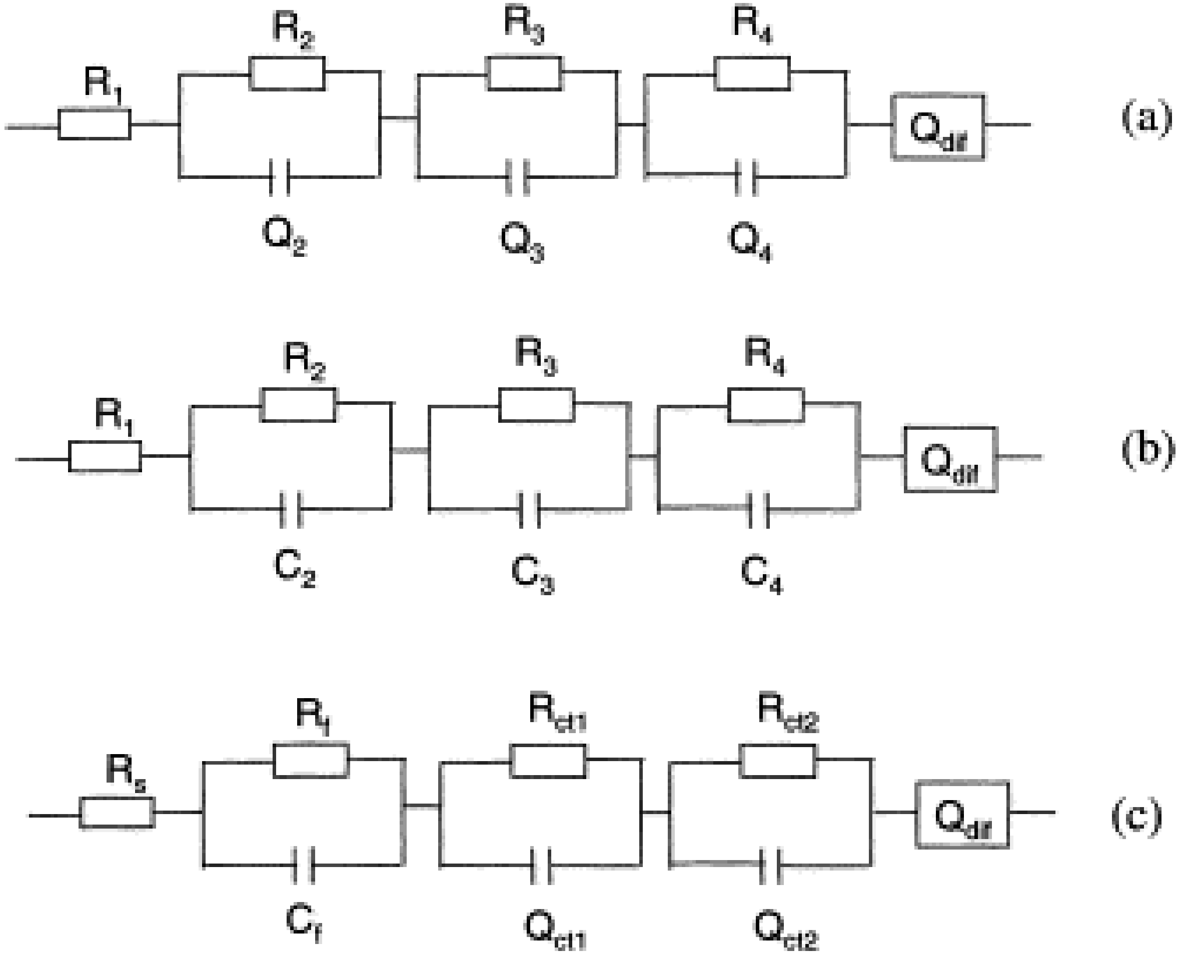


Fig. 4. Three possible equivalent circuit analogs for a lithium-ion cell. R, C, and Q stand for resistor, capacitor, and constant phase element, respectively. The subscripts s, f, ct, and dif stand for the electrolyte solution, surface layer, charge-transfer, and diffusional component, respectively.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

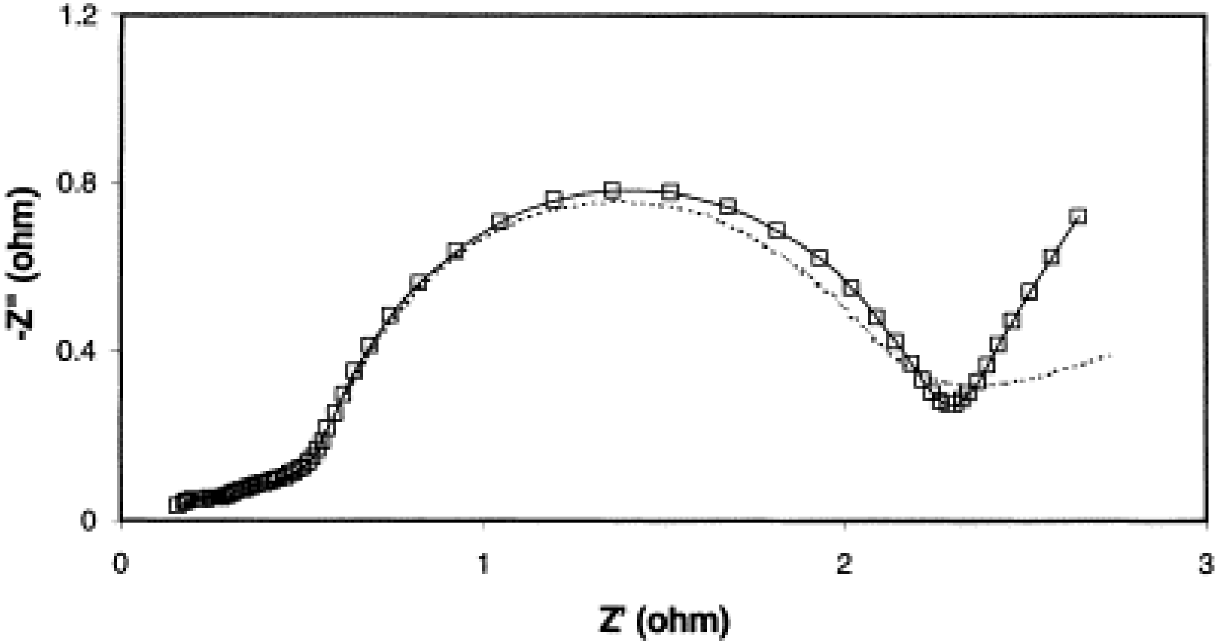


Fig. 5. An ac impedance spectrum of the lithium-ion cell on day 7 of storage (squares) and the simulation results with the equivalent circuits shown in Fig. 4a (solid line) and Fig. 4b (dashed line). The fitting parameters for the solid line are: R_1=0.15 Ω, R_2=0.067 Ω, T_2=59 μF, m_2=1, R_3=0.41 Ω, T_3=0.076 s $\Omega^{-2.1}$, m_3=0.48, R_4=1.60 Ω, T_4=0.075 s $\Omega^{-1.1}$, m_4=0.95, T_{dif}=7.6 s $\Omega^{-1.5}$ and m_{dif}=0.66. The fitting results for the dashed line are: R_1=0.1 Ω, R_2=0.061 Ω, C_2=83.7 μF, R_3=0.062 Ω, C_3=4.26 mF, R_4=1.21 Ω, C_4=81 mF, T_{dif}=1.22 s $\Omega^{-5.5}$ and m_{dif}=0.18.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

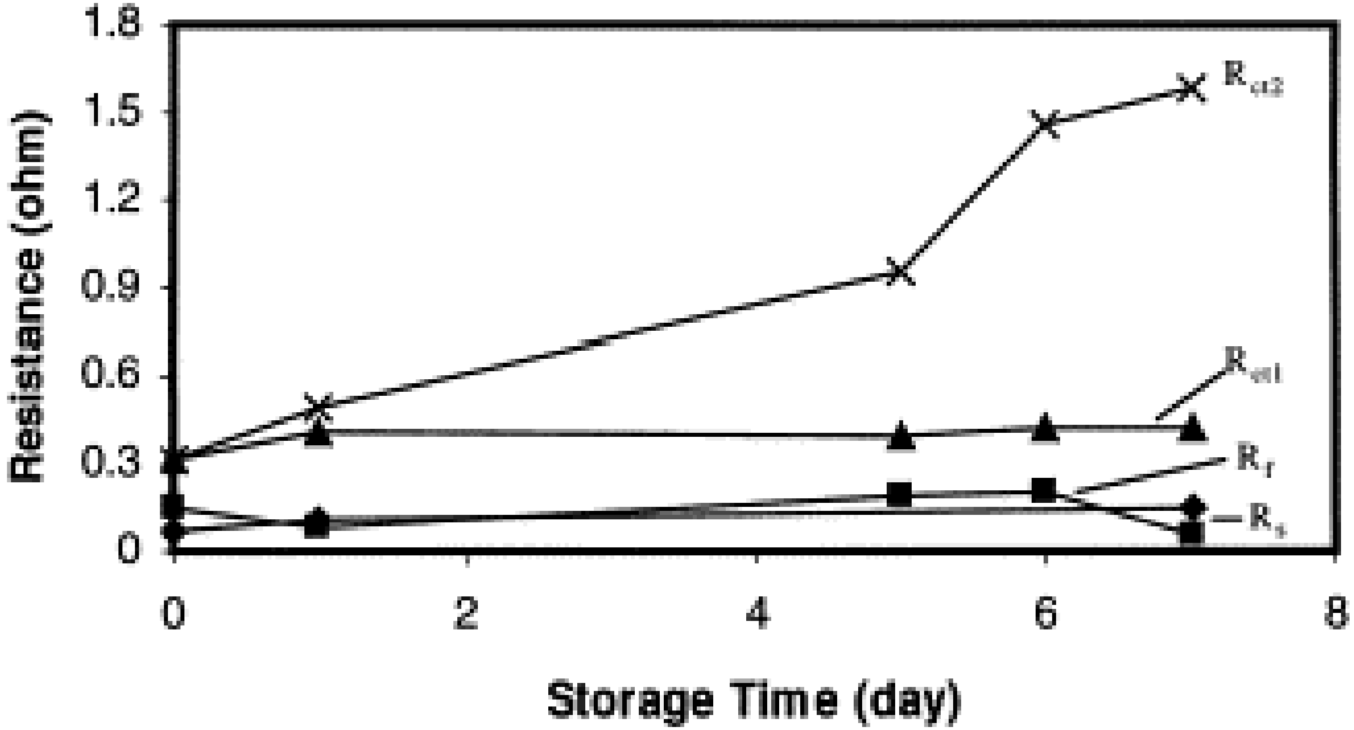


Fig. 6. Fitting results of the lithium-ion cell for the equivalent circuit in Fig. 4c as a function of storage time.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

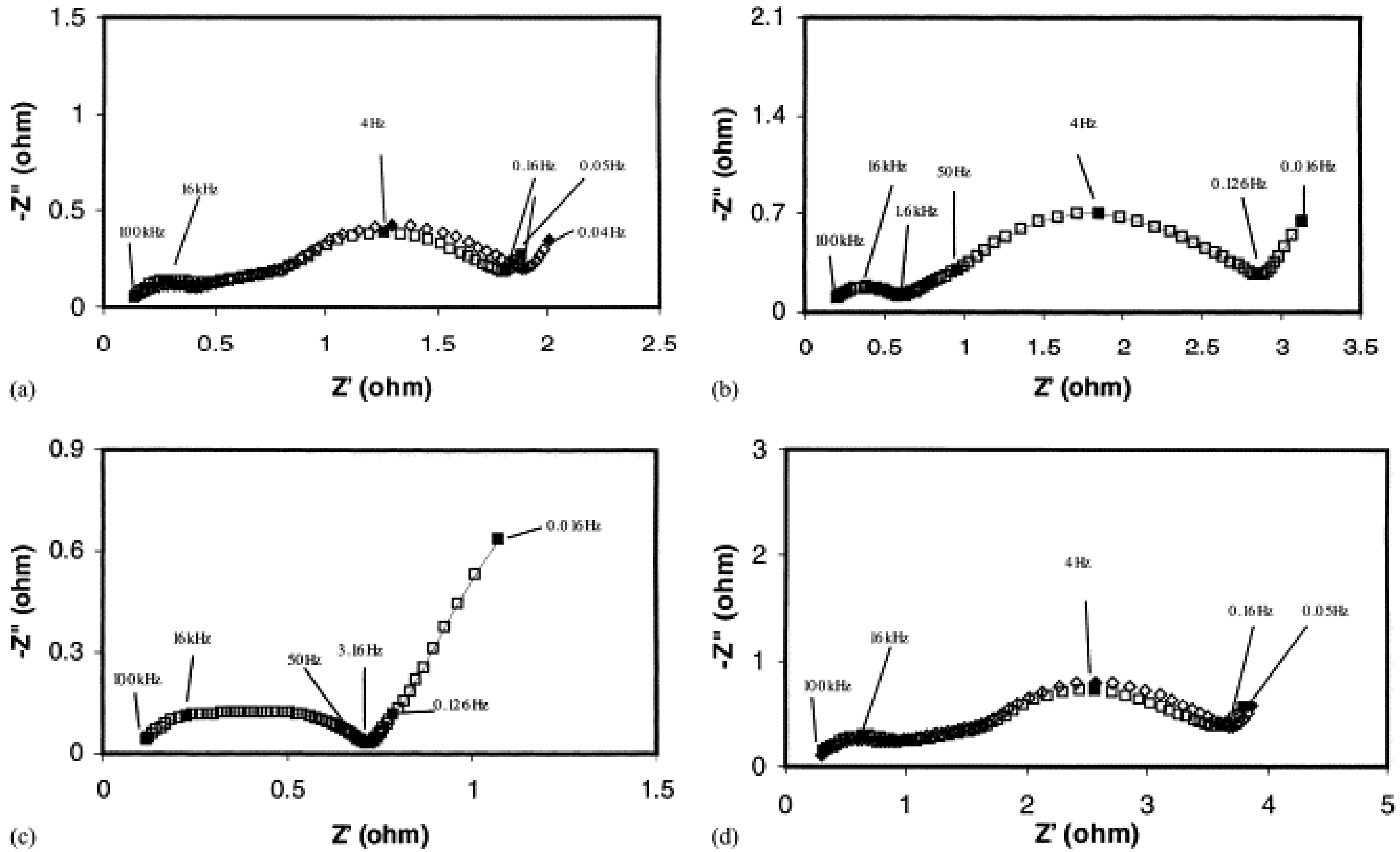


Fig. 7. An ac Impedance spectra of two half-charged lithium-ion cells and their resultant symmetric cells measured immediately after charging: (a) spectra of source cells (diamond marker (): OCV=3.457 V; square marker (□): OCV=3.473 V); (b) spectrum of symmetric cathode cell (OCV=4 mV); (c) spectrum of symmetric anode cell (OCV=22 mV); and (d) summation spectra of the source cells () and symmetric cells (□). Frequencies are indicated for the solid markers.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

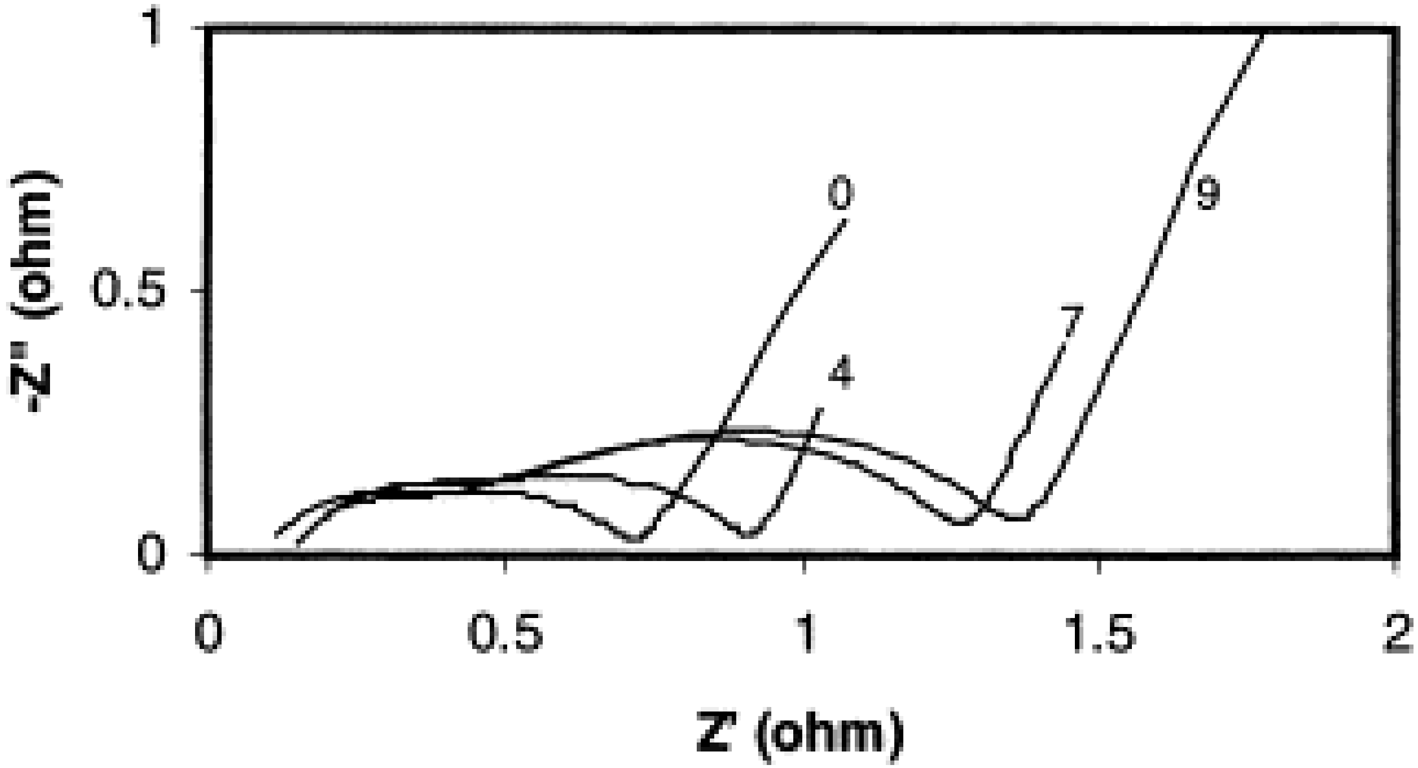


Fig. 8. An ac impedance spectra of the symmetric anode cell (Fig. 7c) as a function of storage time.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

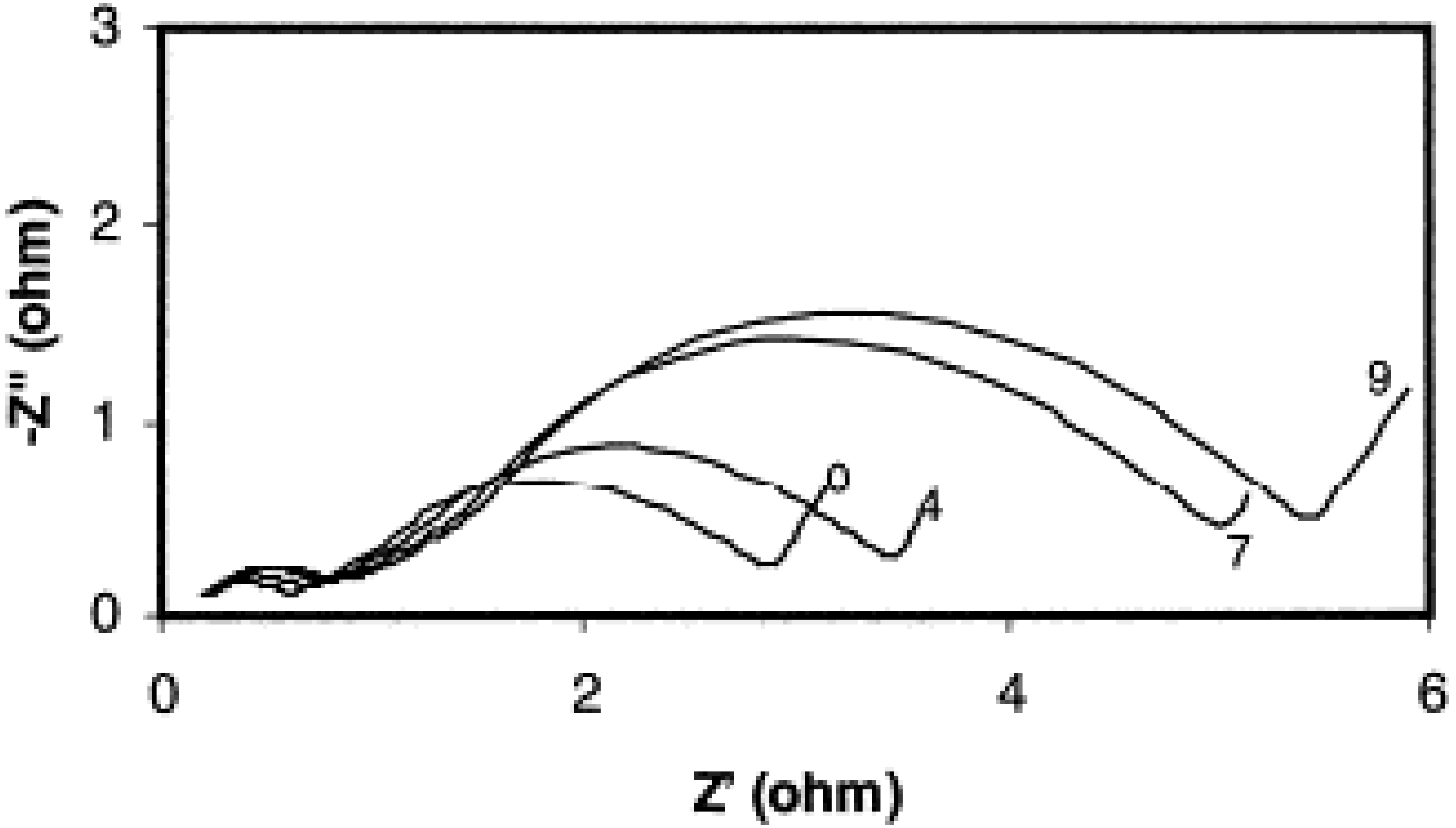


Fig. 9. An ac impedance spectra of the symmetric cathode cell (Fig. 7b) as a function of storage time.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

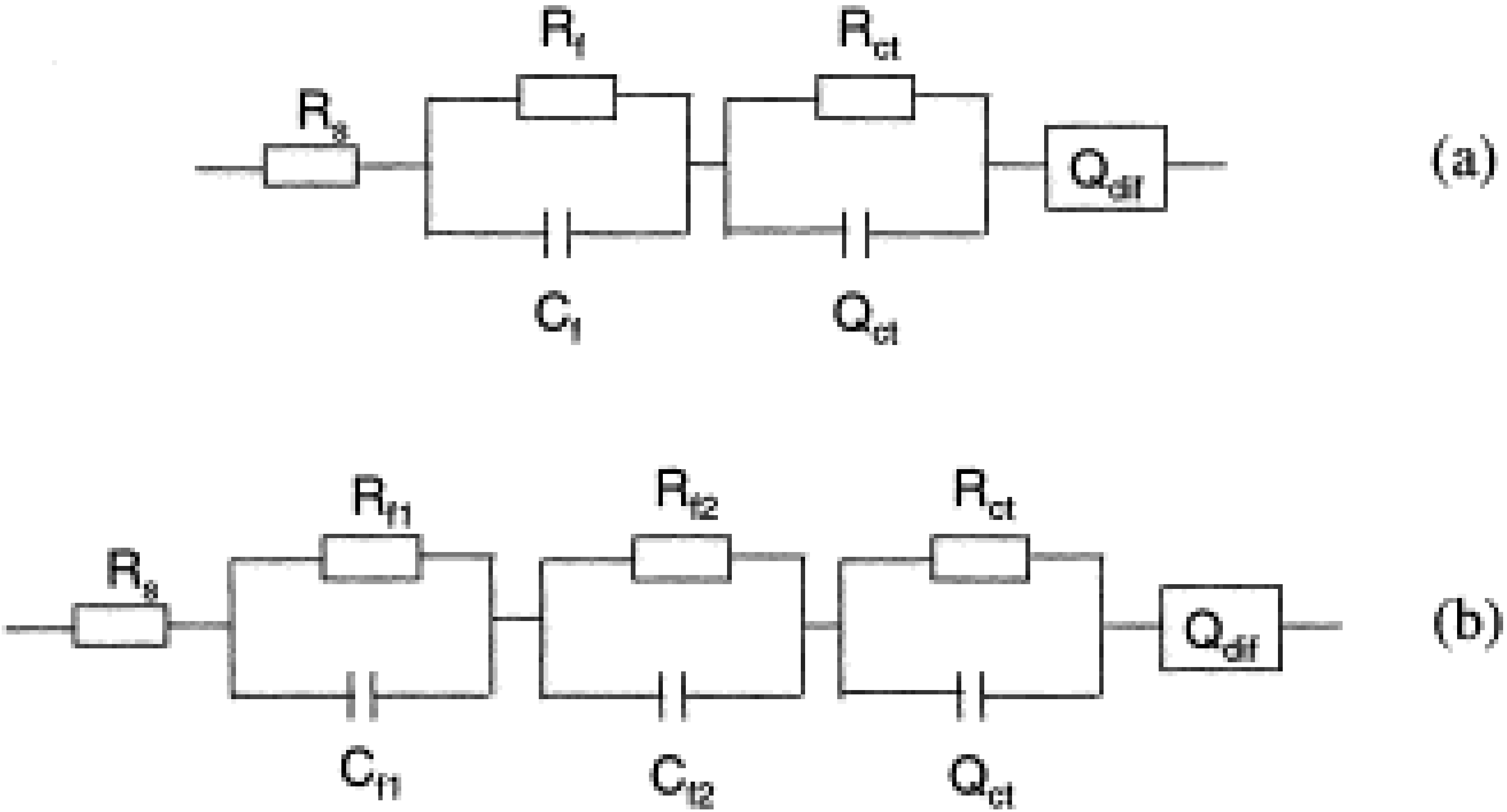


Fig. 10. Equivalent circuits for (a) the symmetric anode cell and (b) the symmetric cathode cell.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

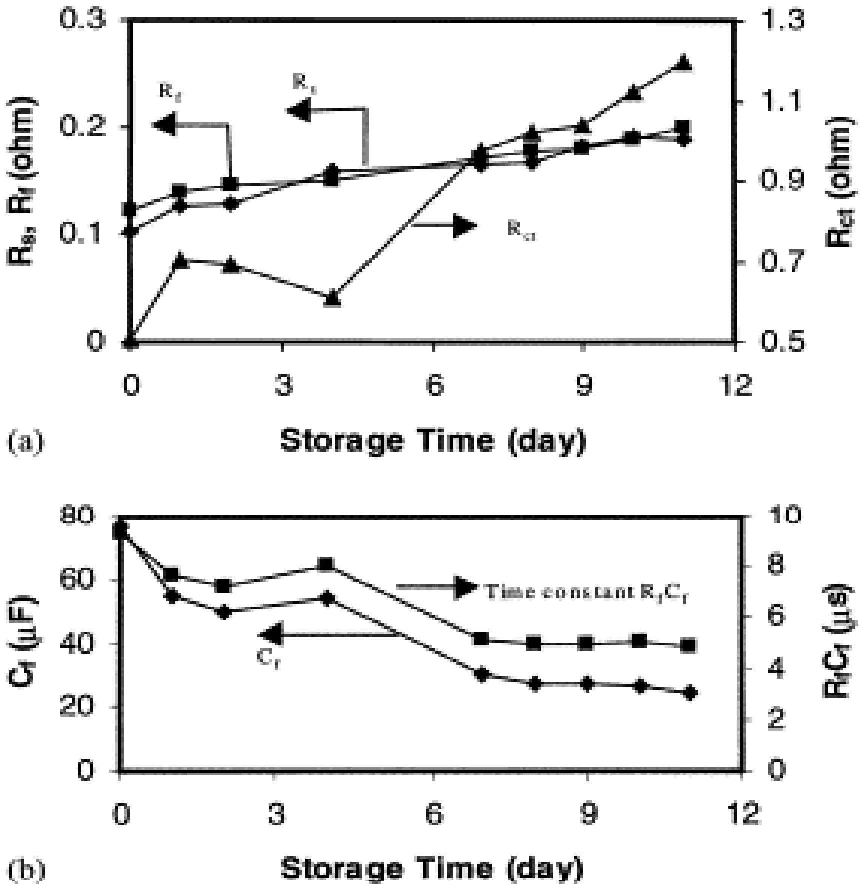


Fig. 11. Fitting results for the symmetric anode cell as a function of storage time: (a) resistance parameters and (b) surface-layer capacitance.

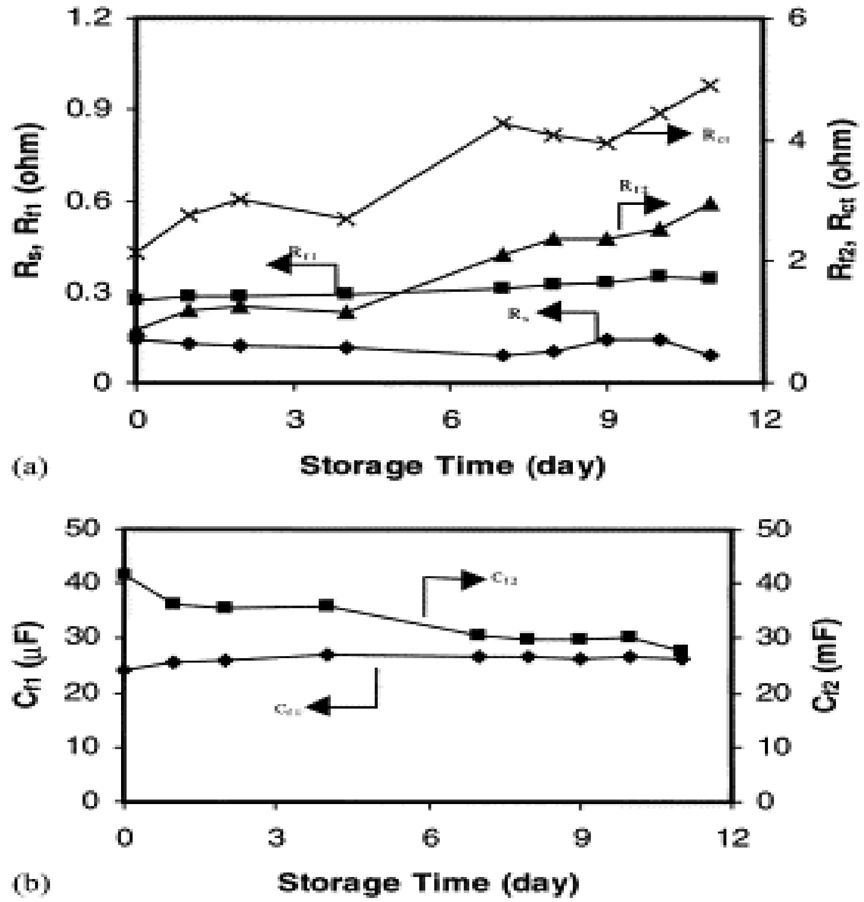


Fig. 12. Fitting results for the symmetric cathode cell as a function of storage time: (a) resistance parameters and (b) capacitance parameters.

Symmetric cell approach
(J. Power Sources 96 (2001) 321)

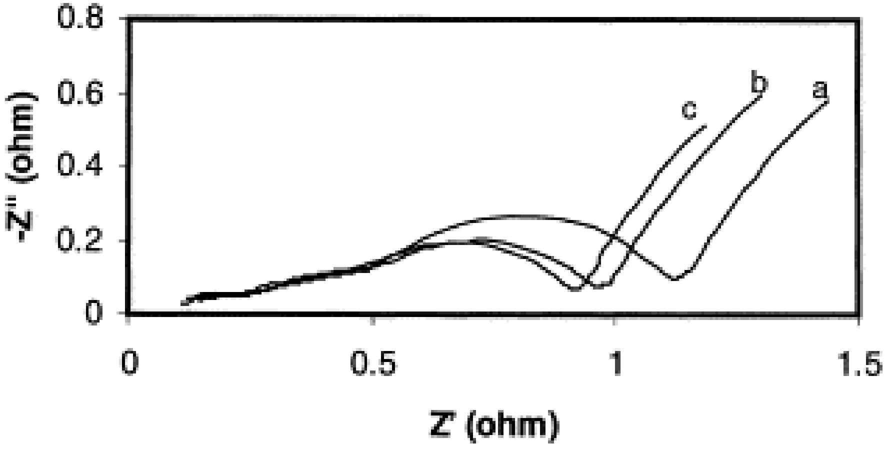


Fig. 13. An ac impedance spectra of three fully charged lithium-ion cells using different solvents in the electrolyte solutions: (a) EC:DEC; (b) 2EC:DEC:2DMC; (c) EC:4EMC. The electrode area was 20.3 cm^2.

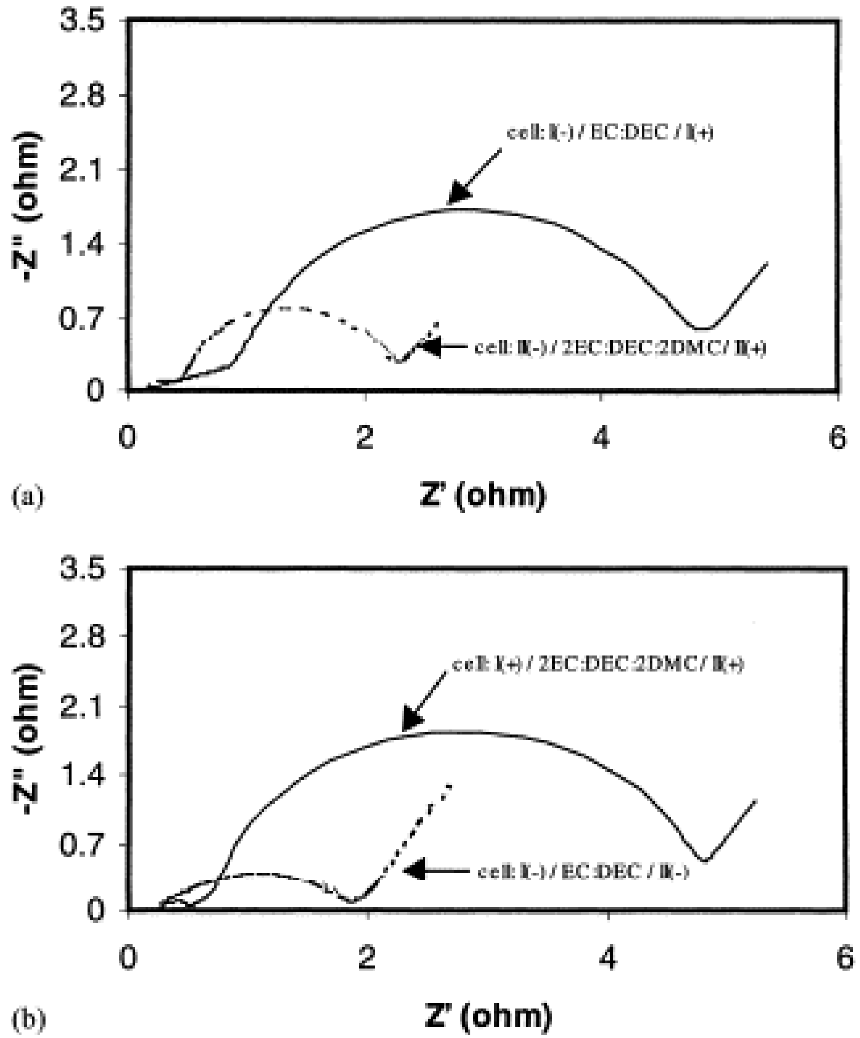


Fig. 14. An ac impedance spectra of (a) two fully charged cells using different solvents and (b) their resultant symmetric cells. The structures of the cells are given in the plots.