Ac-impedance - Electrochemical Impedance Spectroscopy (EIS) (II)

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1. Introduction

Systems

Characterization of systems = Equivalent Circuits

Parameters of systems = Electric parameters (R, C, L..)

Mechanisms = Combination of Circuits

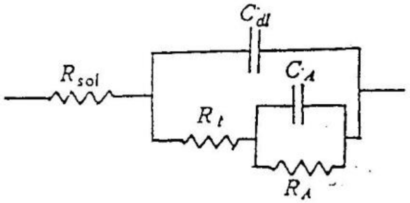
Ex. Electrochemical Systems

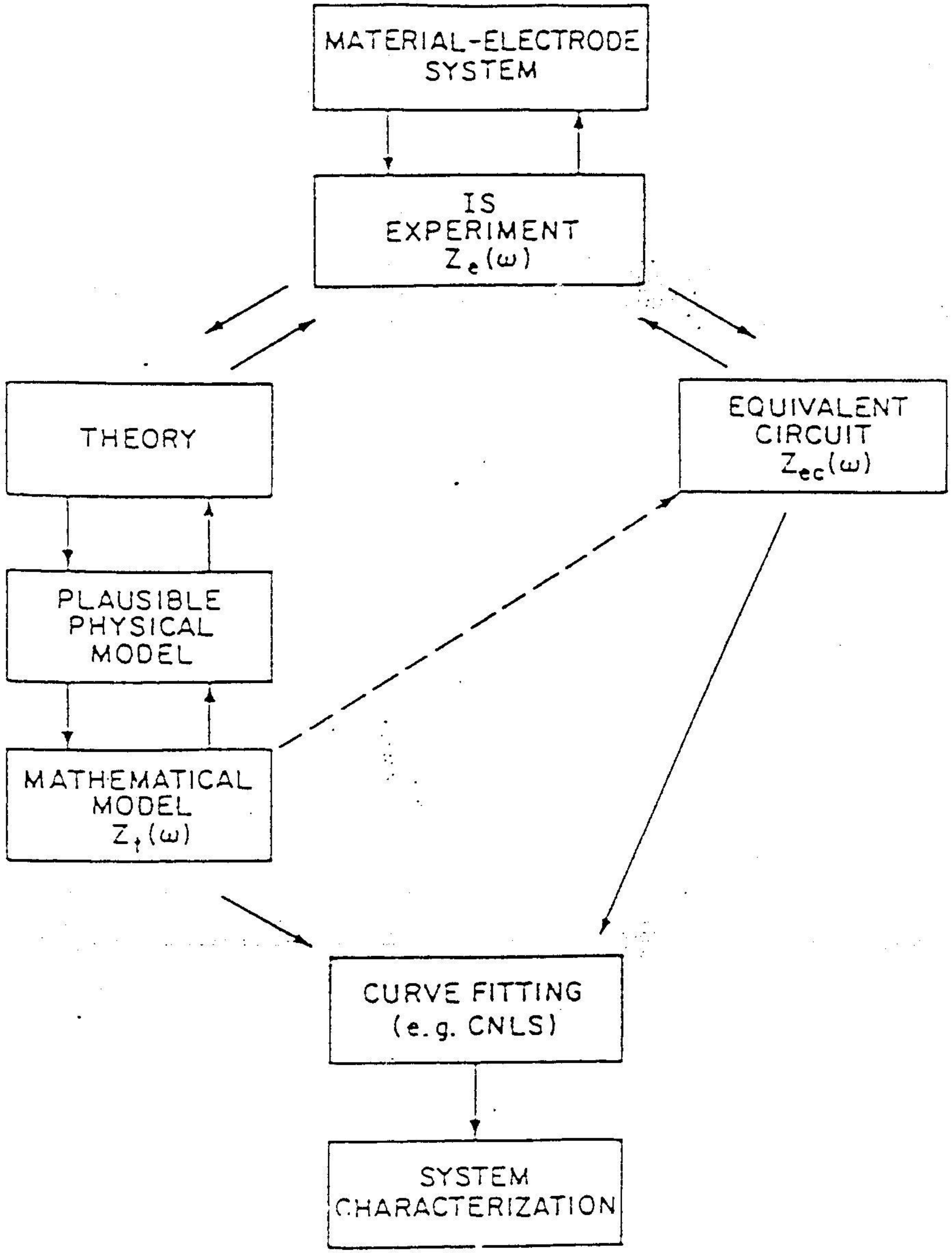
Kinetics of systems = Equivalent Circuits

Kinetic parameters of systems = Electric parameters

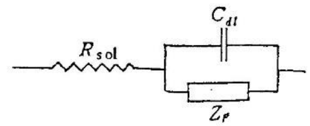
Kinetic mechanisms = Combination of Circuits

$$\underset{1-\theta}{M} + X^- \rightleftharpoons \underset{\theta}{(MX)_{ad}} + e$$
$$\underset{\theta}{(MX)_{ad}} \longrightarrow MX^+_{sol} + e$$
$$MX^+_{sol} \rightleftharpoons M^+ + X^-$$




MATERIAL-ELECTRODE SYSTEM
IS EXPERIMENT $Z_e(\omega)$
THEORY
EQUIVALENT CIRCUIT $Z_{ec}(\omega)$
PLAUSIBLE PHYSICAL MODEL
MATHEMATICAL MODEL $Z_t(\omega)$
CURVE FITTING (e.g. CNLS)
SYSTEM CHARACTERIZATION

B. Kinetic Systems



$$I = f(E, C_\alpha, \theta_\beta) \quad (\alpha = 1,2....n \; ; \; \beta = 1,2....m) \qquad [31]$$

At steady state

$$dE/dt = 0 \; ; \; dC_\alpha/dt = 0 \; ; \; d\theta_\beta/dt = 0 \qquad [32]$$

Pertubation of potential $E \rightarrow E + \delta E$

$$\delta I = (\partial f/\partial E)_{C_\alpha, \theta_\beta} \delta E + \sum_{\alpha=1}^{n} (\partial f/\partial C_\alpha)_{E, C_{\alpha'} \neq C_\alpha, \theta_\beta} \delta C_\alpha$$

$$+ \sum_{\beta=1}^{m} (\partial f/\partial \theta_\beta)_{E, C_\alpha, \theta_{\beta'} \neq \theta_\beta} \delta \theta_\beta \qquad [33]$$

$$\delta E = \Delta E \, e^{j\omega t} \qquad [34]$$

Admitance

$$Y_F = (\partial f/\partial E)_{C_\alpha, \theta_\beta} + \sum_{\alpha=1}^{n} (\partial f/\partial C_\alpha)_{E, C_{\alpha'} \neq C_\alpha, \theta_\beta} \delta C_\alpha / \delta E$$

$$+ \sum_{\beta=1}^{m} (\partial f/\partial \theta_\beta)_{E, C_\alpha, \theta_{\beta'} \neq \theta_\beta} \delta \theta_\beta / \delta E \qquad [35]$$

Case 1 : $\delta C_\alpha=0$, $\delta \theta_\beta=0$

$$Y_F = (\partial f/\partial E)_{C_\alpha, \theta_\beta} \quad [36]$$

Function

$$I = I_o[e^{\alpha nF(E-Ee)/RT} - e^{-(1-\alpha)nF(E-Ee)/RT}] \quad [37]$$

If α = 0.5 and at equilibrium

$$Z_F = 1/Y_F = (\partial f/\partial E)_{Ee} = RT/nFI_o \quad [38]$$

If α = 0.5 and far away from the equilibrium

$$Z_F = 1/Y_F = (\partial f/\partial E)_E = \beta_a/I \quad [39]$$

where

$$\beta_a = RT/\alpha nF \quad [40]$$

Case 2 : Diffusion resistance is not negligible.

Function : $O + ne \rightarrow R$

$$I = -I_o (C_s/C_b)\exp(-(E-E_e)/\beta_c) \quad [41]$$

$$\delta I = (\partial f/\partial E)_{C_s}\delta E + (\partial f/\partial C_s)_E \delta C_s \quad [42]$$

Fick's 2nd law

$$\partial(\delta C)/\partial t = D\partial^2(\delta C)/\partial x^2 \quad [43]$$

$$\partial(\delta C)/\partial t = j\omega\,\delta C \quad [44]$$

$$D\partial^2(\delta C)/\partial x^2 - j\omega\,\delta C = 0 \quad [45]$$

Solution :

$$\delta C = B\exp(-(j\omega/D)^{0.5}x) \quad [46]$$

where

$$B = \delta I/(nF(\omega D j)^{0.5}) \quad [47]$$

$$(\delta C)_{x=0} = \delta C_s = \delta I/(nF(\omega D j)^{0.5}) \quad [48]$$

$$\delta I = (|I_c| / \beta_c)\ \delta E - (|I_c|\ \delta I / C_s nF(\omega D j)^{0.5})$$

[49]

$$Z_F = \delta E / \delta I = (\beta_c / |I_c|)(1 + |I_c| / C_s nF(\omega D j)^{0.5})$$

[50]

where

$$j^{-0.5} = (1-j)/\sqrt{2} \quad [51]$$

Faradaic impedance

$$Z_F = R_t + (R_t |I_c| / (C_s nF(2\omega D)^{0.5}))(1-j) \quad [52]$$

$$= R_t + R_w \quad [53]$$

where R_w is the Warburg impedance.

Surface concentration

$$C_S = ((I_C - |I_C|)/I_C)C_b \qquad [54]$$

Impedance of whole system

$$Z = R_{sol} + R_t(1 + A/\sqrt{\omega} - j/\sqrt{\omega})/(1 + j\omega C_{dl} R_t(+A/\sqrt{\omega} - jA/\sqrt{\omega}))$$

[55]

where

$$A = |I_C| / (nFC_S\sqrt{2D}) \qquad [56]$$

If $\omega >> A^2$

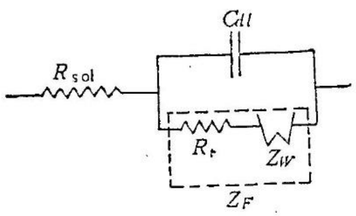
$$Z \fallingdotseq R_{sol} + R_t/(1 + j\omega R_t C_{dl}) \qquad [57]$$

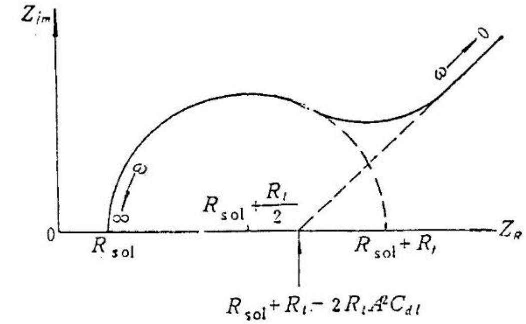
If ω is very small

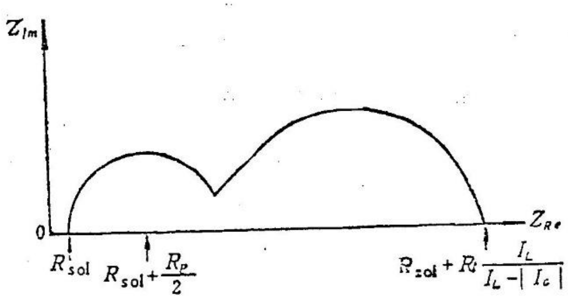
$$Z_{Re} \fallingdotseq R_{sol} + R_t + R_t A/\sqrt{\omega} \qquad [58]$$

$$Z_{Im} \fallingdotseq 2R_t^2 A^2 C_{dl} + R_t A/\sqrt{\omega} \qquad [59]$$

$$\fallingdotseq Z_{Re} - R_{sol} - R_t + 2R_t^2 A^2 C_{dl} \qquad [60]$$


Cdl
R sol
Rt
ZW
ZF


Zim
ω→0
ω
∞
0
R sol
R sol + Rt/2
R sol + Rt
ZR
R sol + Rt − 2Rt A²Cdl


Zim
0
ZRe
Rsol
Rsol + Rp/2

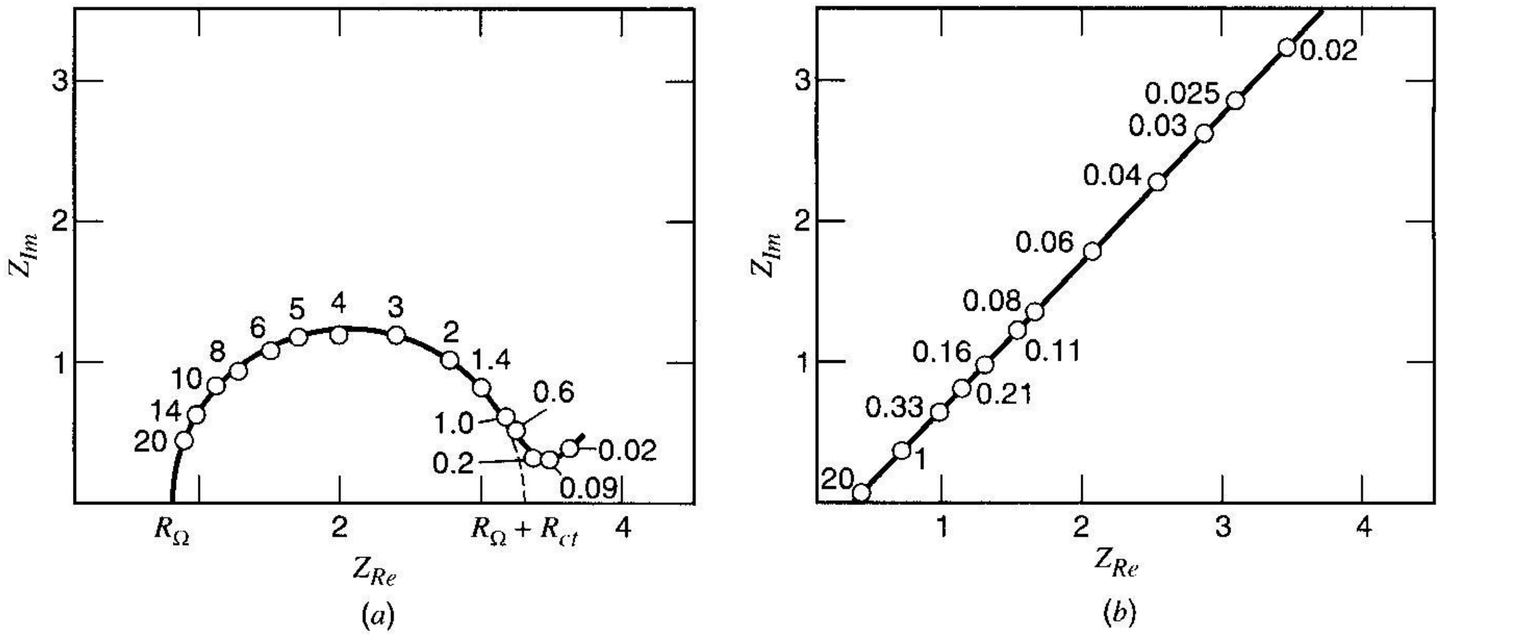


Figure 10.4.5 Impedance plane plots for actual chemical systems. Numbers by points are frequencies in kHz. (*a*) For the electrode reaction $Zn^{2+} + 2e \rightleftarrows Zn(Hg)$. $C^*_{Zn^{2+}} = C^*_{Zn(Hg)} = 8 \times 10^{-3}$ *M*. Electrolyte was 1 *M* $NaClO_4$ plus 10^{-3} *M* $HClO_4$. (b) For the electrode reaction $Hg_2^{2+} + 2e \rightleftarrows Hg$ in 1 *M* $HClO_4$. $C_{Hg_2^{2+}} = 2 \times 10^{-3}$ *M*. [From J. H. Sluyters and J. J. C. Oomen, *Rec. Trav. Chim. Pays-Bas*, **79**, 1101 (1960), with permission.]

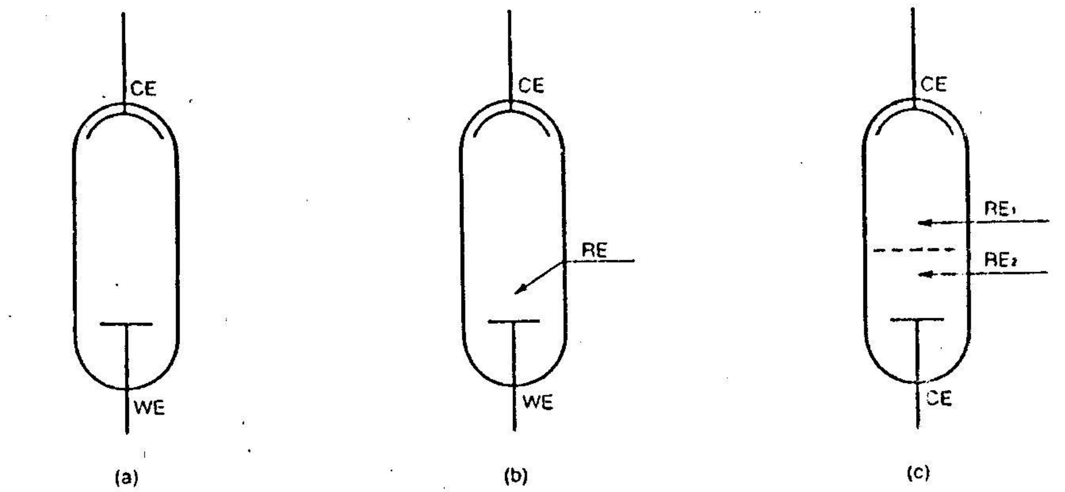
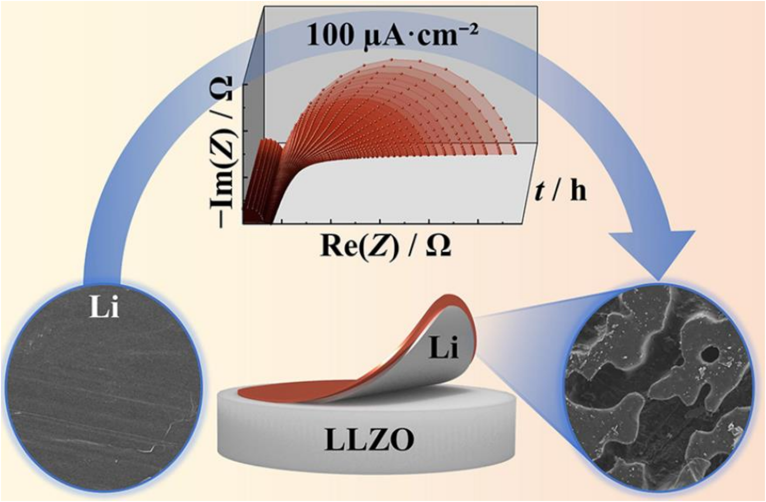
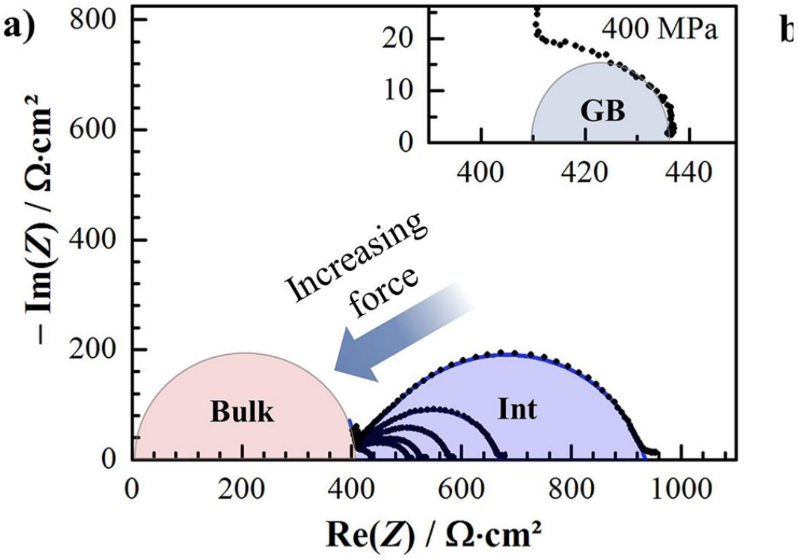


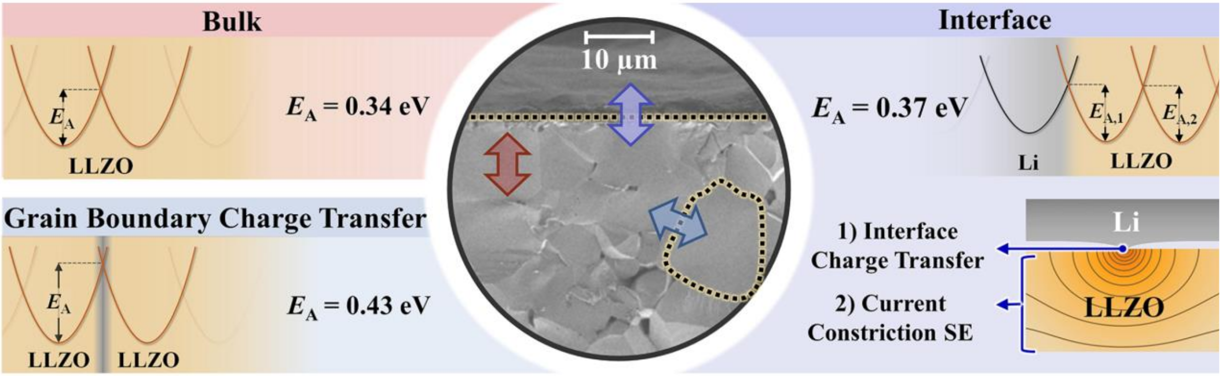
Fig 2.1 *Scheme of experimental electrochemical cells:*

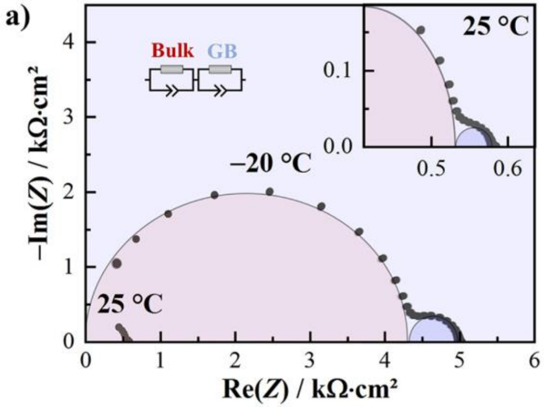
(a)	*2 – electrode cell*	
(b)	*3 – electrode cell*	
(c)	*4 – electrode cell*	

W E	*Working electrode,*
C E	*Counter electrode*
R E	*Reference electrode*









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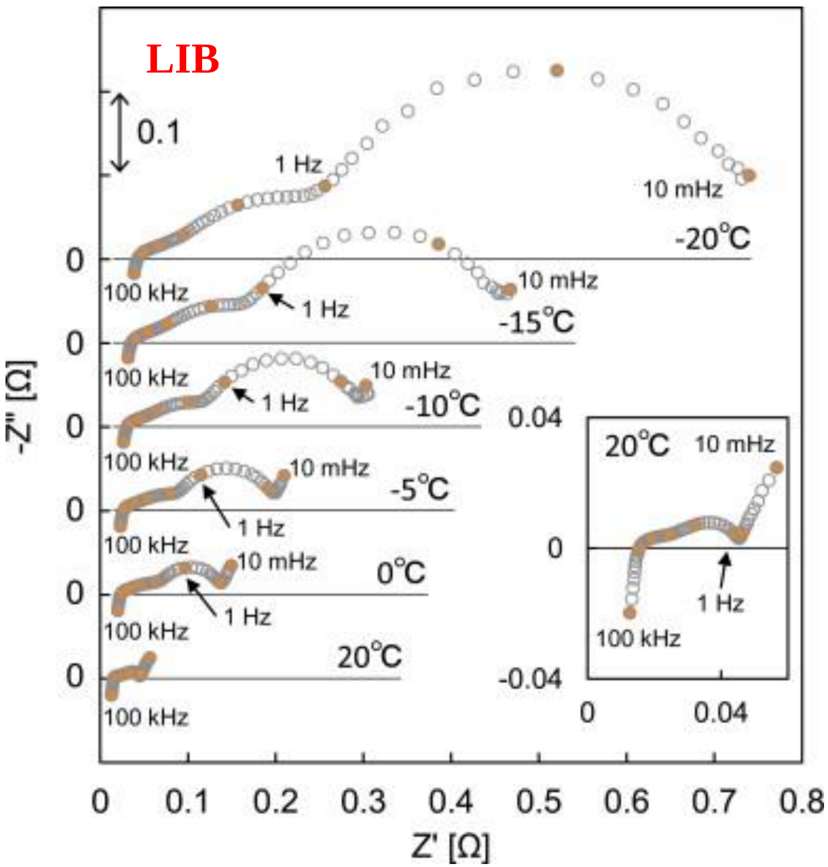
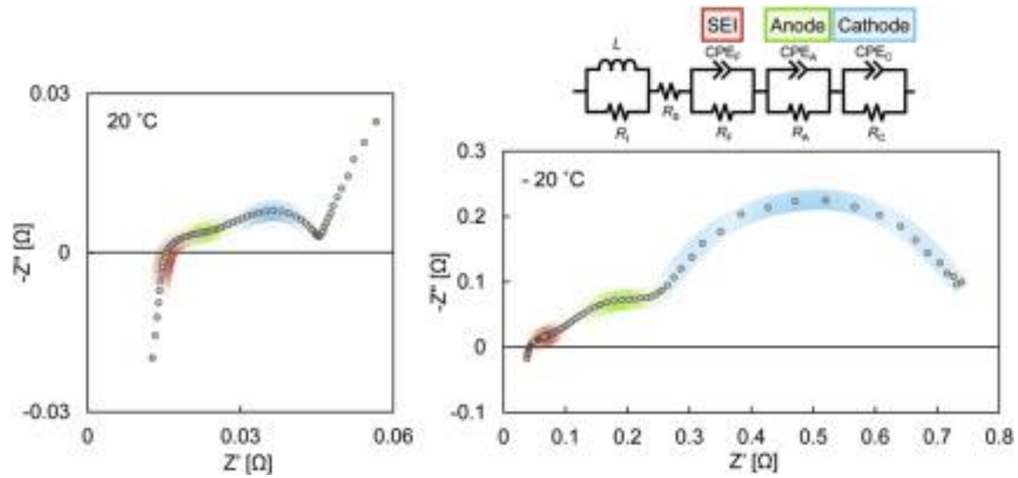
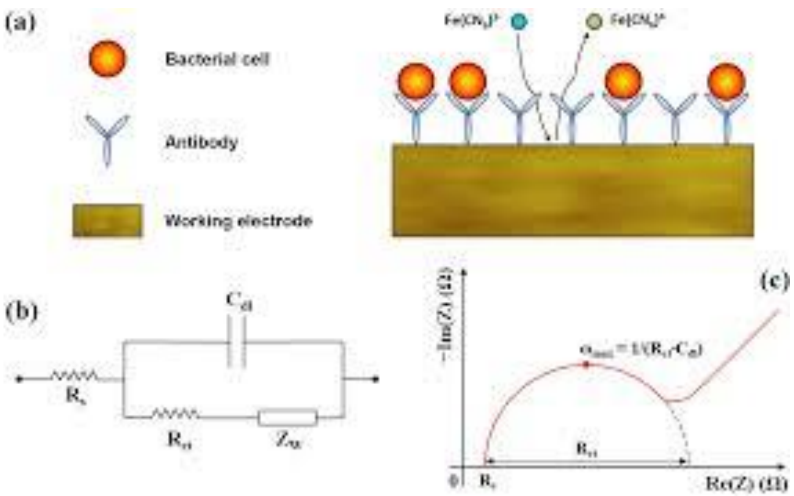
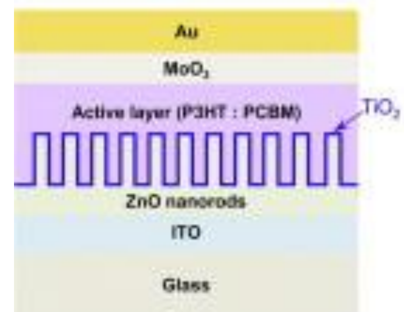
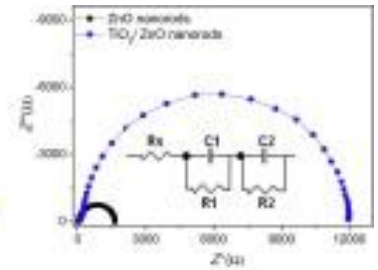
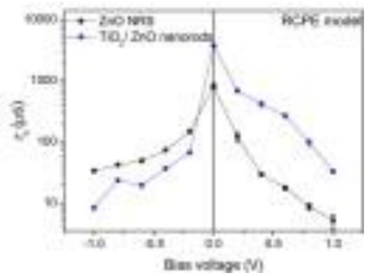

LIB
0.1
1 Hz
10 mHz
-20°C
100 kHz
1 Hz
10 mHz
-15°C
100 kHz
1 Hz
10 mHz
-10°C
100 kHz
1 Hz
10 mHz
-5°C
100 kHz
1 Hz
10 mHz
0°C
100 kHz
20°C
100 kHz
20°C
10 mHz
1 Hz
100 kHz
0.04
0
-0.04
0
0.04
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Z' [Ω]
-Z'' [Ω]


SEI
Anode
Cathode
L
R_l
R_s
CPE_f
R_f
CPE_A
R_A
CPE_C
R_C
20 °C
0.03
0
-0.03
0
0.03
0.06
Z' [Ω]
-Z'' [Ω]
- 20 °C
0.3
0.2
0.1
0
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Z' [Ω]
-Z'' [Ω]









polymer solar cell