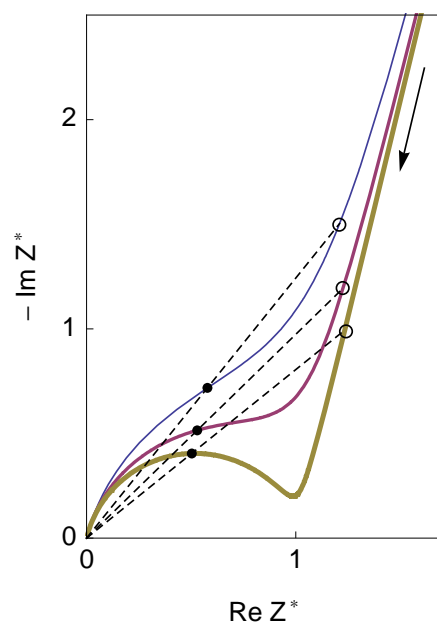


Handbook of Electrochemical Impedance Spectroscopy



ELECTRICAL CIRCUITS CONTAINING CPEs

ER@SE/LEPMI
J.-P. Diard, B. Le Gorrec, C. Montella

Hosted by Bio-Logic @ www.bio-logic.info



March 29, 2013

Contents

1	Circuits containing one CPE	5
1.1	Constant Phase Element (CPE), symbol Q	5
1.2	Circuit (R+Q)	5
1.2.1	Impedance	5
1.2.2	Reduced impedance	6
1.3	Circuit (R/Q)	7
1.3.1	Impedance	7
1.3.2	Reduced impedance	7
1.3.3	Pseudocapacitance #1	7
1.3.4	Pseudocapacitance #2	8
1.4	Circuit (R/Q)+(R/Q)+ .. (Voigt)	9
1.5	Circuit (R ₁ +(R ₂ /Q ₂))	9
1.5.1	Impedance	10
1.5.2	Reduced impedance	10
1.6	Circuit (R ₁ /(R ₂ +Q ₂))	10
1.6.1	Impedance	11
1.6.2	Reduced impedance	11
1.7	Transformation formulae between(R+(R/Q)) and (R/(R+Q))	11
1.7.1	$\alpha_{21} = \alpha_{22}$	11
1.7.2	$\alpha_{21} \neq \alpha_{22}$	11
2	Circuits made of two CPEs	13
2.1	Circuit (Q ₁ +Q ₂)	13
2.1.1	$\alpha_1 = \alpha_2 = \alpha$	13
2.1.2	$\alpha_1 \neq \alpha_2$	13
2.1.3	Reduced impedance	14
2.2	Circuit (Q ₁ /Q ₂)	16
2.2.1	$\alpha_1 = \alpha_2 = \alpha$	16
2.2.2	$\alpha_1 \neq \alpha_2$	16
2.2.3	Reduced impedance	16
3	Circuits made of one R and two CPEs	19
3.1	Circuit ((R ₁ /Q ₁) + Q ₂)	19
3.1.1	$\alpha_1 = \alpha_2 = \alpha$	19
3.1.2	$\alpha_1 \neq \alpha_2$	20
3.2	Circuit ((R ₁ + Q ₁)/Q ₂)	21
3.2.1	$\alpha_1 = \alpha_2 = \alpha$	21

3.2.2	$\alpha_1 \neq \alpha_2$	21
4	Circuits made of two Rs and two CPEs	23
4.1	Circuit $((R_1/Q_1)+(R_2/Q_2))$	23
4.2	Circuit $((R_1+(R_2/Q_2))/Q_1)$	24
4.3	Circuit $((Q_1+(R_2/Q_2))/R_1)$	25
4.4	Circuit $((Q_2+R_2)/R_1)/Q_1)$	26
A	Symbols for CPE	29

Chapter 1

Circuits containing one CPE

1.1 Constant Phase Element (CPE), symbol Q

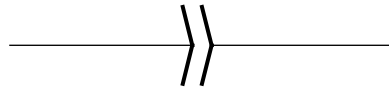


Figure 1.1: Most often used symbol for CPE (see also the Appendix A).

$$Z = \frac{1}{Q (i\omega)^\alpha}, \quad \text{Re } Z = \frac{c_\alpha}{Q \omega^\alpha}, \quad \text{Im } Z = -\frac{s_\alpha}{Q \omega^\alpha}$$

$$c_\alpha = \cos\left(\frac{\pi \alpha}{2}\right), \quad s_\alpha = \sin\left(\frac{\pi \alpha}{2}\right)$$

$$|Z| = \frac{1}{Q \omega^\alpha}, \quad \phi_Z = -\frac{\pi \alpha}{2}$$

The Q unit ($\text{F cm}^{-2} \text{s}^{\alpha-1}$) depends on α ⁽¹⁾.

1.2 Circuit (R+Q)

1.2.1 Impedance

$$Z(\omega) = R + \frac{1}{Q (i\omega)^\alpha}, \quad \text{Re } Z = R + \frac{c_\alpha}{Q \omega^\alpha}, \quad \text{Im } Z = -\frac{s_\alpha}{Q \omega^\alpha}$$

¹ Different equations for CPE: $Z = \frac{Q}{(i\omega)^{1-\alpha}}$ [5], $Z = \frac{1}{(Q i\omega)^\alpha}$ [26].

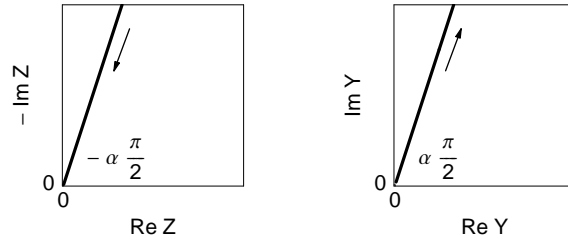


Figure 1.2: Nyquist diagram of the impedance and admittance for the CPE element, plotted for $\alpha = 0.8$. The arrows always indicate the increasing frequency direction.

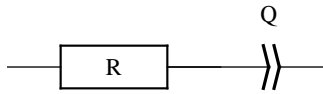


Figure 1.3: Circuit (R+Q).

1.2.2 Reduced impedance

$$Z^*(\omega) = \frac{Z(\omega)}{R} = 1 + \frac{1}{\tau (i\omega)^\alpha}, \quad \tau = RQ$$

The τ unit depends on α : $u_\tau = s^\alpha$.

$$Z^*(u) = 1 + \frac{1}{(iu)^\alpha}, \quad u = \omega \tau^{1/\alpha}$$

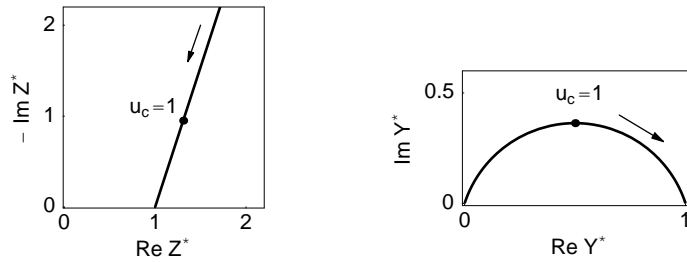


Figure 1.4: Nyquist diagram of the reduced impedance and admittance ($Y^* = RY$) for the (R+Q) circuit, plotted for $\alpha = 0.8$.

1.3 Circuit (R/Q)

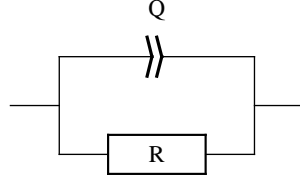


Figure 1.5: Circuit (R/Q).

1.3.1 Impedance

$$Z(\omega) = \frac{R}{1 + \tau (i\omega)^\alpha}; \quad \tau = RQ$$

$$\operatorname{Re} Z(\omega) = \frac{R(1 + \tau \omega^\alpha c_\alpha)}{1 + \tau^2 \omega^{2\alpha} + 2\tau \omega^\alpha c_\alpha}; \quad \operatorname{Im} Z(\omega) = -\frac{R\tau \omega^\alpha s_\alpha}{1 + \tau^2 \omega^{2\alpha} + 2\tau \omega^\alpha c_\alpha}$$

1.3.2 Reduced impedance

$$Z^*(\omega) = \frac{Z(\omega)}{R} = \frac{1}{1 + \tau (i\omega)^\alpha}; \quad \tau = RQ$$

$$\operatorname{Re} Z^*(\omega) = \frac{1 + \tau \omega^\alpha c_\alpha}{1 + \tau^2 \omega^{2\alpha} + 2\tau \omega^\alpha c_\alpha}; \quad \operatorname{Im} Z^*(\omega) = -\frac{\tau \omega^\alpha s_\alpha}{1 + \tau^2 \omega^{2\alpha} + 2\tau \omega^\alpha c_\alpha}$$

$$\frac{d\operatorname{Im} Z^*(\omega)}{d\omega} = \frac{\alpha \tau \omega^{-1+\alpha} (-1 + \tau^2 \omega^{2\alpha}) s_\alpha}{(1 + \tau^2 \omega^{2\alpha} + 2\tau \omega^\alpha c_\alpha)^2} = 0 \Rightarrow \omega_c^\alpha = 1/\tau \quad [6]$$

$$\operatorname{Re} Z^*(\omega_c) = 1/2, \quad \operatorname{Im} Z^*(\omega_c) = -\frac{s_\alpha}{2(1 + c_\alpha)}$$

$$\alpha = \frac{2}{\pi} \arccos \left(-1 + \frac{2}{1 + 4 \operatorname{Im} Z^*(\omega_c)^2} \right)$$

$$Z^*(u) = \frac{1}{1 + (iu)^\alpha}, \quad u = \omega \tau^{1/\alpha}$$

(Fig. 1.6)

1.3.3 Pseudocapacitance #1

The value of the pseudocapacitance C ($C/F \text{ cm}^{-2}$) for the (R/C) circuit giving the same characteristic frequency than that of the (R/Q) circuit (Fig. 1.7) is obtained from:

$$\omega_c = \frac{1}{(RQ)^{1/\alpha}} = \frac{1}{RC} \Rightarrow C = Q^{\frac{1}{\alpha}} R^{\frac{1}{\alpha}-1}$$

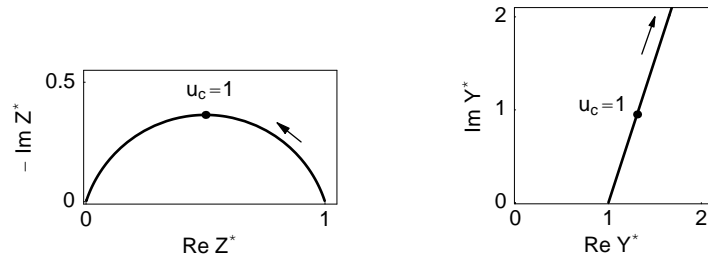


Figure 1.6: Nyquist diagram of the reduced impedance (depressed semi-circle [22]) and admittance ($Y^* = RY$) for the (R/Q) circuit, plotted for $\alpha = 0.8$.

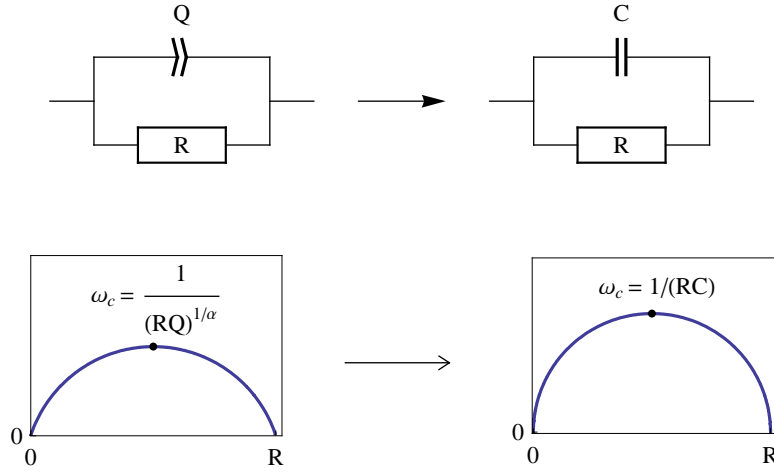


Figure 1.7: (R/Q) and (R/C) circuits with the same characteristic frequency at the apex (or summit) of impedance arc.

1.3.4 Pseudocapacitance #2

The value of the pseudocapacitance C ($C/F \text{ cm}^{-2}$) for the (R_C/C) circuit giving the same impedance for the characteristic frequency of the (R_Q/Q) circuit (Fig. 1.7) is obtained from [2, 9]:

$$C = Q^{1/\alpha} R_Q^{(1/\alpha)-1} \sin(\alpha \pi/2), \quad R_C = \frac{R_Q}{2 (\cos(\alpha \pi/4))^2}$$

with:

$$\tau_{(R_C/C)} = (R_Q Q)^{1/\alpha} \tan(\alpha \pi/4)$$

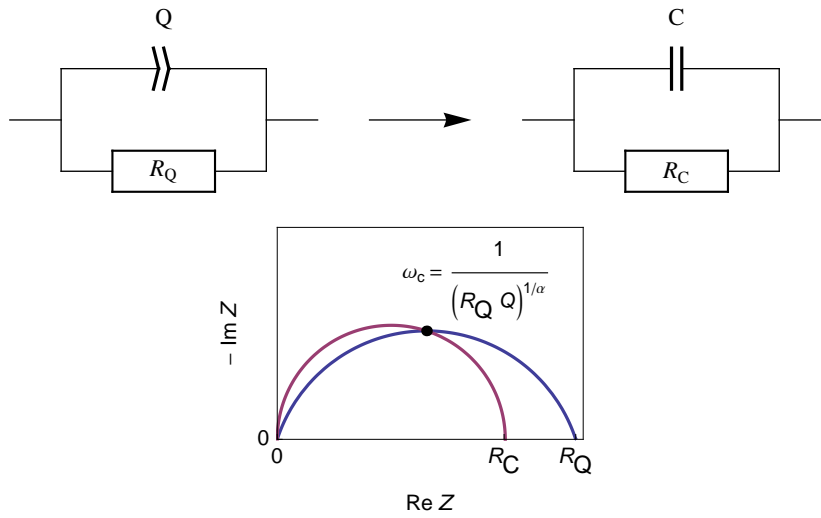


Figure 1.8: (R_Q/Q) and (R_C/C) circuits with the same impedance for the characteristic frequency of the (R_Q/Q) circuit.

1.4 Circuit $(R/Q)+(R/Q)+ \dots$ (Voigt)

$$Z(\omega) = \sum_{i=1}^{n_{RQ}} \frac{R_i}{1 + \tau_i (i\omega)^{\alpha_i}} ; \tau_i = R_i Q_i$$

$$\text{Re } Z(\omega) = \sum_{i=1}^{n_{RQ}} \frac{R_i (1 + \tau_i \omega^{\alpha_i} c_{\alpha i})}{1 + \tau_i^2 \omega^{2\alpha_i} + 2 \tau_i \omega^{\alpha_i} c_{\alpha i}}$$

$$\text{Im } Z(\omega) = - \sum_{i=1}^{n_{RQ}} \frac{R_i \tau_i \omega^{\alpha_i} s_{\alpha i}}{1 + \tau_i^2 \omega^{2\alpha_i} + 2 \tau_i \omega^{\alpha_i} c_{\alpha i}}$$

1.5 Circuit $(R_1+(R_2/Q_2))$

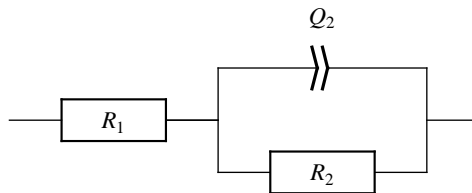


Figure 1.9: Circuit $(R_1+(R_2/Q_2))$.

1.5.1 Impedance

$$Z(\omega) = R_1 + \frac{1}{(i\omega)^{\alpha_2} Q_2 + \frac{1}{R_2}}$$

$$Z(\omega) = \frac{(R_1 + R_2) (1 + (i\omega)^{\alpha_2} \tau_2)}{1 + (i\omega)^{\alpha_2} \tau_1}, \quad \tau_1 = R_2 Q_2, \quad \tau_2 = \frac{R_1 R_2 Q_2}{R_1 + R_2}$$

1.5.2 Reduced impedance

$$Z^*(u) = \frac{Z(u)}{R_1 + R_2} = \frac{1 + T (i u)^{\alpha_2}}{1 + (i u)^{\alpha_2}} \tag{1.1}$$

$$u = \tau_1^{1/\alpha_2} \omega, \quad T = \tau_2/\tau_1 = R_1/(R_1 + R_2) < 1$$

$$\text{Re } Z^*(u) = \frac{T c_\alpha u^{\alpha_2} + c_\alpha u^{\alpha_2} + T u^{2\alpha_2} + 1}{2 c_\alpha u^{\alpha_2} + u^{2\alpha_2} + 1}$$

$$\text{Im } Z^*(u) = -\frac{(1 - T) u^{\alpha_2} s_\alpha}{2 c_\alpha u^{\alpha_2} + u^{2\alpha_2} + 1}$$

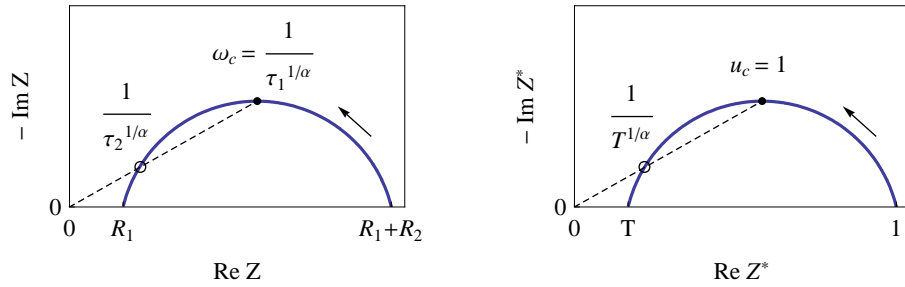


Figure 1.10: Nyquist diagrams of the impedance and reduced impedance for the $(R_1+(R_2/Q_2))$ circuit.

1.6 Circuit $(R_1/(R_2+Q_2))$

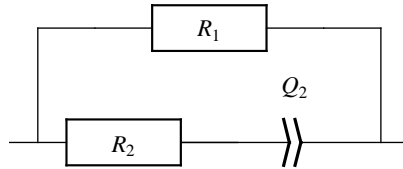


Figure 1.11: Circuit $(R_1/(R_2+Q_2))$.

1.6.1 Impedance

$$Z(\omega) = \frac{R_1 (1 + \tau_2 (i\omega)^{\alpha_2})}{1 + \tau_1 (i\omega)^{\alpha_2}}, \quad \tau_1 = (R_1 + R_2) Q_2, \quad \tau_2 = R_2 Q_2$$

$$\operatorname{Re} Z(\omega) = \frac{R_1 \left(\cos\left(\frac{\pi\alpha_2}{2}\right) (\tau_1 + \tau_2) \omega^{\alpha_2} + \tau_1 \tau_2 \omega^{2\alpha_2} + 1 \right)}{\tau_1 \left(\tau_1 \omega^{\alpha_2} + 2 \cos\left(\frac{\pi\alpha_2}{2}\right) \right) \omega^{\alpha_2} + 1}$$

$$\operatorname{Im} Z(\omega) = -\frac{\omega^{\alpha_2} \sin\left(\frac{\pi\alpha_2}{2}\right) R_1 (\tau_1 - \tau_2)}{\tau_1 \left(\tau_1 \omega^{\alpha_2} + 2 \cos\left(\frac{\pi\alpha_2}{2}\right) \right) \omega^{\alpha_2} + 1}$$

1.6.2 Reduced impedance

$$Z^*(u) = \frac{Z(u)}{R_1} = \frac{1 + T (iu)^{\alpha_2}}{1 + (iu)^{\alpha_2}}$$

$$u = \tau_1^{1/\alpha_2} \omega, \quad T = \tau_2/\tau_1 = R_2/(R_1 + R_2) < 1$$

cf. Eq. (1.1) and Fig. 1.10.

1.7 Transformation formulae between $(R+(R/Q))$ and $(R/(R+Q))$

1.7.1 $\alpha_{21} = \alpha_{22}$

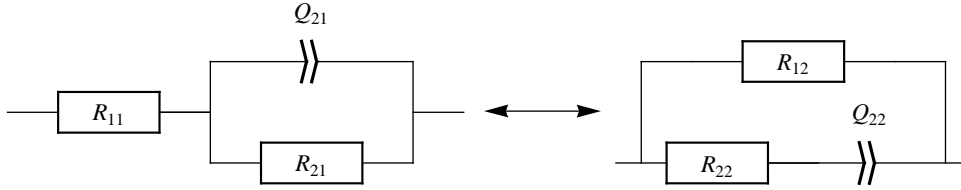


Figure 1.12: The $(R+(R/Q))$ and $(R/(R+Q))$ circuits are non-distinguishable for $\alpha_{21} = \alpha_{22}$ [1].

Transformations formulae $(R+(R/Q)) \rightarrow (R/(R+Q))$

$$R_{12} = R_{11} + R_{21}, \quad R_{22} = \frac{R_{11}^2}{R_{21}} + R_{11}, \quad Q_{22} = \frac{Q_{21} R_{21}^2}{(R_{11} + R_{21})^2}$$

Transformations formulae $(R/(R+Q)) \rightarrow (R+(R/Q))$

$$Q_{21} = \frac{Q_{22} (R_{12} + R_{22})^2}{R_{12}^2}, \quad R_{11} = \frac{R_{12} R_{22}}{R_{12} + R_{22}}, \quad R_{21} = \frac{R_{12}^2}{R_{12} + R_{22}}$$

1.7.2 $\alpha_{21} \neq \alpha_{22}$

The $(R+(R/Q))$ and $(R/(R+Q))$ circuits (Fig. 1.12) are distinguishable for $\alpha_{21} \neq \alpha_{22}$

Chapter 2

Circuits made of two CPEs

2.1 Circuit (Q_1+Q_2)

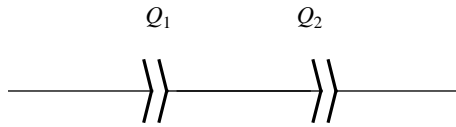


Figure 2.1: Circuit (Q_1+Q_2).

2.1.1 $\alpha_1 = \alpha_2 = \alpha$

$$Z(\omega) = \left(\frac{1}{Q_1} + \frac{1}{Q_2} \right) \frac{1}{(i\omega)^\alpha} = \frac{1}{Q} \frac{1}{(i\omega)^\alpha}, \quad Q = \frac{Q_1 Q_2}{Q_1 + Q_2}$$

cf. § 1.1.

2.1.2 $\alpha_1 \neq \alpha_2$

Impedance

$$Z(\omega) = \frac{1}{Q_1 (i\omega)^{\alpha_1}} + \frac{1}{Q_2 (i\omega)^{\alpha_2}} = \frac{Q_1 (i\omega)^{\alpha_1} + Q_2 (i\omega)^{\alpha_2}}{Q_1 Q_2 (i\omega)^{\alpha_1 + \alpha_2}}$$

$$\operatorname{Re} Z(\omega) = \frac{\cos\left(\frac{\pi\alpha_1}{2}\right) \omega^{-\alpha_1}}{Q_1} + \frac{\cos\left(\frac{\pi\alpha_2}{2}\right) \omega^{-\alpha_2}}{Q_2}$$

$$\operatorname{Im} Z(\omega) = -\frac{\sin\left(\frac{\pi\alpha_1}{2}\right) \omega^{-\alpha_1}}{Q_1} - \frac{\sin\left(\frac{\pi\alpha_2}{2}\right) \omega^{-\alpha_2}}{Q_2}$$

$$|Z_{Q_1}| = |Z_{Q_2}| \Rightarrow \omega = \omega_c = \left(\frac{Q_2}{Q_1} \right)^{\frac{1}{\alpha_1 - \alpha_2}}$$

- $\alpha_1 < \alpha_2$ (Figs. 2.2 and 2.3)

$$\omega \rightarrow 0 \Rightarrow Z(\omega) \approx \frac{1}{Q_2 (i\omega)^{\alpha_2}}, \quad \omega \rightarrow \infty \Rightarrow Z(\omega) \approx \frac{1}{Q_1 (i\omega)^{\alpha_1}}$$

- $\alpha_1 > \alpha_2$

$$\omega \rightarrow 0 \Rightarrow Z(\omega) \approx \frac{1}{Q_1 (i\omega)^{\alpha_1}}, \quad \omega \rightarrow \infty \Rightarrow Z(\omega) \approx \frac{1}{Q_2 (i\omega)^{\alpha_2}}$$

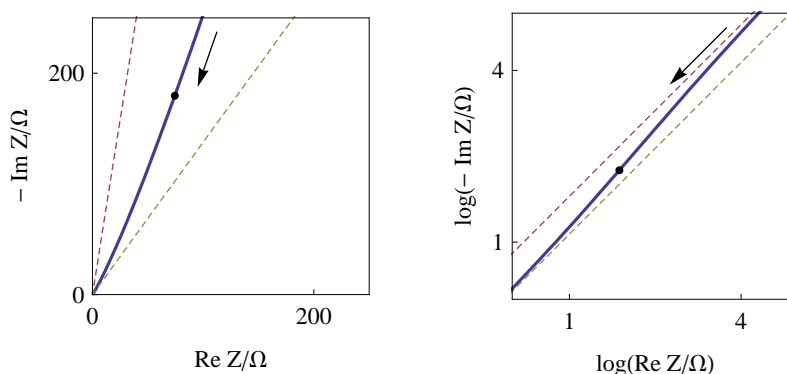


Figure 2.2: Nyquist and log Nyquist [8] diagrams of the impedance for the (Q_1+Q_2) circuit, plotted for $Q_1 = 10^{-2} \text{ F cm}^{-2} \text{ s}^{\alpha_1-1}$, $Q_2 = 10^{-2} \text{ F cm}^{-2} \text{ s}^{\alpha_2-1}$, $\alpha_1 = 0.6$, $\alpha_2 = 0.9$ ($\alpha_1 < \alpha_2$). Dots: $\omega_c = (Q_2/Q_1)^{1/(\alpha_1-\alpha_2)}$.

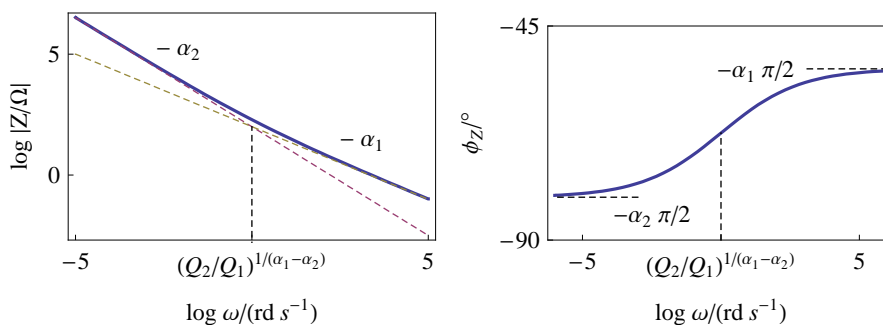


Figure 2.3: Bode diagrams of the impedance for the (Q_1+Q_2) circuit. Same values of parameters as in Fig. 2.2. $\alpha_1 < \alpha_2$.

2.1.3 Reduced impedance

$$Z^*(u) = Q_1 \omega_c^{\alpha_1} Z(\omega) = \frac{1}{(iu)^{\alpha_1}} + \frac{1}{(iu)^{\alpha_2}}, \quad u = \frac{\omega}{\omega_c}$$

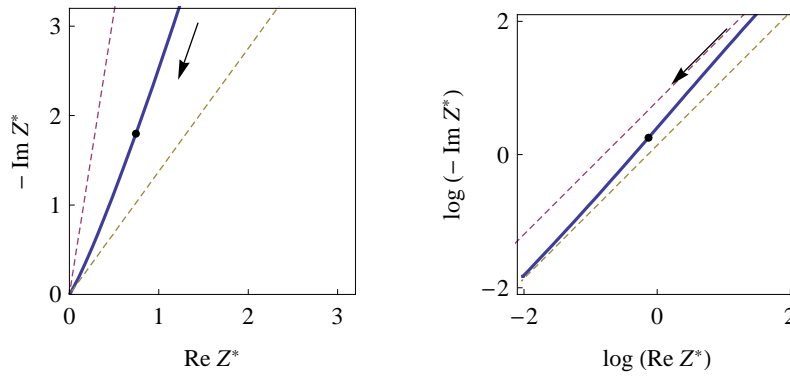


Figure 2.4: Nyquist and log Nyquist [8] diagrams of the reduced impedance for the (Q_1+Q_2) circuit, plotted for $\alpha_1 = 0.6, \alpha_2 = 0.9$ ($\alpha_1 < \alpha_2$). Dots: $u_c = 1$.

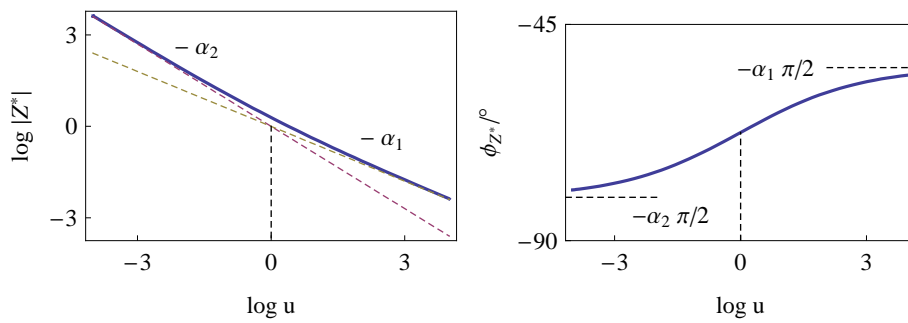
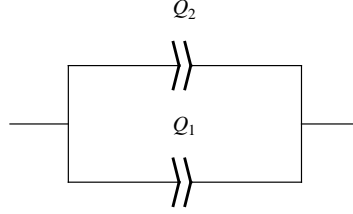


Figure 2.5: Bode diagrams of the impedance for the (Q_1+Q_2) circuit. Same values of parameters as in Fig. 2.4. $\alpha_1 < \alpha_2$.

2.2 Circuit (Q_1/Q_2)

Figure 2.6: Circuit (Q_1/Q_2).

2.2.1 $\alpha_1 = \alpha_2 = \alpha$

$$Z(\omega) = \frac{1}{(Q_1 + Q_2)(i\omega)^\alpha} = \frac{1}{Q(i\omega)^\alpha}, \quad Q = Q_1 + Q_2$$

cf. § 1.1.

2.2.2 $\alpha_1 \neq \alpha_2$

Impedance

$$Z(\omega) = \frac{1}{Q_1(i\omega)^{\alpha_1} + Q_2(i\omega)^{\alpha_2}}$$

$$\operatorname{Re} Z(\omega) = \frac{\cos\left(\frac{\pi\alpha_1}{2}\right) Q_1\omega^{\alpha_1} + \cos\left(\frac{\pi\alpha_2}{2}\right) Q_2\omega^{\alpha_2}}{Q_1^2\omega^{2\alpha_1} + Q_2^2\omega^{2\alpha_2} + 2\cos\left(\frac{1}{2}\pi(\alpha_1 - \alpha_2)\right) Q_1Q_2\omega^{\alpha_1 + \alpha_2}}$$

$$\operatorname{Im} Z(\omega) = -\frac{\sin\left(\frac{\pi\alpha_1}{2}\right) Q_1\omega^{\alpha_1} + \sin\left(\frac{\pi\alpha_2}{2}\right) Q_2\omega^{\alpha_2}}{Q_1^2\omega^{2\alpha_1} + Q_2^2\omega^{2\alpha_2} + 2\cos\left(\frac{1}{2}\pi(\alpha_1 - \alpha_2)\right) Q_1Q_2\omega^{\alpha_1 + \alpha_2}}$$

- $\alpha_1 < \alpha_2$ (Figs. 2.7 and 2.8)

$$\omega \rightarrow 0 \Rightarrow Z(\omega) \approx \frac{1}{Q_1(i\omega)^{\alpha_1}}, \quad \omega \rightarrow \infty \Rightarrow Z(\omega) \approx \frac{1}{Q_2(i\omega)^{\alpha_2}}$$

- $\alpha_1 > \alpha_2$

$$\omega \rightarrow 0 \Rightarrow Z(\omega) \approx \frac{1}{Q_2(i\omega)^{\alpha_2}}, \quad \omega \rightarrow \infty \Rightarrow Z(\omega) \approx \frac{1}{Q_1(i\omega)^{\alpha_1}}$$

2.2.3 Reduced impedance

$$Z^*(u) = Q_1\omega_c^{\alpha_1} Z(\omega) = \frac{1}{(iu)^{\alpha_1} + (iu)^{\alpha_2}}, \quad u = \frac{\omega}{\omega_c}$$

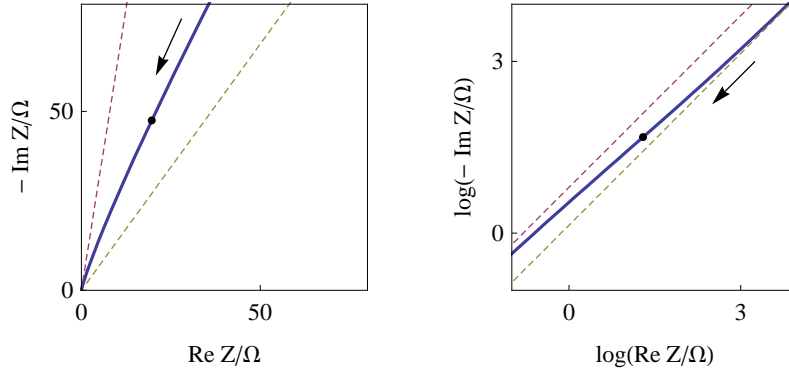


Figure 2.7: Nyquist and log Nyquist [8] diagrams of the impedance for the (Q_1/Q_2) circuit plotted for $Q_1 = 10^{-2} \text{ F cm}^{-2} \text{ s}^{\alpha_1-1}$, $Q_2 = 10^{-2} \text{ F cm}^{-2} \text{ s}^{\alpha_2-1}$, $\alpha_1 = 0.6$, $\alpha_2 = 0.9$ ($\alpha_1 < \alpha_2$). Dots: $\omega_c = (Q_2/Q_1)^{1/(\alpha_1-\alpha_2)}$.

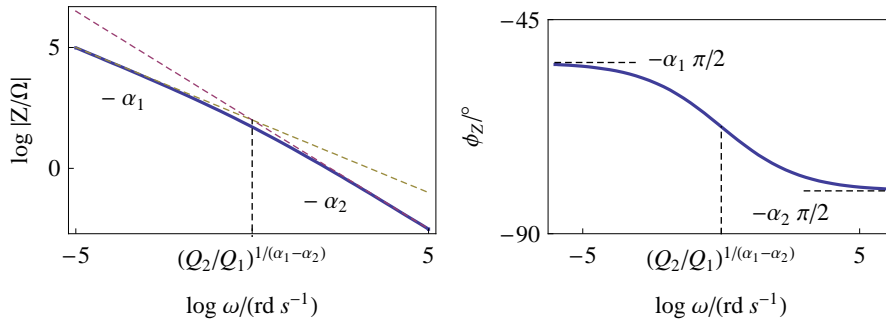


Figure 2.8: Bode diagrams of the impedance for the (Q_1/Q_2) circuit. Same values of parameters as in Fig. 2.7. $\alpha_1 < \alpha_2$.

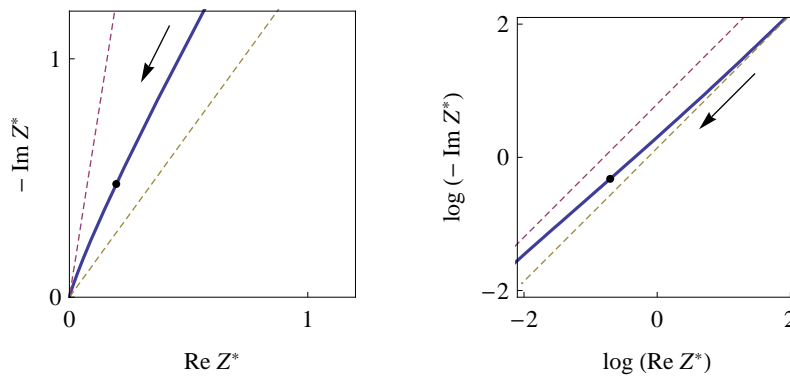


Figure 2.9: Nyquist and log Nyquist [8] diagrams of the reduced impedance for the (Q_1/Q_2) circuit, plotted for $\alpha_1 = 0.6$, $\alpha_2 = 0.9$ ($\alpha_1 < \alpha_2$). Dots: $u_c = 1$.

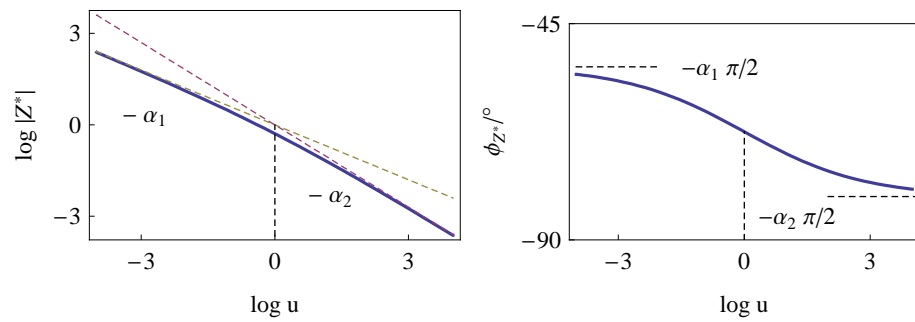


Figure 2.10: Bode diagrams of the impedance for the (Q_1/Q_2) circuit. Same values of parameters as in Fig. 2.9. $\alpha_1 < \alpha_2$.

Chapter 3

Circuits made of one R and two CPEs

3.1 Circuit $((R_1/Q_1) + Q_2)$

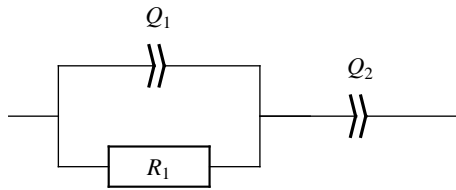


Figure 3.1: Circuit $((R_1/Q_1)+Q_2)$.

3.1.1 $\alpha_1 = \alpha_2 = \alpha$

Impedance

$$Z(\omega) = \frac{1}{\frac{1}{R_1} + Q_1 (i\omega)^\alpha} + \frac{1}{Q_2 (i\omega)^\alpha}$$

$$Z(\omega) = \frac{1 + (i\omega)^\alpha \tau_2}{(i\omega)^\alpha Q_2 (1 + (i\omega)^\alpha \tau_1)}, \quad \tau_1 = R_1 Q_1, \quad \tau_2 = (Q_1 + Q_2) R_1, \quad \tau_1 < \tau_2$$

$$\operatorname{Re} Z(\omega) = -\frac{\cos\left(\frac{\pi\alpha}{2}\right) (\tau_1 \tau_2 \omega^{2\alpha} + 1) \omega^{-\alpha} + \cos(\pi\alpha) \tau_1 + \tau_2}{Q_2 (\tau_1 (\tau_1 \omega^\alpha + 2 \cos\left(\frac{\pi\alpha}{2}\right)) \omega^\alpha + 1)}$$

$$\operatorname{Im} Z(\omega) = -\frac{\sin\left(\frac{\pi\alpha}{2}\right) (\tau_1 \tau_2 \omega^{2\alpha} + 1) \omega^{-\alpha} + \sin(\pi\alpha) \tau_1}{Q_2 (\tau_1 (\tau_1 \omega^\alpha + 2 \cos\left(\frac{\pi\alpha}{2}\right)) \omega^\alpha + 1)}$$

Reduced impedance

$$Z^*(u) = \frac{Z(u)}{R_1} = \frac{1}{T-1} \frac{1 + T(iu)^\alpha}{(iu)^\alpha (1 + (iu)^\alpha)} \quad (3.1)$$

$$u = \omega \tau^{1/\alpha}, \quad T = \tau_2/\tau_1 = 1 + Q_2/Q_1 > 1$$

$$\operatorname{Re} Z^*(u) = \frac{u^{-\alpha} \left((T + \cos(\alpha\pi))u^\alpha + (Tu^{2\alpha} + 1) \cos\left(\frac{\alpha\pi}{2}\right) \right)}{(T-1) \left(2 \cos\left(\frac{\alpha\pi}{2}\right) u^\alpha + u^{2\alpha} + 1 \right)}$$

$$\operatorname{Im} Z^*(u) = u^{-\alpha} \left(\frac{1}{1-T} - \frac{u^{2\alpha}}{2 \cos\left(\frac{\alpha\pi}{2}\right) u^\alpha + u^{2\alpha} + 1} \right) \sin\left(\frac{\alpha\pi}{2}\right)$$

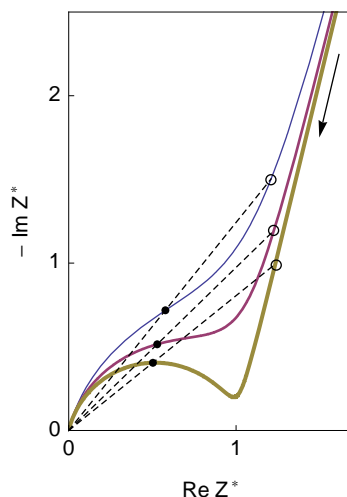


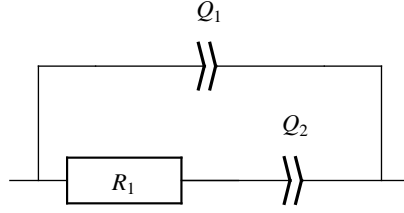
Figure 3.2: Nyquist diagram of the reduced impedance for the $((R_1/Q_1)+Q_2)$ circuit (Fig. 3.1, Eq. (3.1)), plotted for $T = 4, 9, 90$ and $\alpha = 0.85$. The line thickness increases with increasing T . Dots: reduced characteristic angular frequency $u_{c1} = 1$; circles: reduced characteristic angular frequency $u_{c2} = 1/T^{1/\alpha}$ ($\phi_{u_{c1}} = \phi_{u_{c2}}$).

3.1.2 $\alpha_1 \neq \alpha_2$ **Impedance**

$$Z(\omega) = \frac{1}{\frac{1}{R_1} + Q_1 (i\omega)^{\alpha_1}} + \frac{1}{Q_2 (i\omega)^{\alpha_2}}$$

$$\operatorname{Re} Z(\omega) = \frac{\cos\left(\frac{\pi\alpha_2}{2}\right) \omega^{-\alpha_2}}{Q_2} + \frac{R_1 \left(\cos\left(\frac{\pi\alpha_1}{2}\right) Q_1 R_1 \omega^{\alpha_1} + 1 \right)}{Q_1 R_1 \left(Q_1 R_1 \omega^{\alpha_1} + 2 \cos\left(\frac{\pi\alpha_1}{2}\right) \right) \omega^{\alpha_1} + 1}$$

$$\operatorname{Im} Z(\omega) = -\frac{\sin\left(\frac{\pi\alpha_1}{2}\right) Q_1 R_1^2 \omega^{\alpha_1}}{Q_1 R_1 \left(Q_1 R_1 \omega^{\alpha_1} + 2 \cos\left(\frac{\pi\alpha_1}{2}\right) \right) \omega^{\alpha_1} + 1} - \frac{\sin\left(\frac{\pi\alpha_2}{2}\right) \omega^{-\alpha_2}}{Q_2}$$

Figure 3.3: Circuit $((R_1+Q_2)/Q_1)$.

3.2 Circuit $((R_1 + Q_1)/Q_2)$

3.2.1 $\alpha_1 = \alpha_2 = \alpha$

Impedance

$$Z(\omega) = \frac{1}{(i\omega)^\alpha Q_1 + \frac{1}{R_1 + \frac{1}{(i\omega)^\alpha Q_2}}} = \frac{1 + Q_2 R_1 (i\omega)^\alpha}{(i\omega)^\alpha (Q_1 + Q_2) \left(1 + \frac{(i\omega)^\alpha Q_1 Q_2 R_1}{Q_1 + Q_2}\right)}$$

$$Z(\omega) = \frac{1 + \tau_2 (i\omega)^\alpha}{(i\omega)^\alpha (Q_1 + Q_2) (1 + (i\omega)^\alpha \tau_1)}, \quad \tau_1 = \frac{Q_1 Q_2 R_1}{Q_1 + Q_2}, \quad \tau_2 = Q_2 R_1$$

$$\operatorname{Re} Z(\omega) = \frac{\omega^{-\alpha} (\cos(\pi\alpha)\omega^\alpha + \tau_2\omega^\alpha + \cos(\frac{\pi\alpha}{2}) (\tau_2\omega^{2\alpha} + 1))}{(2 \cos(\frac{\pi\alpha}{2}) \omega^\alpha + \omega^{2\alpha} + 1) (Q_1 + Q_2) \tau_1}$$

$$\operatorname{Im} Z(\omega) = -\frac{\omega^{-\alpha} \sin(\frac{\pi\alpha}{2}) (2 \cos(\frac{\pi\alpha}{2}) \omega^\alpha + \tau_2\omega^{2\alpha} + 1)}{(2 \cos(\frac{\pi\alpha}{2}) \omega^\alpha + \omega^{2\alpha} + 1) (Q_1 + Q_2) \tau_1}$$

Reduced impedance

$$Z^*(u) = \frac{Z(u)}{R_1} = \frac{T-1}{T^2} \frac{1 + T (iu)^\alpha}{(iu)^\alpha (1 + (iu)^\alpha)} \quad (3.2)$$

$$u = \omega \tau^{1/\alpha}, \quad T = \tau_2/\tau_1 = 1 + Q_2/Q_1 > 1$$

$$\operatorname{Re} Z^*(u) = \frac{(T-1)u^{-\alpha} ((T + \cos(\alpha\pi))u^\alpha + (Tu^{2\alpha} + 1) \cos(\frac{\alpha\pi}{2}))}{T^2 (2 \cos(\frac{\alpha\pi}{2}) u^\alpha + u^{2\alpha} + 1)}$$

$$\operatorname{Im} Z^*(u) = -\frac{(T-1)u^{-\alpha} (2 \cos(\frac{\alpha\pi}{2}) u^\alpha + Tu^{2\alpha} + 1) \sin(\frac{\alpha\pi}{2})}{T^2 (2 \cos(\frac{\alpha\pi}{2}) u^\alpha + u^{2\alpha} + 1)}$$

3.2.2 $\alpha_1 \neq \alpha_2$

$$Z(\omega) = \frac{\frac{1}{(i\omega)^{\alpha_2} Q_2} + R_1}{(i\omega)^{\alpha_1} Q_1 \left(\frac{1}{(i\omega)^{\alpha_1} Q_1} + \frac{1}{(i\omega)^{\alpha_2} Q_2} + R_1\right)}$$

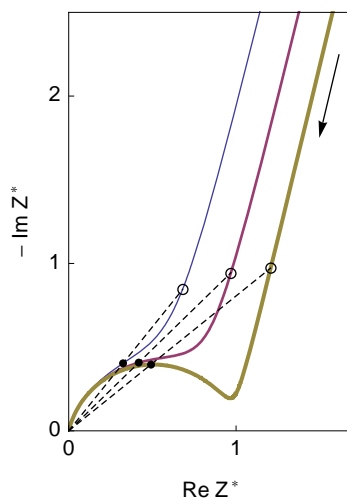


Figure 3.4: Nyquist diagram of the reduced impedance for the $((R_1+Q_1)/Q_2)$ circuit (Fig. 3.3, Eq. (3.2)), plotted for $T = 4, 9, 90$ and $\alpha = 0.85$. The line thickness increases with increasing T . Dots: reduced characteristic angular frequency $u_{c1} = 1$; circles: reduced characteristic angular frequency $u_{c2} = 1/T^{1/\alpha}$ ($\phi_{u_{c1}} = \phi_{u_{c2}}$).

$$Z(\omega) = \frac{1 + \tau (i\omega)^{\alpha_2}}{(i\omega)^{\alpha_1} Q_1 + (i\omega)^{\alpha_2} Q_2 + \tau (i\omega)^{\alpha_1 + \alpha_2} Q_1}, \quad \tau = R_1 Q_2$$

$$\begin{aligned} \text{Re } Z(\omega) = & \\ & \frac{(\omega^{\alpha_1} c_{\alpha_1} (1 + \tau^2 \omega^{2\alpha_2} + 2\tau \omega^{\alpha_2} c_{\alpha_2}) Q_1 + \omega^{\alpha_2} (\tau \omega^{\alpha_2} + c_{\alpha_2}) Q_2)}{(\omega^{2\alpha_1} (1 + \tau^2 \omega^{2\alpha_2} + 2\tau \omega^{\alpha_2} c_{\alpha_2}) Q_1^2 + 2\omega^{\alpha_1 + \alpha_2} (\tau \omega^{\alpha_2} c_{\alpha_1} + c_{\alpha_1 m \alpha_2}) Q_1 Q_2 + \omega^{2\alpha_2} Q_2^2)} \end{aligned}$$

$$c_{\alpha_1 m \alpha_2} = \cos\left(\frac{\pi (\alpha_1 - \alpha_2)}{2}\right)$$

$$\begin{aligned} \text{Im } Z(\omega) = & \\ & \frac{(-\omega^{\alpha_1} (1 + \tau^2 \omega^{2\alpha_2} + 2\tau \omega^{\alpha_2} c_{\alpha_2}) Q_1 s_{\alpha_1} - \omega^{\alpha_2} Q_2 s_{\alpha_2})}{(\omega^{2\alpha_1} (1 + \tau^2 \omega^{2\alpha_2} + 2\tau \omega^{\alpha_2} c_{\alpha_2}) Q_1^2 + 2\omega^{\alpha_1 + \alpha_2} (\tau \omega^{\alpha_2} c_{\alpha_1} + c_{\alpha_1 m \alpha_2}) Q_1 Q_2 + \omega^{2\alpha_2} Q_2^2)} \end{aligned}$$

Chapter 4

Circuits made of two Rs and two CPEs

4.1 Circuit $((R_1/Q_1)+(R_2/Q_2))$

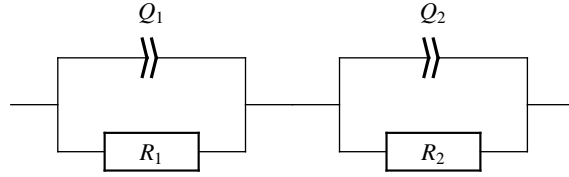


Figure 4.1: Circuit $((R_1/Q_1)+(R_2/Q_2))$.

$$Z(\omega) = \frac{1}{(i\omega)^{\alpha_1} Q_1 + \frac{1}{R_1}} + \frac{1}{(i\omega)^{\alpha_2} Q_2 + \frac{1}{R_2}}$$

$$Z(\omega) = \frac{R_1}{1 + (i\omega)^{\alpha_1} \tau_1} + \frac{R_2}{1 + (i\omega)^{\alpha_2} \tau_2}, \quad \tau_1 = R_1 Q_1, \quad \tau_2 = R_2 Q_2$$

$$Z(\omega) = \frac{R_1 + R_2 + (i\omega)^{\alpha_1} R_2 \tau_1 + (i\omega)^{\alpha_2} R_1 \tau_2}{(1 + (i\omega)^{\alpha_1} \tau_1) (1 + (i\omega)^{\alpha_2} \tau_2)}$$

$$\text{Re } Z(\omega) = \frac{R_1 (1 + \omega^{\alpha_1} c_{\alpha_1} \tau_1)}{1 + \omega^{\alpha_1} \tau_1 (2 c_{\alpha_1} + \omega^{\alpha_1} \tau_1)} + \frac{R_2 (1 + \omega^{\alpha_2} c_{\alpha_2} \tau_2)}{1 + \omega^{\alpha_2} \tau_2 (2 c_{\alpha_2} + \omega^{\alpha_2} \tau_2)}$$

$$\text{Im } Z(\omega) = -\frac{\omega^{\alpha_1} R_1 s_{\alpha_1} \tau_1}{1 + \omega^{\alpha_1} \tau_1 (2 c_{\alpha_1} + \omega^{\alpha_1} \tau_1)} - \frac{\omega^{\alpha_2} R_2 s_{\alpha_2} \tau_2}{1 + \omega^{\alpha_2} \tau_2 (2 c_{\alpha_2} + \omega^{\alpha_2} \tau_2)}$$

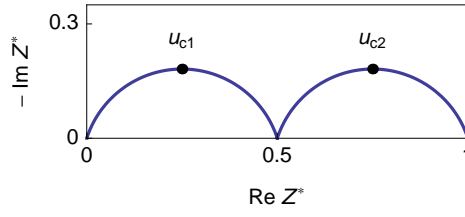


Figure 4.2: Nyquist diagrams of the reduced impedance for the $((R_1/Q_1)+(R_2/Q_2))$ circuit (Fig. 4.1). $R_1 = R_2$, $\alpha_1 = \alpha_2$, $Q_2 \gg Q_1$.

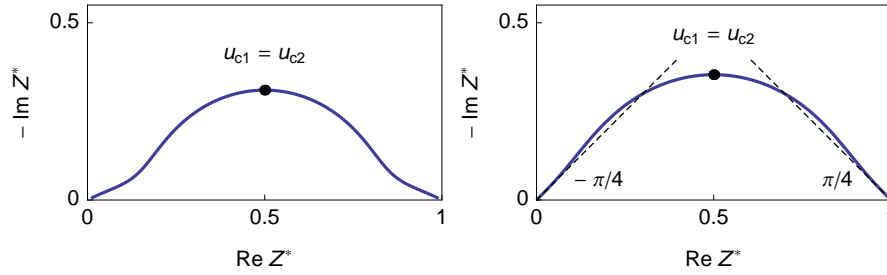


Figure 4.3: Unusual Nyquist diagrams of the reduced impedance for the $((R_1/Q_1)+(R_2/Q_2))$ circuit (Fig. 4.1). $R_1 = R_2$, $Q_2 = Q_1$, $\alpha_1 = 1$. Left: $\alpha_2 = 0.3$, right: $\alpha_2 = 0.5$.

4.2 Circuit $((R_1+(R_2/Q_2))/Q_1)$

$$Z(\omega) = \frac{1}{(i\omega)^{\alpha_1} Q_1 + \frac{1}{R_1 + \frac{1}{(i\omega)^{\alpha_2} Q_2 + \frac{1}{R_2}}}}$$

$$Z(\omega) = \frac{R_1 + R_2 + (i\omega)^{\alpha_2} Q_2 R_1 R_2}{1 + (i\omega)^{\alpha_1} Q_1 (R_1 + R_2) + (i\omega)^{\alpha_2} Q_2 R_2 + (i\omega)^{\alpha_1 + \alpha_2} Q_1 Q_2 R_1 R_2}$$

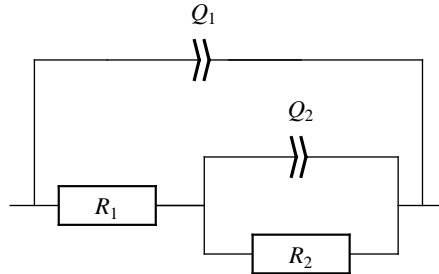


Figure 4.4: Circuit $((R_1+(R_2/Q_2))/Q_1)$.

$$\begin{aligned} \operatorname{Re} Z(\omega) = & (R_1 + R_2 + \omega^{2\alpha_2} Q_2^2 R_1 (1 + \omega^{\alpha_1} C_{\alpha_1} Q_1 R_1) R_2^2 + \\ & \omega^{\alpha_1} C_{\alpha_1} Q_1 (R_1 + R_2)^2 + \omega^{\alpha_2} C_{\alpha_2} Q_2 R_2 (R_2 + 2 R_1 (1 + \omega^{\alpha_1} C_{\alpha_1} Q_1 (R_1 + R_2)))) / \\ & (1 + \omega^{2\alpha_2} Q_2^2 (1 + \omega^{\alpha_1} Q_1 R_1 (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 R_1)) R_2^2 + \\ & \omega^{\alpha_1} Q_1 (R_1 + R_2) (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 (R_1 + R_2)) + 2 \omega^{\alpha_2} Q_2 R_2 \\ & \times (C_{\alpha_2} + \omega^{\alpha_1} Q_1 (C_{\alpha_1 m \alpha_2} R_2 + C_{\alpha_2} R_1 (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 (R_1 + R_2)))))) \end{aligned}$$

$$c_{\alpha_1 m \alpha_2} = \cos\left(\frac{\pi (\alpha_1 - \alpha_2)}{2}\right)$$

$$\begin{aligned} \operatorname{Im} Z(\omega) = & (\omega^{\alpha_1} Q_1 (-\omega^{2\alpha_2} Q_2^2 R_1^2 R_2^2 - 2 \omega^{\alpha_2} C_{\alpha_2} Q_2 R_1 R_2 (R_1 + R_2) - \\ & (R_1 + R_2)^2) S_{\alpha_1} - \omega^{\alpha_2} Q_2 R_2^2 S_{\alpha_2}) / \\ & (1 + \omega^{2\alpha_2} Q_2^2 (1 + \omega^{\alpha_1} Q_1 R_1 (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 R_1)) R_2^2 + \\ & \omega^{\alpha_1} Q_1 (R_1 + R_2) (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 (R_1 + R_2)) + 2 \omega^{\alpha_2} Q_2 R_2 \\ & \times (C_{\alpha_2} + \omega^{\alpha_1} Q_1 (C_{\alpha_1 m \alpha_2} R_2 + C_{\alpha_2} R_1 (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 (R_1 + R_2)))))) \end{aligned}$$

4.3 Circuit $((Q_1+(R_2/Q_2))/R_1)$

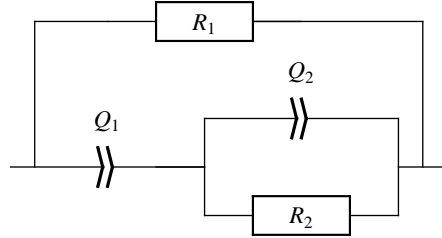


Figure 4.5: Circuit $((Q_1+(R_2/Q_2))/R_1)$.

$$Z(\omega) = \frac{1}{\frac{1}{R_1} + \frac{1}{\frac{1}{(i\omega)^{\alpha_1} Q_1} + \frac{1}{(i\omega)^{\alpha_2} Q_2 + \frac{1}{R_2}}}}$$

$$Z(\omega) = \frac{R_1 (1 + (i\omega)^{\alpha_1} Q_1 R_2 + (i\omega)^{\alpha_2} Q_2 R_2)}{1 + (i\omega)^{\alpha_1} Q_1 (R_1 + R_2) + (i\omega)^{\alpha_2} Q_2 R_2 + (i\omega)^{\alpha_1 + \alpha_2} Q_1 Q_2 R_1 R_2}$$

$$\begin{aligned} \operatorname{Re} Z(\omega) = & (R_1 (1 + \omega^{\alpha_2} Q_2 R_2 (2 C_{\alpha_2} + \omega^{\alpha_2} Q_2 R_2) + \omega^{2\alpha_1} Q_1^2 R_2 \\ & \times (R_2 + R_1 (1 + \omega^{\alpha_2} C_{\alpha_2} Q_2 R_2)) + \omega^{\alpha_1} Q_1 (2 R_2 (C_{\alpha_1} + \omega^{\alpha_2} C_{\alpha_1 m \alpha_2} Q_2 R_2) + \\ & C_{\alpha_1} R_1 (1 + \omega^{\alpha_2} Q_2 R_2 (2 C_{\alpha_2} + \omega^{\alpha_2} Q_2 R_2)))) / \\ & (1 + \omega^{2\alpha_2} Q_2^2 (1 + \omega^{\alpha_1} Q_1 R_1 (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 R_1)) R_2^2 + \\ & \omega^{\alpha_1} Q_1 (R_1 + R_2) (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 (R_1 + R_2)) + \\ & 2 \omega^{\alpha_2} Q_2 R_2 (C_{\alpha_2} + \omega^{\alpha_1} Q_1 (C_{\alpha_1 m \alpha_2} R_2 + C_{\alpha_2} R_1 (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 (R_1 + R_2)))))) \end{aligned}$$

$$\begin{aligned} \operatorname{Im} Z(\omega) = & -\omega^{\alpha_1} Q_1 R_2^2 (S_{\alpha_1} + \omega^{\alpha_2} Q_2 R_2 ((2 C_{\alpha_2} + \omega^{\alpha_2} Q_2 R_2) S_{\alpha_1} + \omega^{\alpha_1} Q_1 R_2 S_{\alpha_2})) / \\ & (1 + \omega^{2\alpha_2} Q_2^2 (1 + \omega^{\alpha_1} Q_1 R_1 (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 R_1)) R_2^2 + \\ & \omega^{\alpha_1} Q_1 (R_1 + R_2) (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 (R_1 + R_2)) + \\ & 2 \omega^{\alpha_2} Q_2 R_2 (C_{\alpha_2} + \omega^{\alpha_1} Q_1 (C_{\alpha_1 m \alpha_2} R_2 + C_{\alpha_2} R_1 (2 C_{\alpha_1} + \omega^{\alpha_1} Q_1 (R_1 + R_2)))))) \end{aligned}$$

$$Z(\omega) = \frac{R_1 (1 + \tau_1 (i\omega)^{\alpha_1} + \tau_2 (i\omega)^{\alpha_2})}{1 + (1 + R_1/R_2) \tau_1 (i\omega)^{\alpha_1} + \tau_2 (i\omega)^{\alpha_2} + \tau_1 \tau_2 (R_1/R_2) (i\omega)^{\alpha_1 + \alpha_2}}$$

$$\tau_1 = Q_1 R_2, \quad \tau_2 = Q_2 R_2$$

4.4 Circuit $((Q_2 + R_2)/R_1)/Q_1$

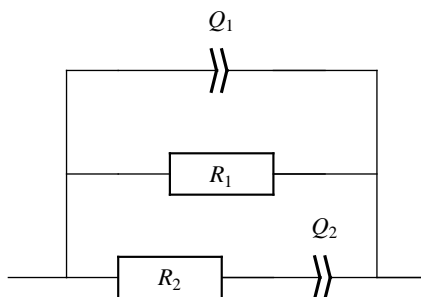


Figure 4.6: Circuit $((Q_2 + R_2)/R_1)/Q_1$.

$$Z(\omega) = \frac{1}{(i\omega)^{\alpha_1} Q_1 + \frac{1}{R_1} + \frac{1}{\frac{1}{(i\omega)^{\alpha_2} Q_2} + R_2}}$$

$$Z(\omega) = \frac{R_1 (1 + (i\omega)^{\alpha_2} Q_2 R_2)}{1 + (i\omega)^{\alpha_1} Q_1 R_1 + (i\omega)^{\alpha_2} Q_2 R_1 + (i\omega)^{\alpha_2} Q_2 R_2 + (i\omega)^{\alpha_1 + \alpha_2} Q_1 Q_2 R_1 R_2}$$

$$\begin{aligned} \operatorname{Re} Z(\omega) = & (R_1 (1 + \omega^{\alpha_2} Q_2 (\omega^{\alpha_2} Q_2 R_2 (R_1 + R_2) + C_{\alpha_2} (R_1 + 2 R_2)) + \\ & \omega^{\alpha_1} C_{\alpha_1} Q_1 R_1 (1 + \omega^{\alpha_2} Q_2 R_2 (2 C_{\alpha_2} + \omega^{\alpha_2} Q_2 R_2))) / \\ & (1 + \omega^{\alpha_2} Q_2 (R_1 + R_2) (2 C_{\alpha_2} + \omega^{\alpha_2} Q_2 (R_1 + R_2)) + \\ & \omega^{2\alpha_1} Q_1^2 R_1^2 (1 + \omega^{\alpha_2} Q_2 R_2 (2 C_{\alpha_2} + \omega^{\alpha_2} Q_2 R_2)) + 2\omega^{\alpha_1} Q_1 R_1 \\ & \times (C_{\alpha_1} + \omega^{\alpha_2} Q_2 (C_{\alpha_1 m \alpha_2} R_1 + 2 C_{\alpha_1} C_{\alpha_2} R_2 + \omega^{\alpha_2} C_{\alpha_1} Q_2 R_2 (R_1 + R_2)))) \end{aligned}$$

$$\begin{aligned} \operatorname{Im} Z(\omega) = & (R_1^2 (-\omega^{\alpha_1} Q_1 (1 + \omega^{\alpha_2} Q_2 R_2 (2 C_{\alpha_2} + \omega^{\alpha_2} Q_2 R_2)) S_{\alpha_1}) - \omega^{\alpha_2} Q_2 S_{\alpha_2}) / \\ & (1 + \omega^{\alpha_2} Q_2 (R_1 + R_2) (2 C_{\alpha_2} + \omega^{\alpha_2} Q_2 (R_1 + R_2)) + \\ & \omega^{2\alpha_1} Q_1^2 R_1^2 (1 + \omega^{\alpha_2} Q_2 R_2 (2 C_{\alpha_2} + \omega^{\alpha_2} Q_2 R_2)) + 2\omega^{\alpha_1} Q_1 R_1 \\ & \times (C_{\alpha_1} + \omega^{\alpha_2} Q_2 (C_{\alpha_1 m \alpha_2} R_1 + 2 C_{\alpha_1} C_{\alpha_2} R_2 + \omega^{\alpha_2} C_{\alpha_1} Q_2 R_2 (R_1 + R_2)))) \end{aligned}$$

$$Z(\omega) = \frac{R_1 (1 + (i\omega)^{\alpha_2} \tau_2)}{1 + (i\omega)^{\alpha_1} \tau_1 + (1 + R_1/R_2) (i\omega)^{\alpha_2} \tau_2 + (i\omega)^{\alpha_1 + \alpha_2} \tau_1 \tau_2}$$

$$\tau_1 = Q_1 R_1, \tau_2 = Q_2 R_2$$

Appendix A

Symbols for CPE

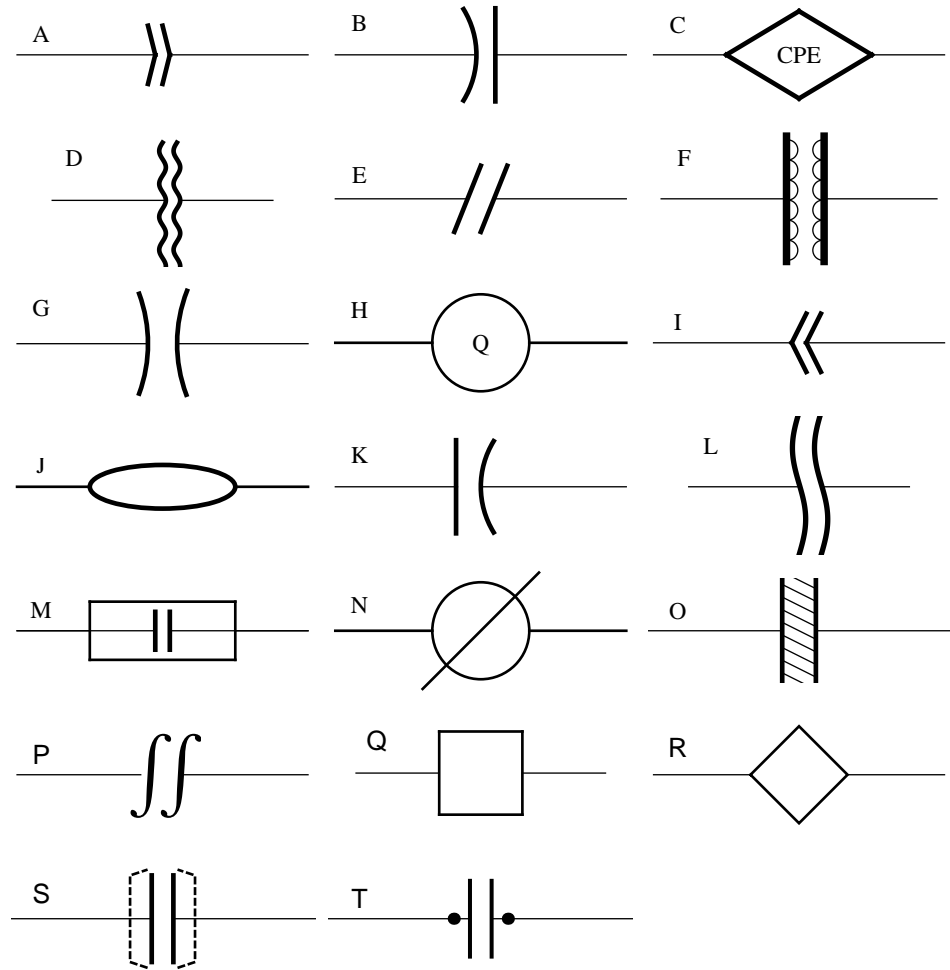


Figure A.1: Some CPE symbols, taken from A: [13], B: [19], C: [23], D: [5], E: [10], F: [17], G: [18], H: [21], I: [12], J: [15], K: [20], L: [2, 9], M: [11], N: [3, 4], O: [14], P: [24], Q, R [25], S [7], T [16].

Bibliography

- [1] BERTHIER, F., DIARD, J.-P., AND MONTELLA, C. Distinguishability of equivalent circuits containing CPEs. I. Theoretical part. *J. Electroanal. Chem.* 510 (2001), 1–11.
- [2] BOILLOT, M. *Validation expérimentale d'outil de modélisation d'une pile à combustible de type PEM*. PhD thesis, INPL, Nancy, Oct. 2005.
- [3] BOMMERSBACH, P., ALEMANY-DUMONT, C., MILLET, J., AND NORMAND, B. Formation and behaviour study of an environment-friendly corrosion inhibitor by electrochemical methods. *Electrochim. Acta* 51, 6 (2005), 1076 – 1084.
- [4] BOMMERSBACH, P., ALEMANY-DUMONT, C., MILLET, J.-P., AND NORMAND, B. Hydrodynamic effect on the behaviour of a corrosion inhibitor film: Characterization by electrochemical impedance spectroscopy. *Electrochimica Acta* 51, 19 (2006), 4011 – 4018.
- [5] BRUG, G. J., VAN DEN EEDEN, A. L. G., SLUYTERS-REHBACH, M., AND SLUYTERS, J. H. The analysis of electrode impedance complicated by the presence of a constant phase element. *J. Electroanal. Chem.* 176 (1984), 275–295.
- [6] CHABLI, A., DIACO, T., AND DIARD, J.-P. Détermination de la séquence de pondération d'une pile Leclanché à l'aide d'une méthode d'intercorrélacion. *J. Applied Electrochem.* 11 (1981), 661.
- [7] DING, S.-J., CHANG, B.-W., WU, C.-C., LAI, M.-F., AND CHANG, H.-C. Impedance spectral studies of self-assembly of alkanethiols with different chain lengths using different immobilization strategies on au electrodes. *Analytica Chimica Acta* 554 (2005), 43 – 51.
- [8] FOURNIER, J., WRONA, P. K., LASIA, A., LACASSE, R., LALANCETTE, J.-M., MENARD, H., AND BROSSARD, L. *J. Electrochem. Soc.* 139 (1992), 2372.
- [9] FRANCK-LACAZE, L., BONNET, C., BESSE, S., AND LAPICQUE, F. Effect of ozone on the performance of a polymer electrolyte membrane fuel cell. *Fuel Cells* 09 (2009), 562–569.
- [10] HAN, D. G., AND CHOI, G. M. Computer simulation of the electrical conductivity of composites: the effect of geometrical arrangement. *Solid State Ionics* 106 (1998), 71–87.

- [11] HERNANDO, J., LUD, S. Q., BRUNO, P., GRUEN, D. M., STUTZMANN, M., AND GARRIDO, J. A. Electrochemical impedance spectroscopy of oxidized and hydrogen-terminated nitrogen-induced conductive ultranocrystalline diamond. *Electrochim. Acta* 54 (2009), 1909–1915.
- [12] HOLZAPFEL, M., MARTINENT, A., ALLOIN, F., B. LE GORREC, YAZAMI, R., AND MONTELLA, C. First lithiation and charge/discharge cycles of graphite materials, investigated by electrochemical impedance spectroscopy. *J. Electroanal. Chem.* 546 (2003), 41–50.
- [13] JANSEN, R., AND BECK, F. *Electrochim. Acta* 39 (1994), 921.
- [14] JONSCHER, A. K., AND BARI, M. A. Admittance spectroscopy of sealed primary batteries. *J. Electrochem. Soc.* 135 (1988), 1618–1625.
- [15] KULOVA, T. L., SKUNDIN, A. M., PLESKOV, Y. V., TERUKOV, E. I., AND KON'KOV, O. I. Lithium insertion into amorphous silicon thin-film electrode. *J. Electroanal. Chem.* 600 (2007), 217–225.
- [16] LAES, K., BEREZNEV, S., LAND, R., TVERJANOVICH, A., VOLOBUJEVA, O., TRAKSMAA, R., RAADIK, T., AND ÖPIK, A. The impedance spectroscopy of photoabsorber films prepared by high vacuum evaporation technique. *Energy Procedia* 2, 1 (2010), 119 – 131.
- [17] MATTHEW-ESTEBAN, J., AND ORAZEM, M. E. On the application of the Kramers-Kronig relations to evaluate the consistency of electrochemical impedance data. *J. Electrochem. Soc.* 138 (1991), 67–76.
- [18] MESSAOUDI, B., JOIRET, S., KEDDAM, M., AND TAKENOUTI, H. Anodic behaviour of manganese in alkaline medium. *Electrochim. Acta* 46 (2001), 2487–2498.
- [19] ORAZEM, M. E., SHUKLA, P. S., AND MEMBRINO, M. A. Extension of the measurement model approach for deconvolution of underlying distributions for impedance measurements. *Electrochim. Acta* 47 (2002), 2027–2034.
- [20] QUINTIN, M., DEVOS, O., DELVILLE, M. H., AND CAMPET, G. Study of the lithium insertion-deinsertion mechanism in nanocrystalline γ -Fe₂O₃ electrodes by means of electrochemical impedance spectroscopy. *Electrochim. Acta* 51 (2006), 6426–6434.
- [21] SEKI, S., KOBAYASHI, Y., MIYASHIRO, H., YAMANAKA, A., MITA, Y., AND IWAHORI, T. Degradation mechanism analysis of all solid-state lithium polymer rechargeable batteries. In *IMBL 12 Meeting* (2004), The Electrochemical Society. Abs. 386.
- [22] SLUYTERS-REHBACH, M. Impedance of electrochemical systems: Terminology, nomenclature and representation-Part I: Cells with metal electrodes and liquid solution (IUPAC Recommendations 1994). *Pure & Appl. Chem.* 66 (1994), 1831–1891.
- [23] TOMCZYK, P., AND MOSIALEK, M. Investigation of the oxygen electrode reaction in basic molten carbonates using electrochemical impedance spectroscopy. *Electrochim. Acta* 46 (2001), 3023–3032.

- [24] VANDERNOOT, T. J., AND ABRAHAMS, I. The use of genetic algorithms in the non-linear regression of immittance data. *J. Electroanal. Chem.* 448 (1998), 17–23.
- [25] YANG, B. Y., AND KIM, K. Y. The oxidation behavior of Ni-50%Co alloy electrode in molten Li + K carbonate eutectic. *Electrochim. Acta* 44 (1999), 2227–2234.
- [26] ZOLTOWSKI, P. *J. Electroanal. Chem.* 443 (1998), 149.