SOFC and Electrolysis

Electrochemical Characterisation-Impedance Fundamentals

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Outline

- Fysisk Kemi 2, 2009. Exercise 3 (1 hour)
- Pause (15 min)
- Chapter 4 in Mark E. Orazem and Bernard Tribollet, *Electrochemical Impedance Spectroscopy*, Willey, Hoboken, NJ, 2008 (15 min)
- Exercises in relation to chapter 4 (45 min)
- Pause (15 min)
- Chapter 7 in Mark E. Orazem and Bernard Tribollet, *Electrochemical Impedance Spectroscopy*, Willey, Hoboken, NJ, 2008 (30 min)
- Exercises in relation to chapter 7 (45 min)

Electrical Circuits

Chapter 4 in EIS by Orazem and Tribollet, Wiley 2008

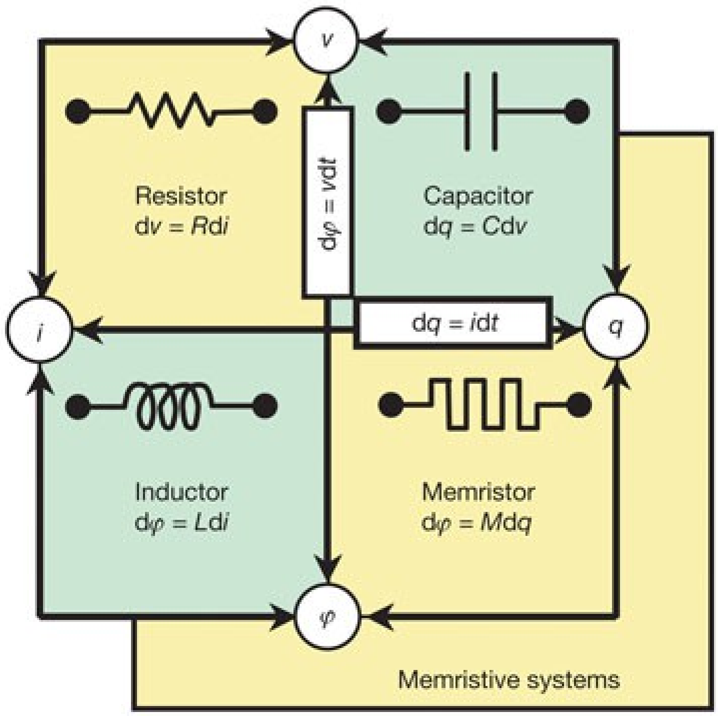
(a) Resistor (b) Inductor (c) Capacitor

$$V(t) = RI(t)$$

$$C = \frac{dq(t)}{dV(t)}$$

$$V(t) = L\frac{dI(t)}{dt}$$

Electrical Circuits



Leon Chua 1971

Electrical Circuits

Chapter 4 in EIS by Orazem and Tribollet, Wiley 2008

$$V(t) = |\Delta V| \cos(\omega t)$$

$$I(t) = |\Delta I| \cos(\omega t + \varphi)$$

$$= \mathrm{Re}\left\{ |\Delta I| \exp(j\varphi) \exp(j\omega t) \right\}$$

$$= \mathrm{Re}\left\{ \Delta I \exp(j\omega t) \right\} \qquad \text{where } \Delta I = |\Delta I| \exp(j\varphi).$$

Electrical Circuits

Chapter 4 in EIS by Orazem and Tribollet, Willey 2008

$$\frac{dI(t)}{dt} = \mathrm{Re}\left\{ j\omega \Delta I \exp(j\omega t) \right\}$$

$$\frac{dV(t)}{dt} = \mathrm{Re}\left\{ j\omega \Delta V \exp(j\omega t) \right\}$$

Electrical Circuits
-Inductor

$$V(t) = L\frac{dI(t)}{dt}$$

$$\mathrm{Re}\left\{\Delta V \exp(j\omega t)\right\} = L\mathrm{Re}\left\{j\omega\Delta I \exp(j\omega t)\right\}$$

$$\Delta V = j\omega L\Delta I$$

$$Z = \frac{\Delta V}{\Delta I}$$

$$Z_{\mathrm{inductor}} = j\omega L$$

Electrical Circuits
-Exercise

Derive the impedance of a capacitor

Electrical Circuits

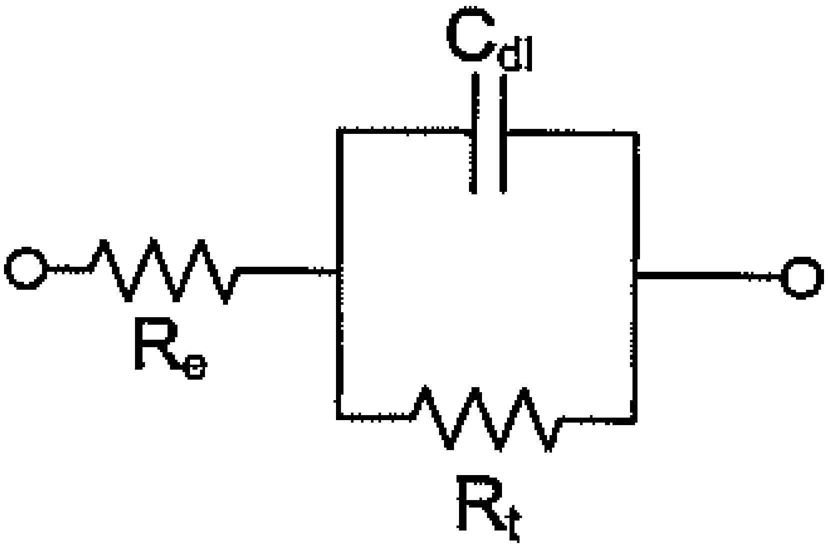
-Exercise

$$Z_{\text{resistor}} = R$$

$$Z_{\text{capacitor}} = \frac{1}{j\omega C}$$

$$Z_{\text{inductor}} = j\omega L$$

Electrical Circuits
-Series and Parallel Connections



$$Z = R_e + \frac{R_t}{1 + j\omega R_t C_{dl}}$$

Show this

Electrical Circuits
-Exercise

1. Draw Nyquist plot and Bode plots of the impedances of a resistor, inductor and capacitor
2. Draw the impedance of $Z = R_e + \frac{R_t}{1 + j\omega R_t C_{dl}}$ a Z_r , Z_I plot with R_e = 1 Ohm, R_t = 2 Ohm and C_{dl} = 0.1 F
3. Exercise 4.1, 4.2, 4.3, 4.4, (extra 4.6)

Pause (15 minutes)

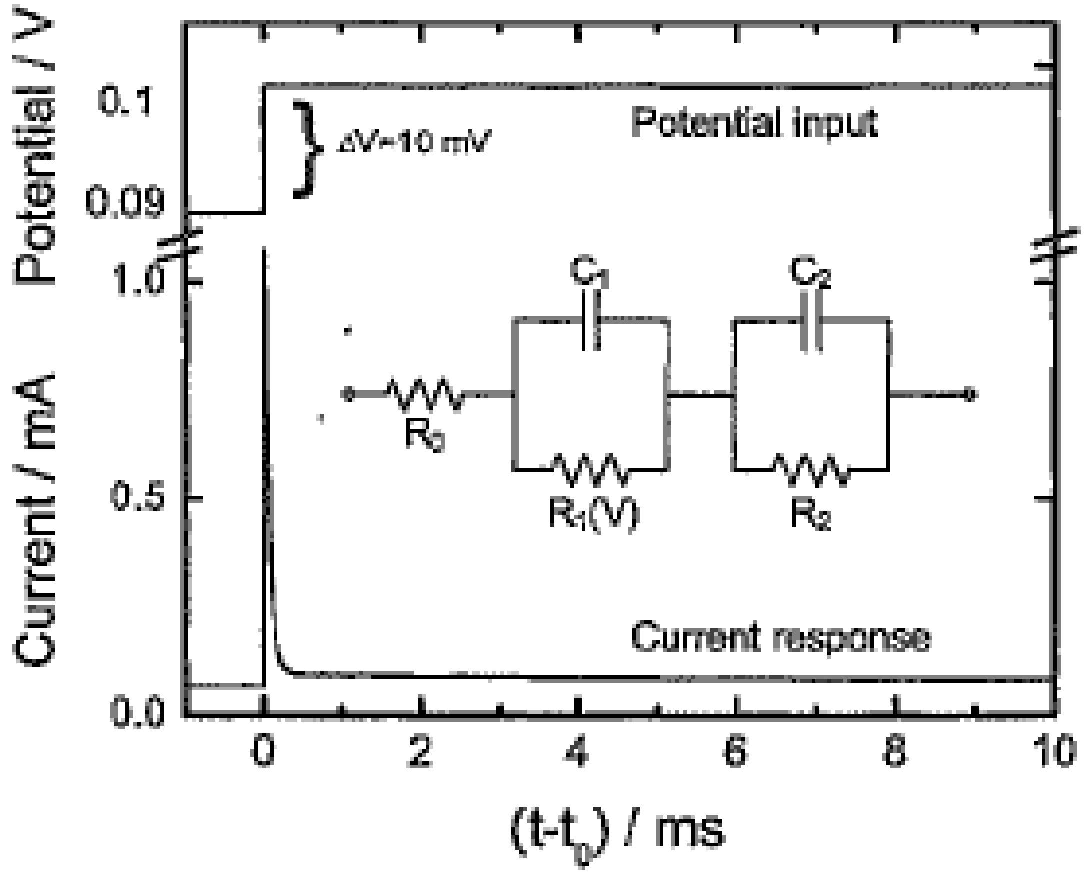
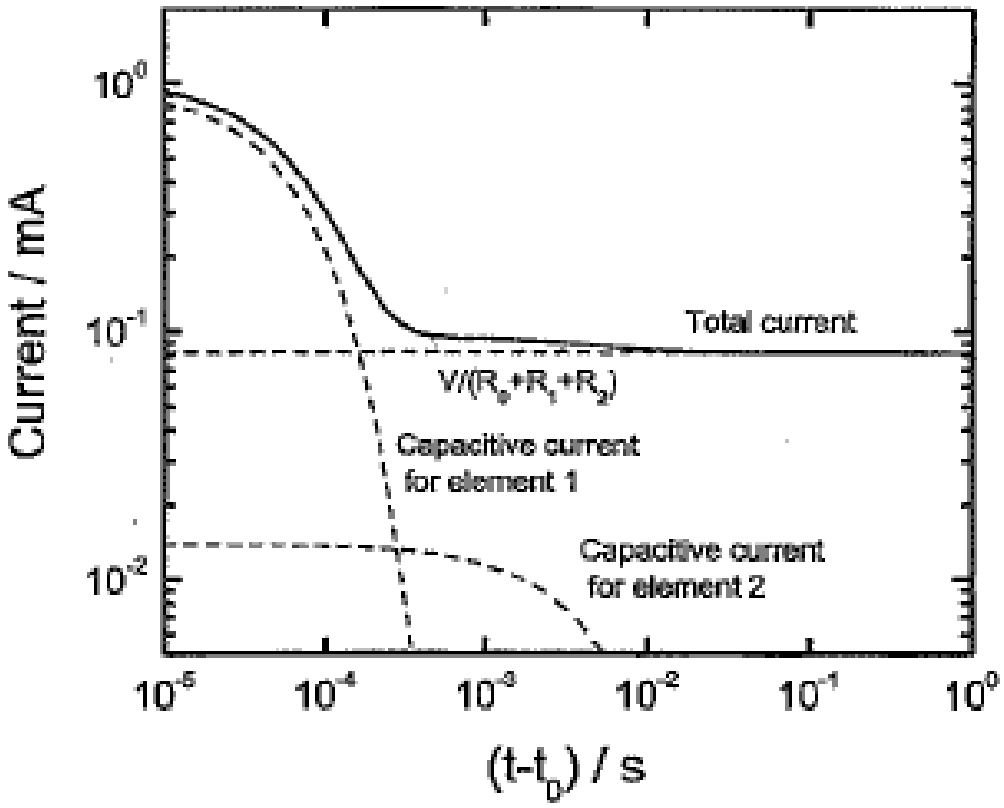


Figure 7.1: The current response of an electrochemical system to a 10 mV step change in applied potential from 0.09 V to 0.1 V for the inserted electrical circuit with parameters $R_0 = 1\ \Omega$, $R_1 = 10^{4-V/0.060}\ \Omega$, $C_1 = 10\ \mu F$, $R_2 = 10^3\ \Omega$, and $C_2 = 20\ \mu F$. The potential dependence of parameter R_1 is consistent with the behavior of the charge-transfer resistance described in Chapter 10.

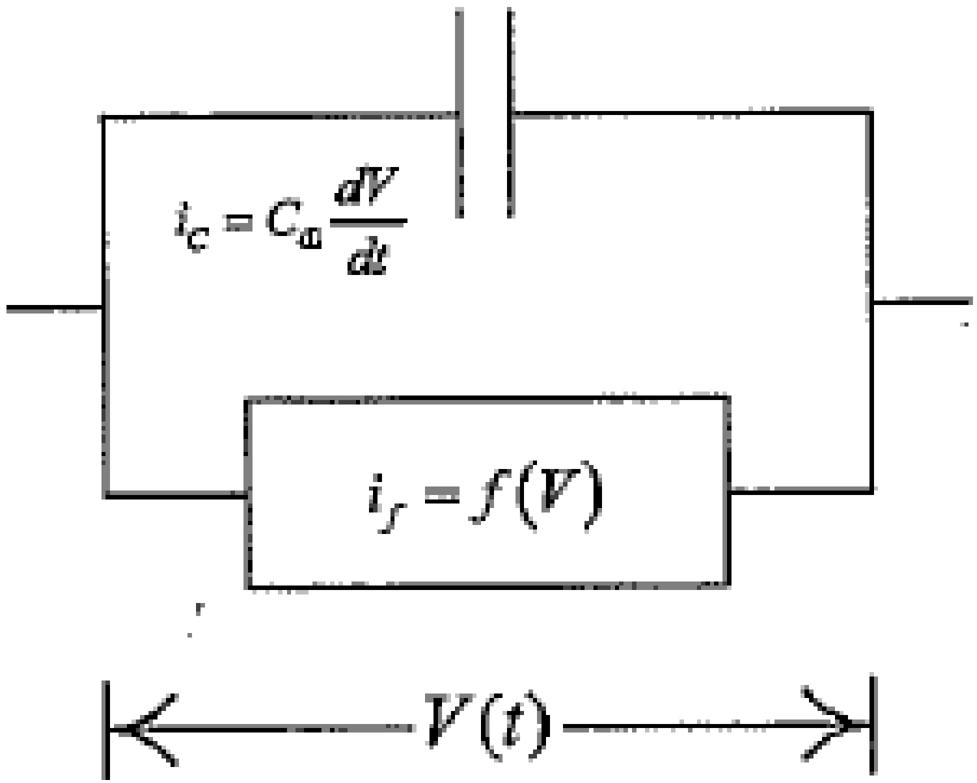

Current / mA
10^{0}
10^{-1}
10^{-2}
Total current
$V/(R_0+R_1+R_2)$
Capacitive current
for element 1
Capacitive current
for element 2
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
$(t-t_0)$ / s

- Applied Voltage: $V = \overline{V} + \Delta V \cos(2\pi f t)$
- Faradaic current response: $i_f = nFk_a \exp(b_a \overline{V}) - nFk_c \exp(-b_c \overline{V})$
- Capacitive current response: $i_C = -C_{dl} \frac{dV}{dt} = 2\pi f \Delta V C_{dl} \sin(2\pi f t)$

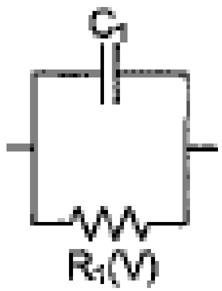
Charge Transfer resistance : $R_t = \frac{1}{(b_a nFk_a \exp(b_a \overline{V}) + b_c nFk_c \exp(-b_c \overline{V}))}$

↑

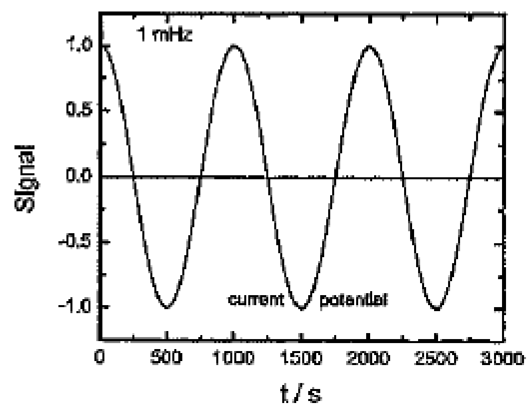
Derive this



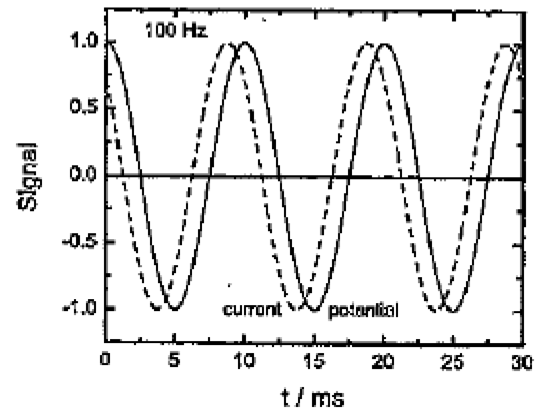
$i_C = C_{dl}\frac{dV}{dt}$
$i_f = f(V)$
$V(t)$



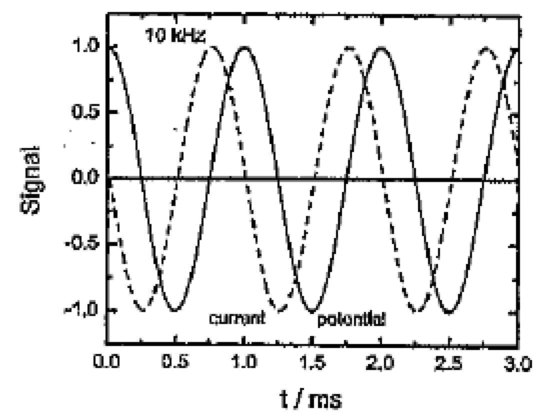
Equiv. circuit



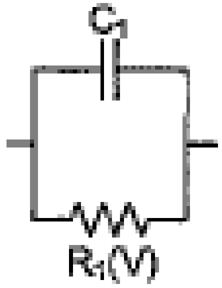
(a)



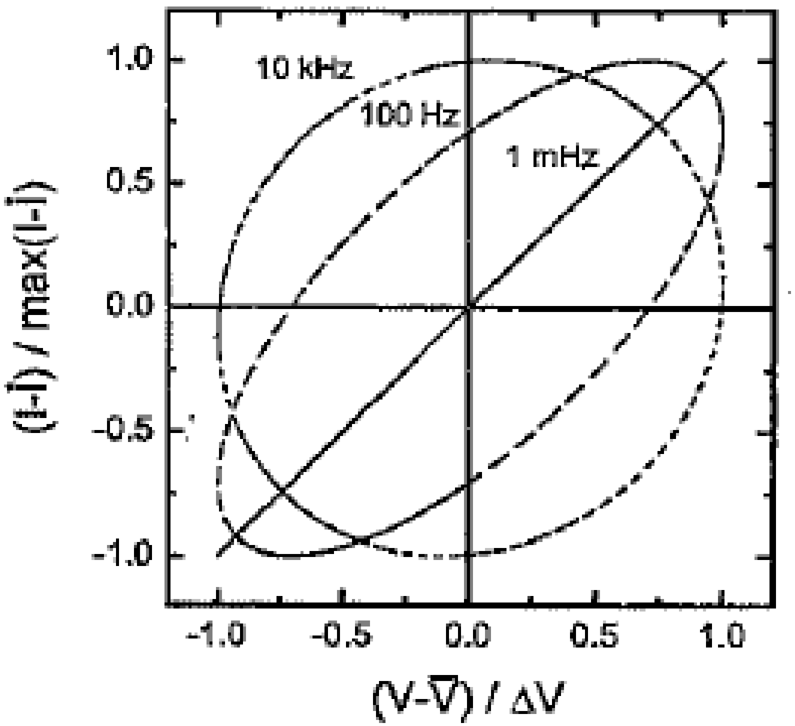
(b)



(c)

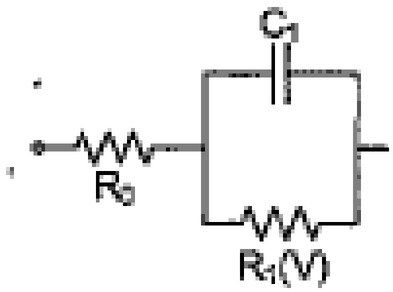


Equiv. circuit

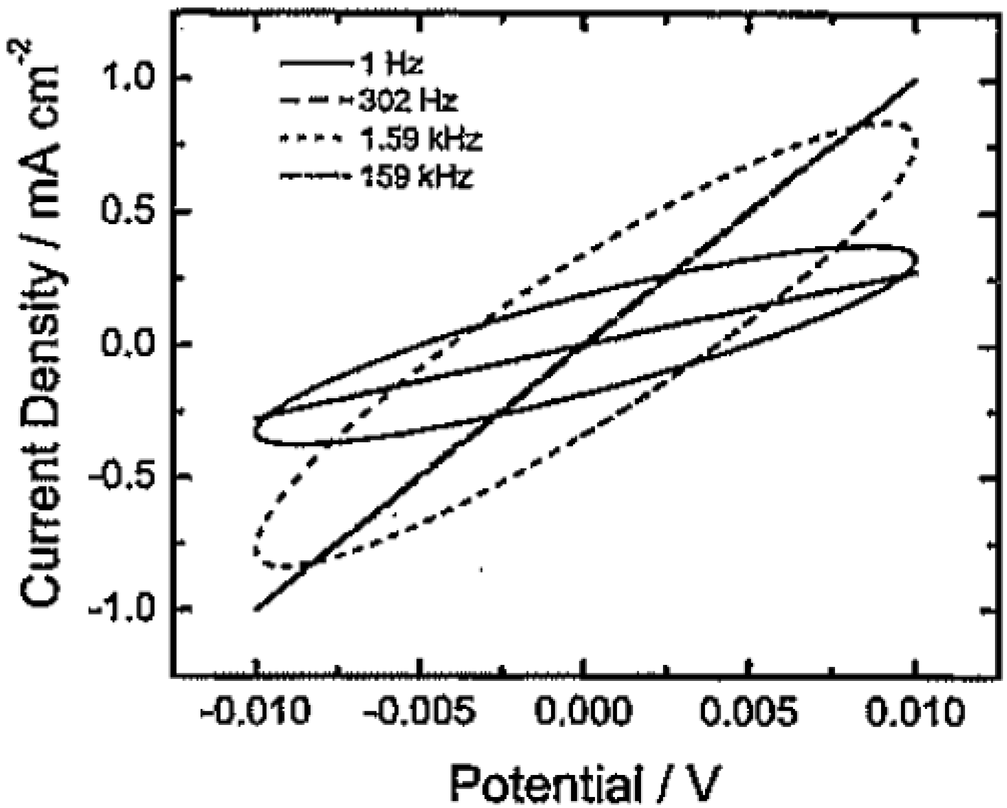


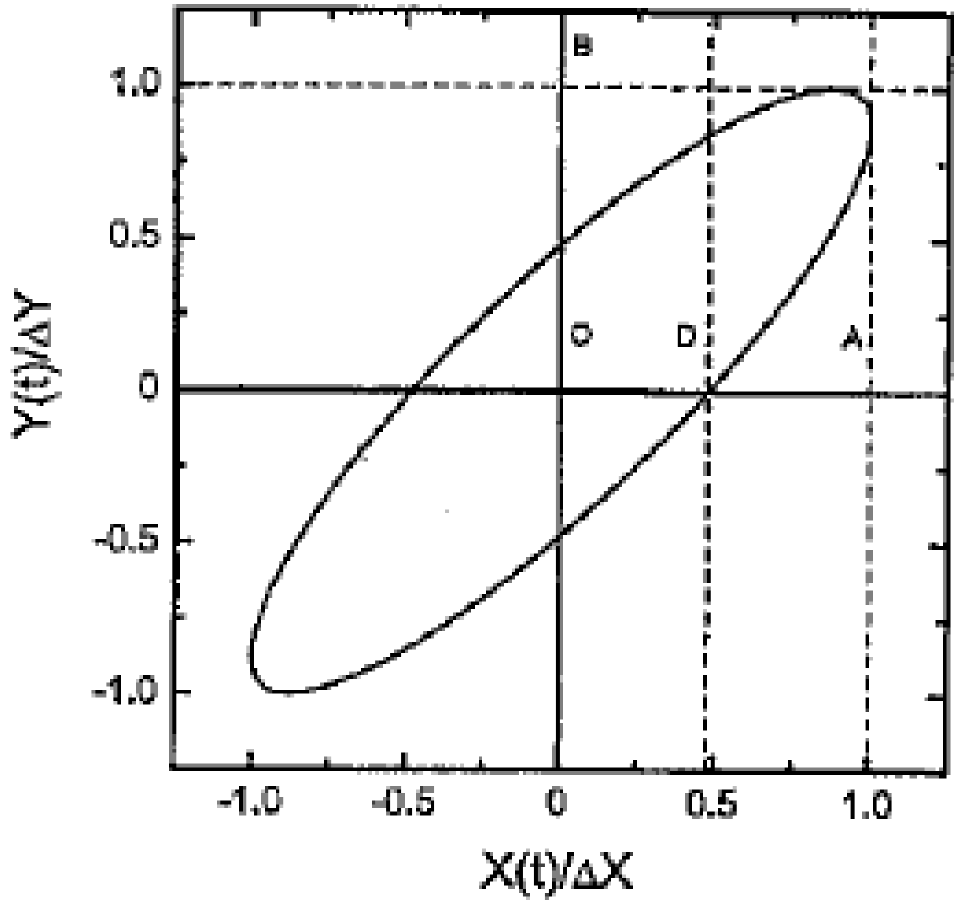
Lissajous representation of the signals presented in Figure 7.4

- What happens with max(i-I) for a constant ΔV when the frequency increases from 1 mHz to 10 kHz?



Equiv. circuit

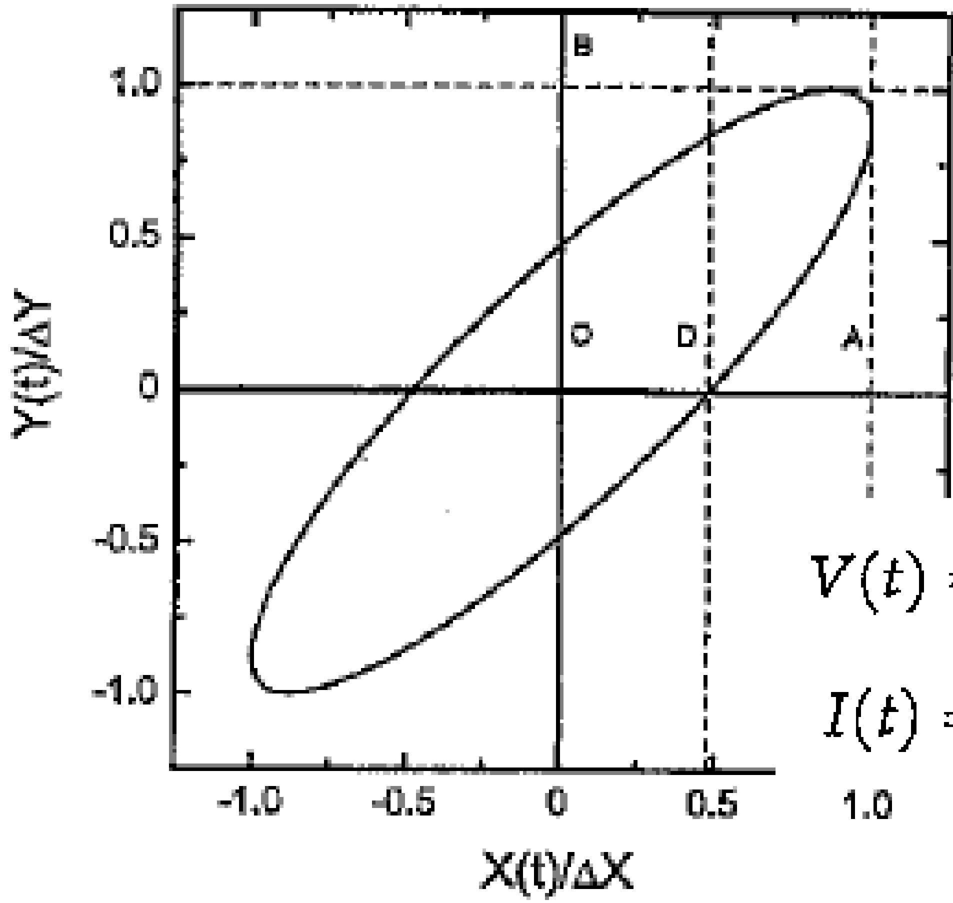




Why?

$$|Z| = \frac{\Delta V}{\Delta I} = \frac{OA}{OB} = \frac{\Delta Y}{\Delta X}$$

$$\sin(\phi) = -\frac{OD}{OA}$$



$$V(t) = |\Delta V| \cos(\omega t)$$

$$I(t) = |\Delta I| \cos(\omega t + \varphi)$$

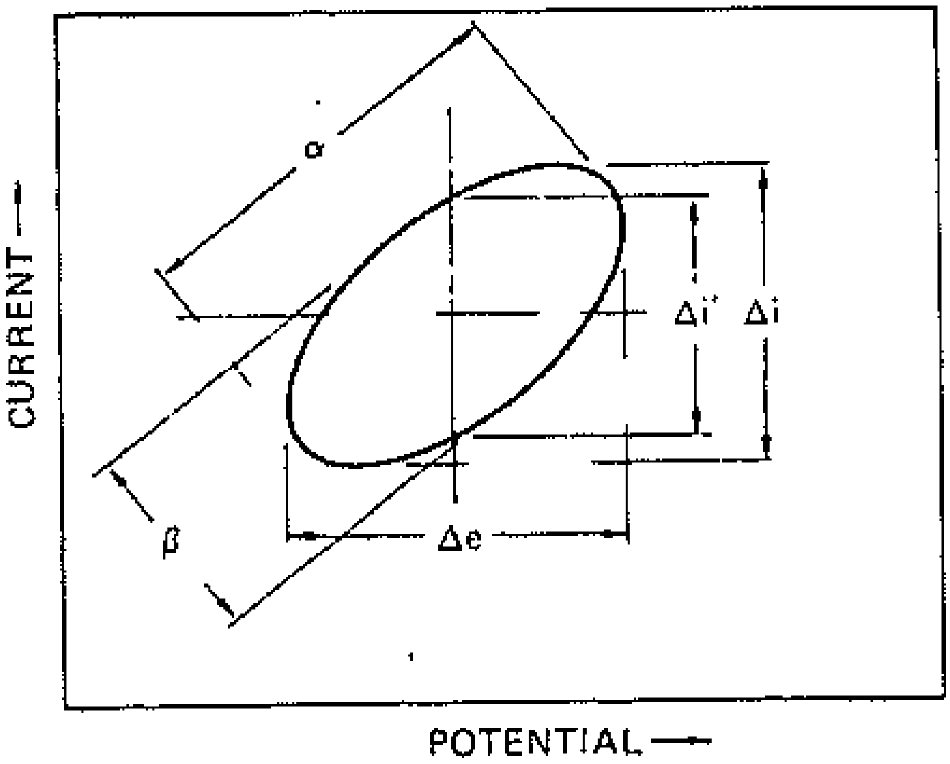
Why?

$$|Z| = \frac{\Delta V}{\Delta I} = \frac{OA}{OB} = \frac{\Delta Y}{\Delta X} \qquad \sin(\phi) = -\frac{OD}{OA}$$

Experimental Methods

Chapter 7 in EIS by Orazem and Tribollet, Wiley 2008

- Lissajous curve



$$|Z| = \Delta e / \Delta i$$

$$\sin(\phi) = \Delta i' / \Delta i = \alpha\beta / (\Delta i \Delta e)$$

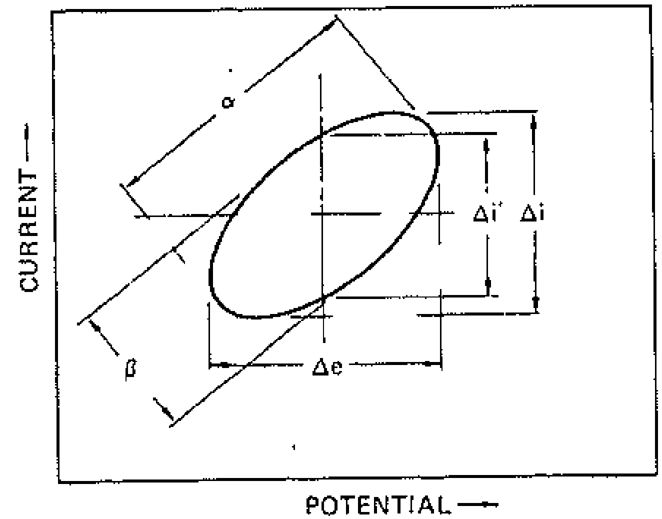
Experimental Methods

Exercise

- Verify the equations

$$|Z| = \Delta e / \Delta i$$

$$\sin(\phi) = \Delta i' / \Delta i = \alpha\beta / (\Delta i \Delta e)$$



Experimental Methods

Phase sensitive methods (Lock-in amplifier)

Signal (AC current)

$$X = \Delta X \sin(\omega t + \phi_X)$$

Ref signal (square)

$$S = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin\left[(2n+1)\,\omega t + \phi_S\right]$$

$$XS = \frac{4\Delta X}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin(\omega t + \phi_X) \sin\left[(2n+1)\,\omega t + \phi_S\right]$$

$$XS = \sum_{n=0}^{\infty} \frac{2\Delta X}{(2n+1)\,\pi} \{\cos\left[-2n\omega + \phi_X - (2n+1)\,\phi_S\right] - \cos\left[(2n+2)\,\omega t + \phi_X + (2n+1)\,\phi_S\right]\}$$

Integration (one period)

$$\frac{\omega}{2\pi} \int_0^{2\pi/\omega} XS dt = \frac{2\Delta X}{\pi} \cos(\phi_X - \phi_S)$$

Experimental Methods

Phase sensitive methods (Lock-in amplifier)

Signal
(AC voltage)

$$Y = \Delta Y \sin(\omega t + \phi_Y)$$

$$\frac{\omega}{2\pi} \int_0^{2\pi/\omega} YS\,dt = \frac{2\Delta Y}{\pi} \cos(\phi_Y - \phi_S)$$

$$|Z| = \frac{\Delta Y}{\Delta X}$$

$$\phi = (\phi_Y - \phi_S) - (\phi_X - \phi_S)$$

Experimental Methods

Single Phase Fourier Analysis

Periodic signal: $$f(t) = a_0 + \sum_{n=1}^{\infty} \left(a_n \cos(n\omega t) + b_n \sin(n\omega t)\right)$$

Complex repr.: $$f(t) = \tilde{c}_0 + \sum_{n=1}^{\infty} \left(\tilde{c}_n \exp(jn\omega t) + \tilde{c}_{-n} \exp(-jn\omega t)\right)$$

$$f(t) = \sum_{n=-\infty}^{\infty} \tilde{c}_n \exp(jn\omega t)$$

Deriv of coeff.: $$\tilde{c}_n = \frac{1}{T} \int_0^T f(t) \exp(-jn\omega t)\, dt$$

Experimental Methods

Single Phase Fourier Analysis

$$V(t) = \Delta V \cos(\omega t)$$

$$I(t) = \Delta I \cos(\omega t + \phi_I)$$

$$I(t) = a_1 \cos(\omega t) + b_1 \sin(\omega t)$$

What is a_1 and b_1?

$a_1 = \cos(\text{phi})$

$b_1 = -\sin(\text{phi})$

$$I_r(\omega) = \frac{1}{T}\int_0^T I(t)\cos(\omega t)dt \qquad I_j(\omega) = -\frac{1}{T}\int_0^T I(t)\sin(\omega t)dt$$

$\cos^2(x) = (1 + \cos(2x))/2$ $\qquad$ $\cos(x)\sin(x) = ½\sin(2x)$

Experimental Methods

Single Phase Fourier Analysis

$$V(t) = \Delta V \cos(\omega t)$$

$$V_r(\omega) = \frac{1}{T}\int_0^T V(t)\cos(\omega t)dt \qquad V_j(\omega) = -\frac{1}{T}\int_0^T V(t)\sin(\omega t)dt$$

$$Z_r(\omega) = \mathrm{Re}\left\{\frac{V_r + jV_j}{I_r + jI_j}\right\} \qquad Z_j(\omega) = \mathrm{Im}\left\{\frac{V_r + jV_j}{I_r + jI_j}\right\}$$

Experimental Methods

Single Phase Fourier Analysis

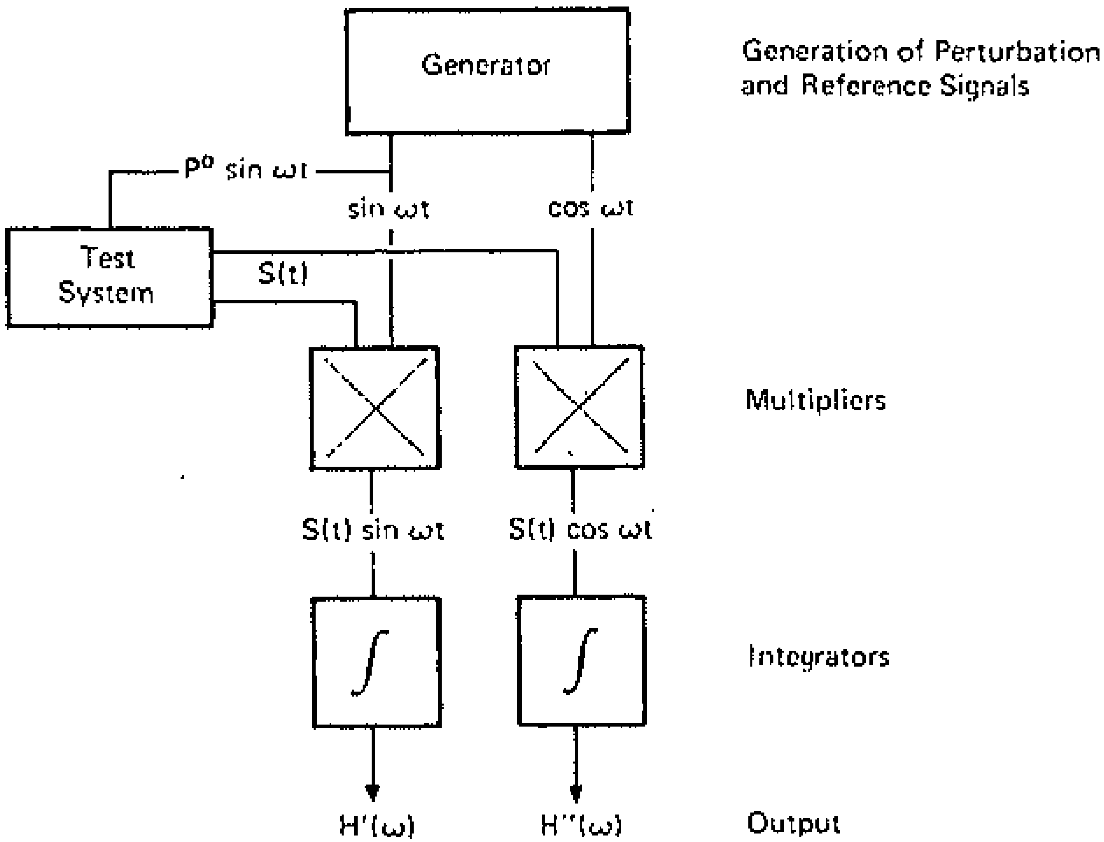


Figure 3.1.10. Schematic of transfer function analyzer.

Experimental Methods

Single Phase Fourier Analysis

$$P(t) = P^0 \sin(\omega t)$$

$$S(t) = P^0 |Z(\omega)| \sin[\omega t + \phi(\omega)] + \sum_m A_m \sin(m\omega t - \phi_m) + N(t)$$

$$|Z(\omega)| e^{j\phi(\omega)}$$

$$H'(\omega) = \frac{1}{T}\int_0^T S(t)\sin(\omega t)dt$$

$$H''(\omega) = \frac{1}{T}\int_0^T S(t)\cos(\omega t)dt$$

$$H'(\omega) = P^0|Z(\omega)|\int_0^T \sin[\omega t + \phi(\omega)]\sin(\omega t)dt + \frac{1}{T}\int_0^T \sum_m A_m \sin(m\omega t - \phi_m)\sin(\tau t)dt + \frac{1}{T}\int_0^T N(t)\sin(\omega t)dt \tag{28}$$

$$H''(\omega) = P^0|Z(\omega)|\int_0^T \sin[\omega t + \phi(\omega)]\cos(\omega t)dt + \frac{1}{T}\int_0^T \sum_m A_m \sin(m\omega t - \phi_m)\cos(\tau t)dt + \frac{1}{T}\int_0^T N(t)\cos(\omega t)dt \tag{29}$$

$$H'(\omega) = P|Z(\omega)|\cos[\phi(\omega)]$$

$$H''(\omega) = P|Z(\omega)|\sin[\phi(\omega)]$$

Experimental Methods

Single Phase Fourier Analysis

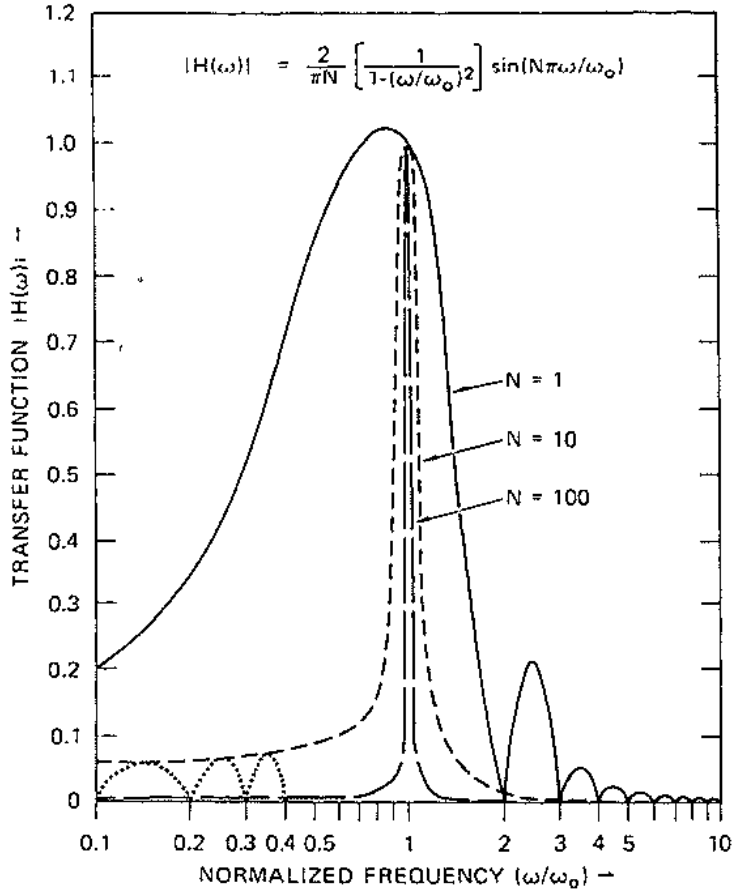
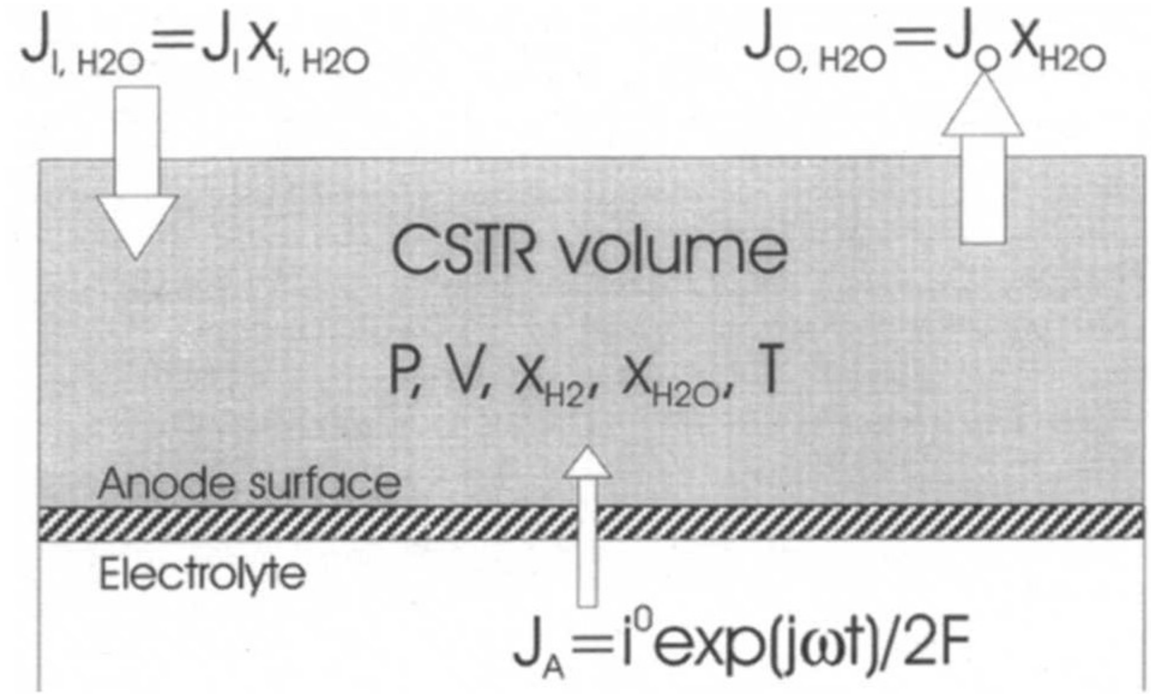


Figure 3.1.11. Frequency response analyzer transfer function vs. normalized frequency, as a function of number of integration cycles.

Pause

Gas Conversion Impedance

Primdahl and Mogensen. *JES* **145**, 2431 (1998)



$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Gas Conversion Impedance

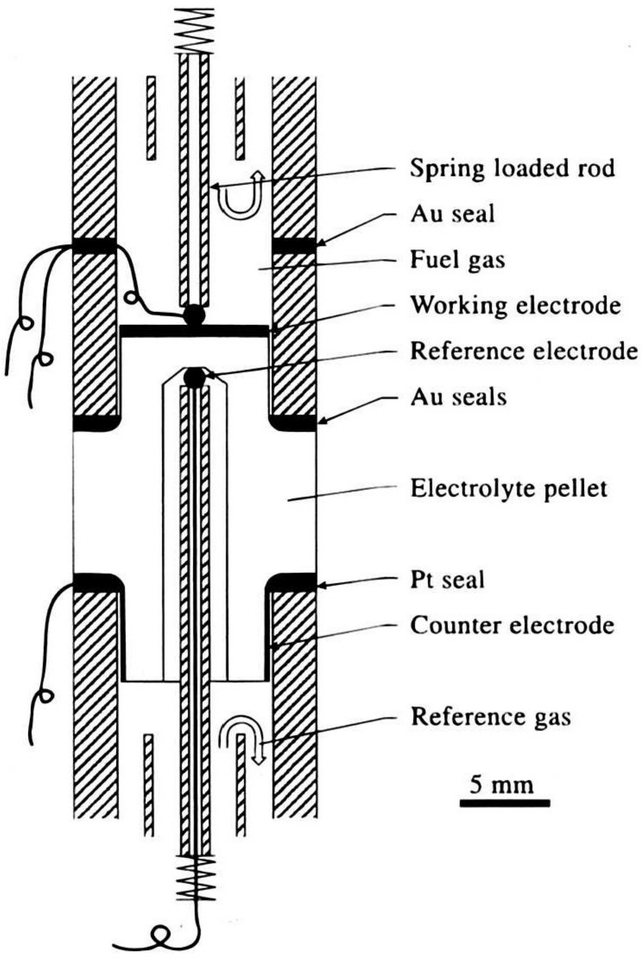
Primdahl and Mogensen. *JES* **145**, 2431 (1998)

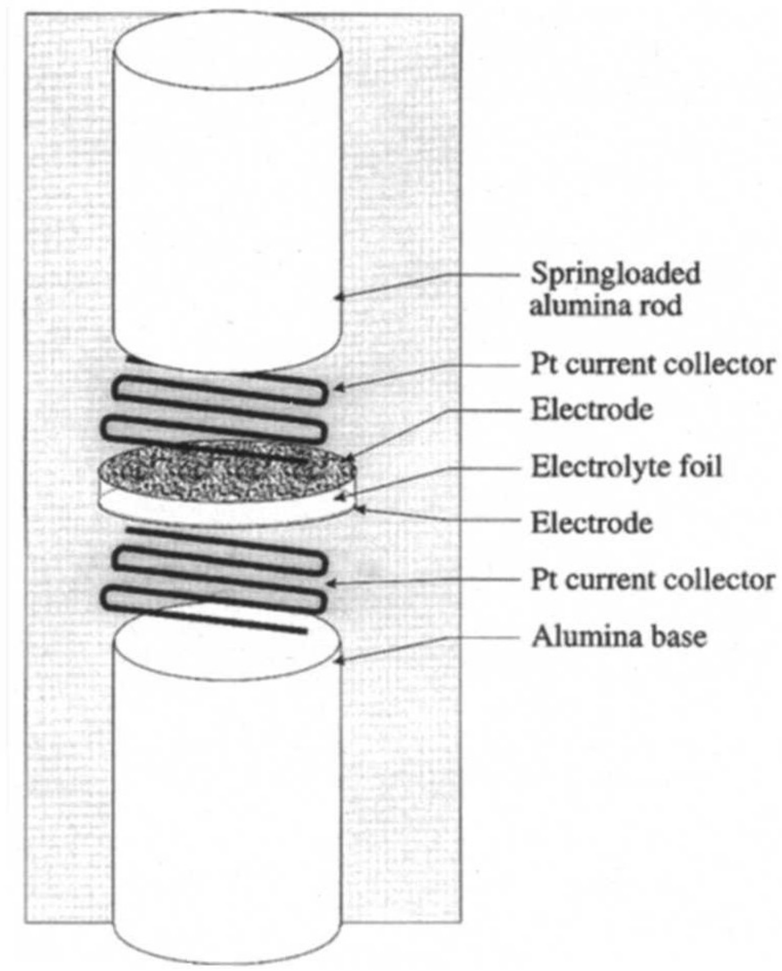
$$E = \frac{RT}{4F} \ln\left(\frac{x_{O_2,\mathrm{red}}}{x_{O_2,\mathrm{ox}}}\right)$$

$$E = E_0 + \frac{RT}{nF} \ln \frac{P_{H_2O}}{P_{H_2}\sqrt{P_{O_2}}}$$

Gas Conversion Impedance

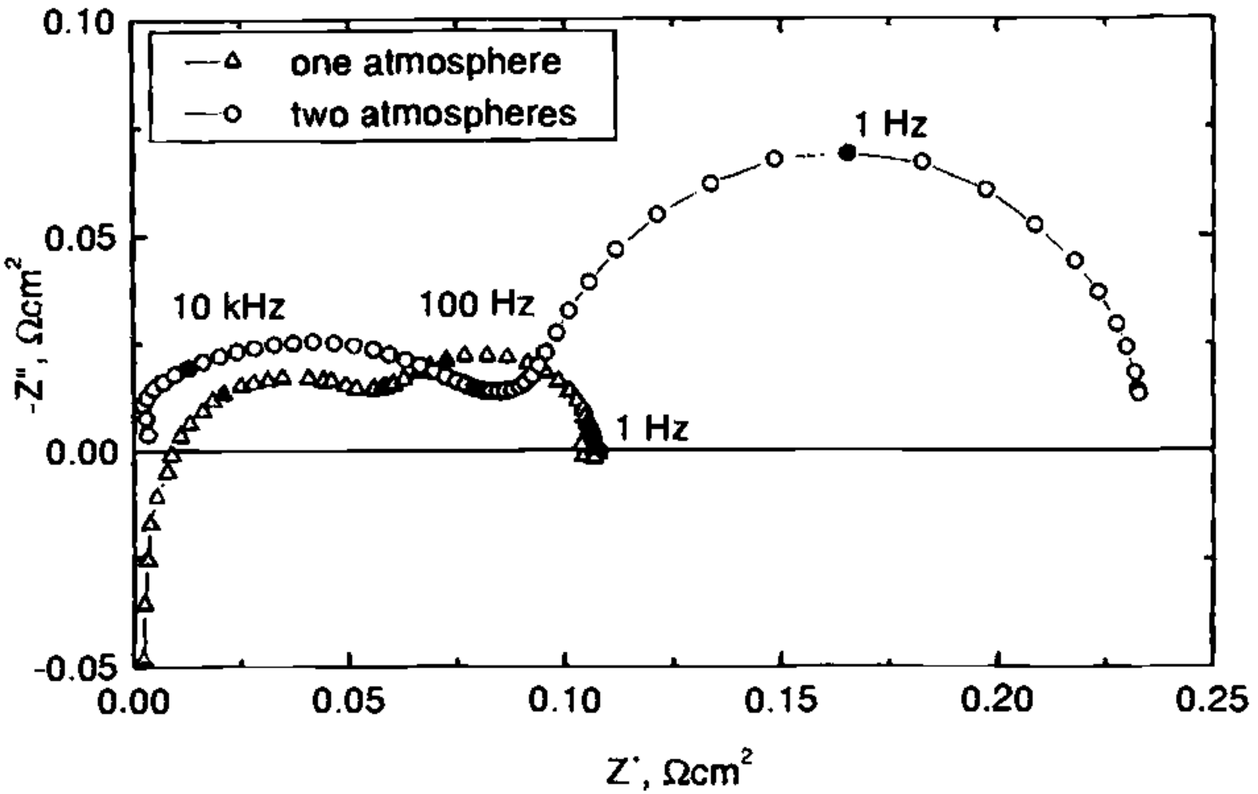
Primdahl and Mogensen. *JES* **145**, 2431 (1998)





Gas Conversion Impedance

Primdahl and Mogensen. *JES* **145**, 2431 (1998)



Gas Conversion Impedance

Primdahl and Mogensen. *JES* **145**, 2431 (1998)

$$R_g = \frac{RT}{4F^2 J_i}\left(\frac{1}{x_{i,H_2O}} + \frac{1}{x_{i,H_2}}\right)$$

$$C_g = \frac{4F^2 PV}{(RT)^2 A}\frac{1}{\frac{1}{x_{i,H_2O}} + \frac{1}{x_{i,H_2}}}$$

$$f_g = \frac{J_i ART}{2\pi PV}$$

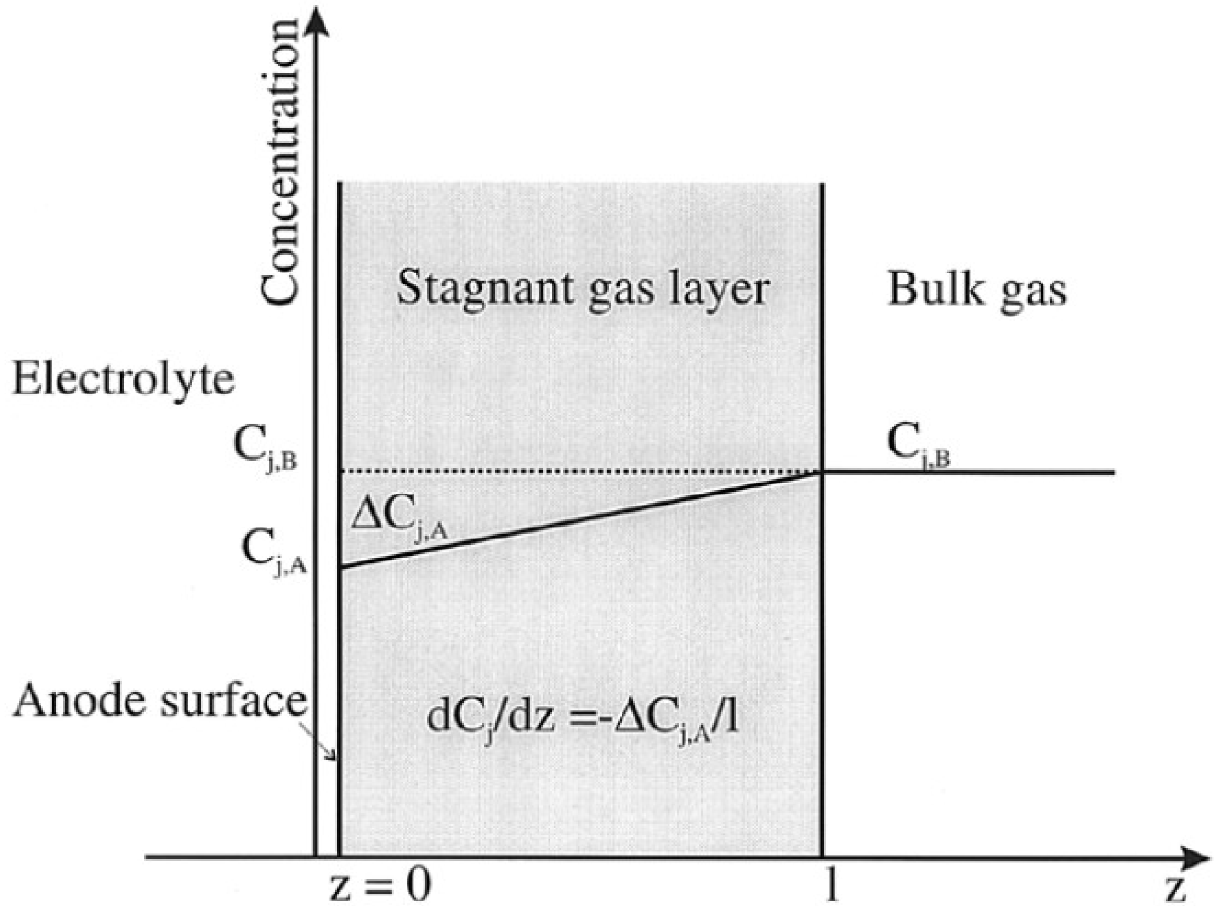
Gas Conversion Impedance

Primdahl and Mogensen. *JES* **145**, 2431 (1998)

- Exercises
  - 1. On Figure 6, the curves have a slope of app. 1 and -1. Why? Why are the curves not linear?
  - 2. On Figure 5 the capacity increases with decreasing flow rate. Why does it increase?
  - 3. The criterion for the expressions for R_g, C_g and f_g is that $\Delta x_{H2O} << x_{H2O}$ and $\Delta x_{H2} << x_{H2}$. Why is it so?
  - 4. Extra: Read Appendix A

Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)



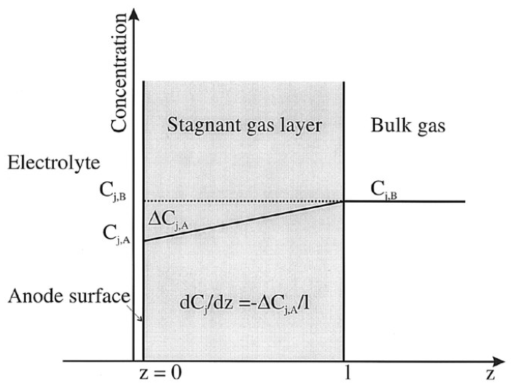
Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)

$$\sum_k \nu_k R_k \rightleftharpoons \sum_l \nu_l X_l + ne^-$$

Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)



$$\frac{dC_j}{dz} = \frac{-\Delta C_j}{l}$$

$$j_{j,A} = -D_{Eff} \frac{dC_{j,A}}{dz}$$

$$D_{12} = \frac{10^{-7} T^{1.75} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{P\left(\sqrt[3]{\nu_1} + \sqrt[3]{\nu_2}\right)^2}$$

Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)

$$j_{\mathrm{j,A}} = \frac{i}{2F}$$

$$\Delta C_{\mathrm{H_2O,A}} = \frac{li}{2FD_{\mathrm{Eff}}} \qquad \Delta C_{\mathrm{H_2,A}} = \frac{-li}{2FD_{\mathrm{Eff}}}$$

Gas Diffusion Impedance

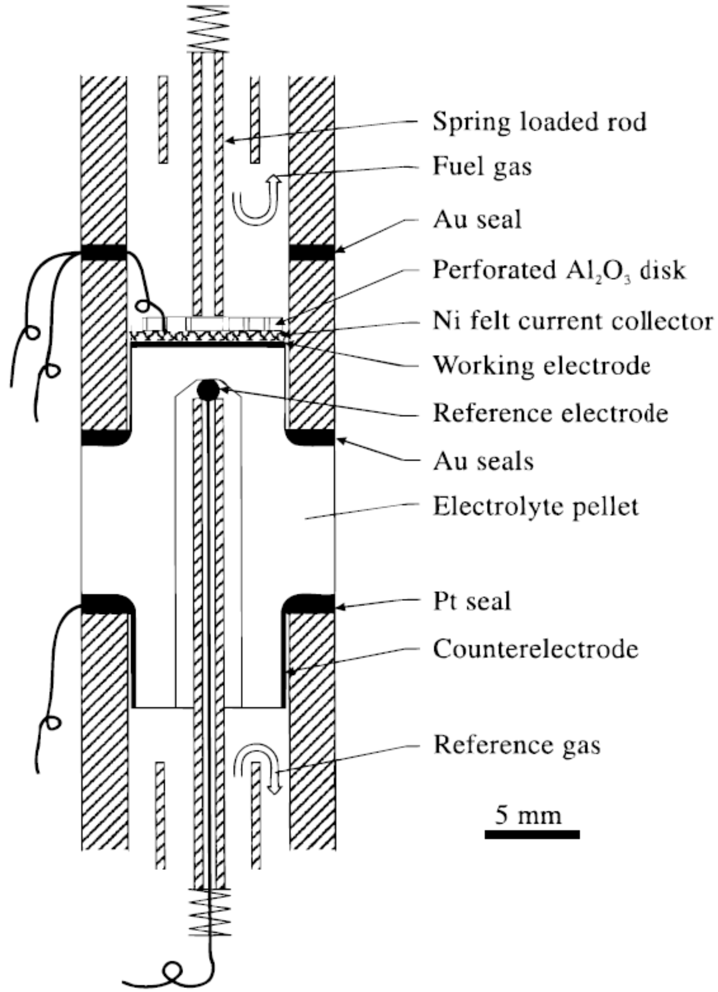
Primdahl and Mogensen. *JES* **146**, 2827 (1999)

$$E = E_0 + \frac{RT}{nF} \ln \frac{P_{H_2O}}{P_{H_2} \sqrt{P_{O_2}}}$$

$$R_D = \frac{\eta_D}{i} = \left(\frac{RT}{2F}\right)^2 \frac{l}{P D_{Eff}} \left(\frac{1}{X_{H_2,B}} + \frac{1}{X_{H_2O,B}}\right)$$

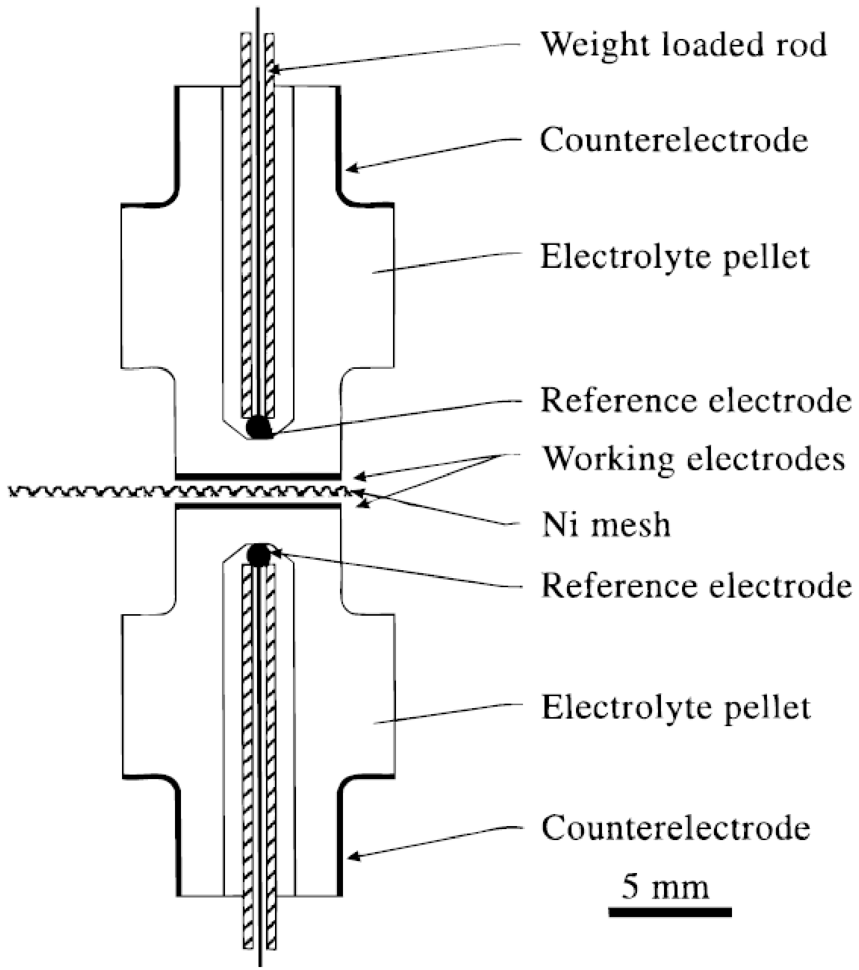
Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)



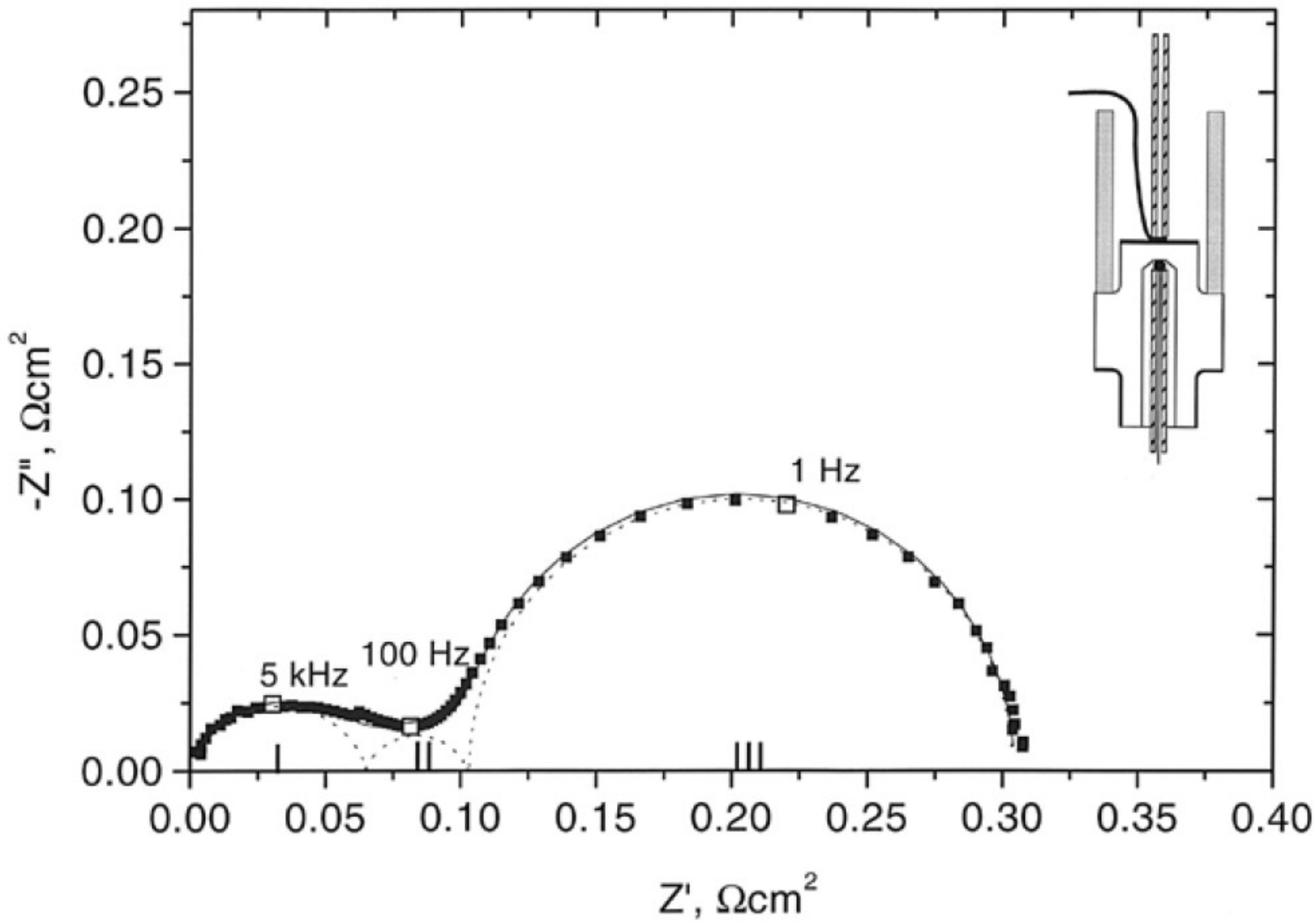
Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)



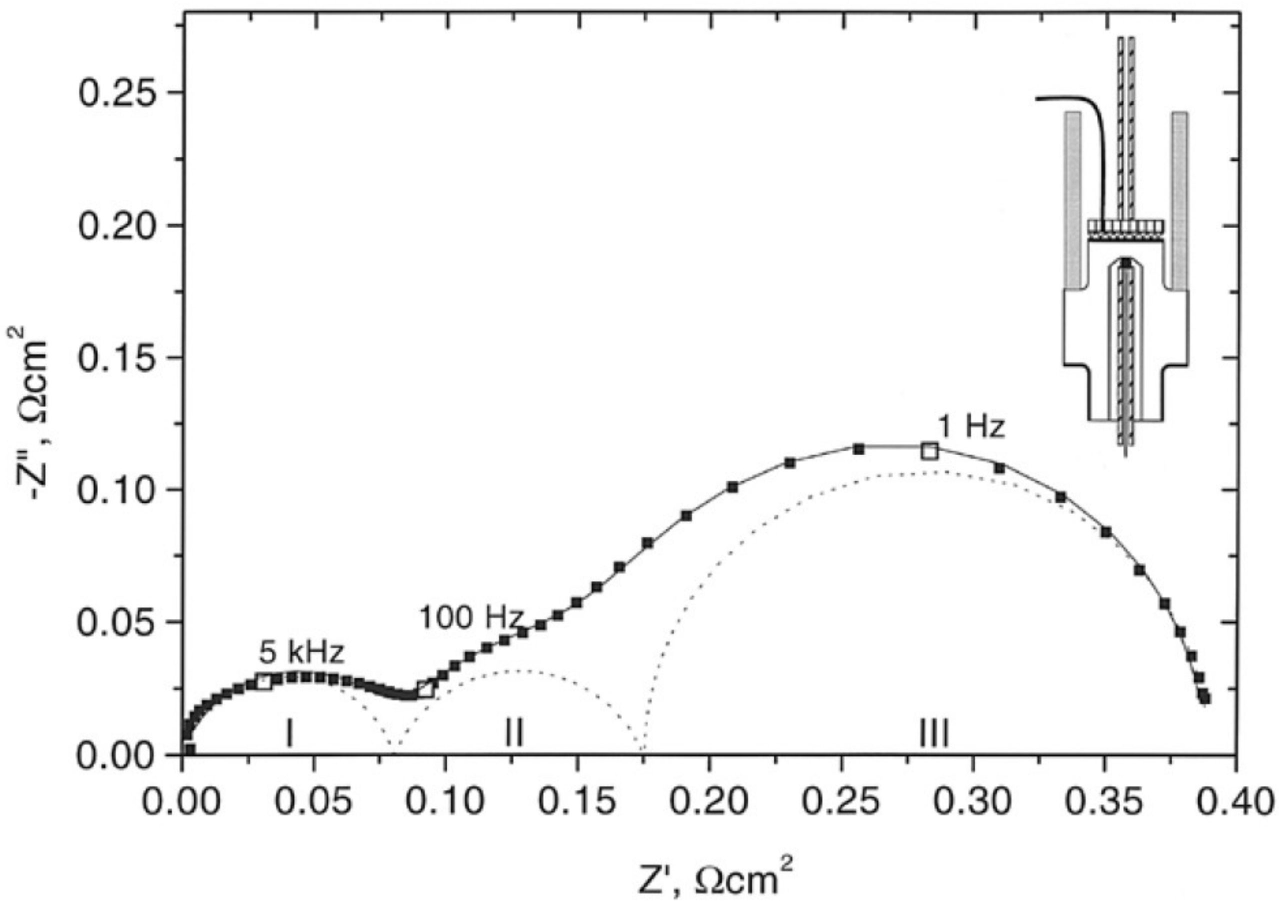
Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)



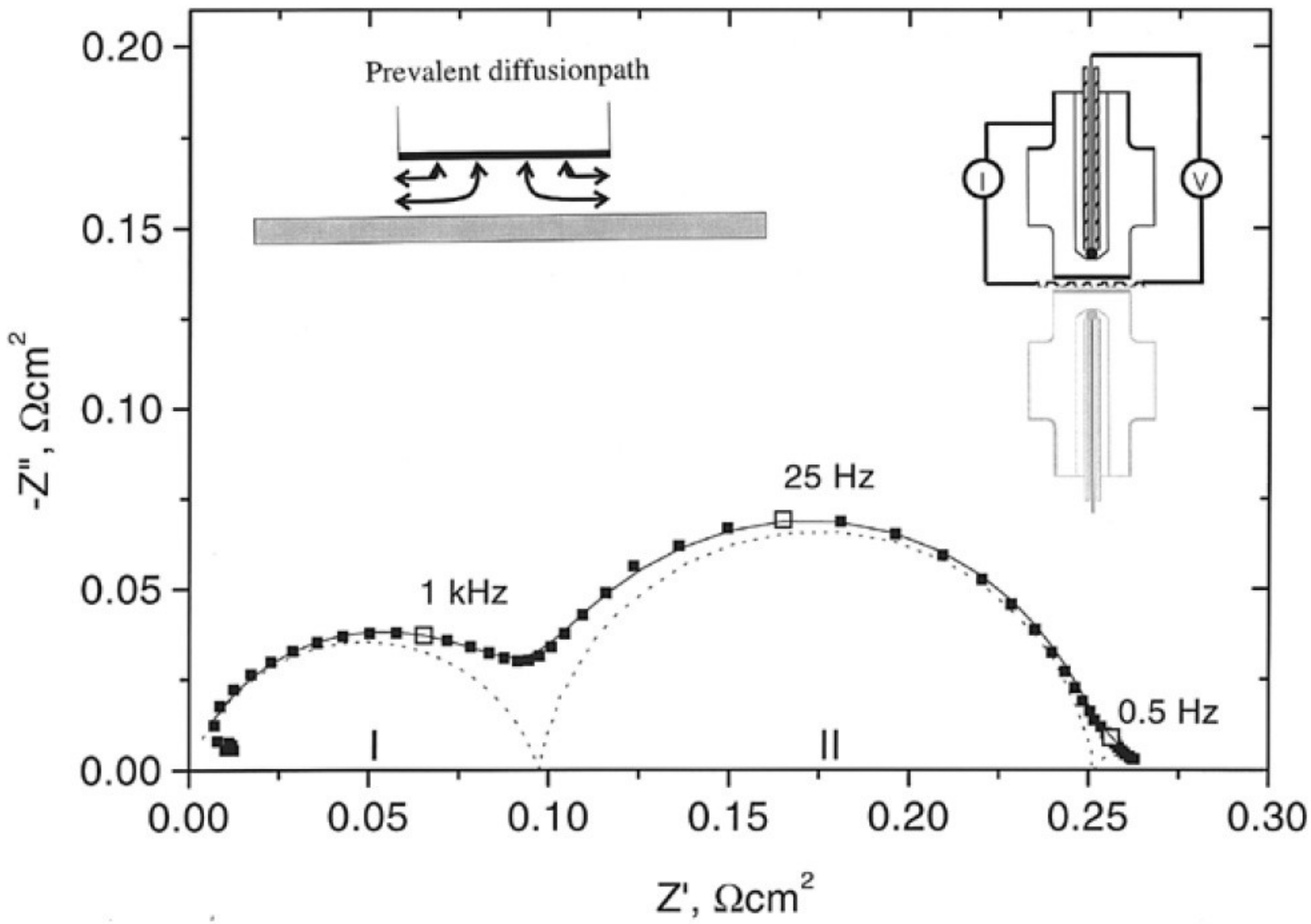
Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)



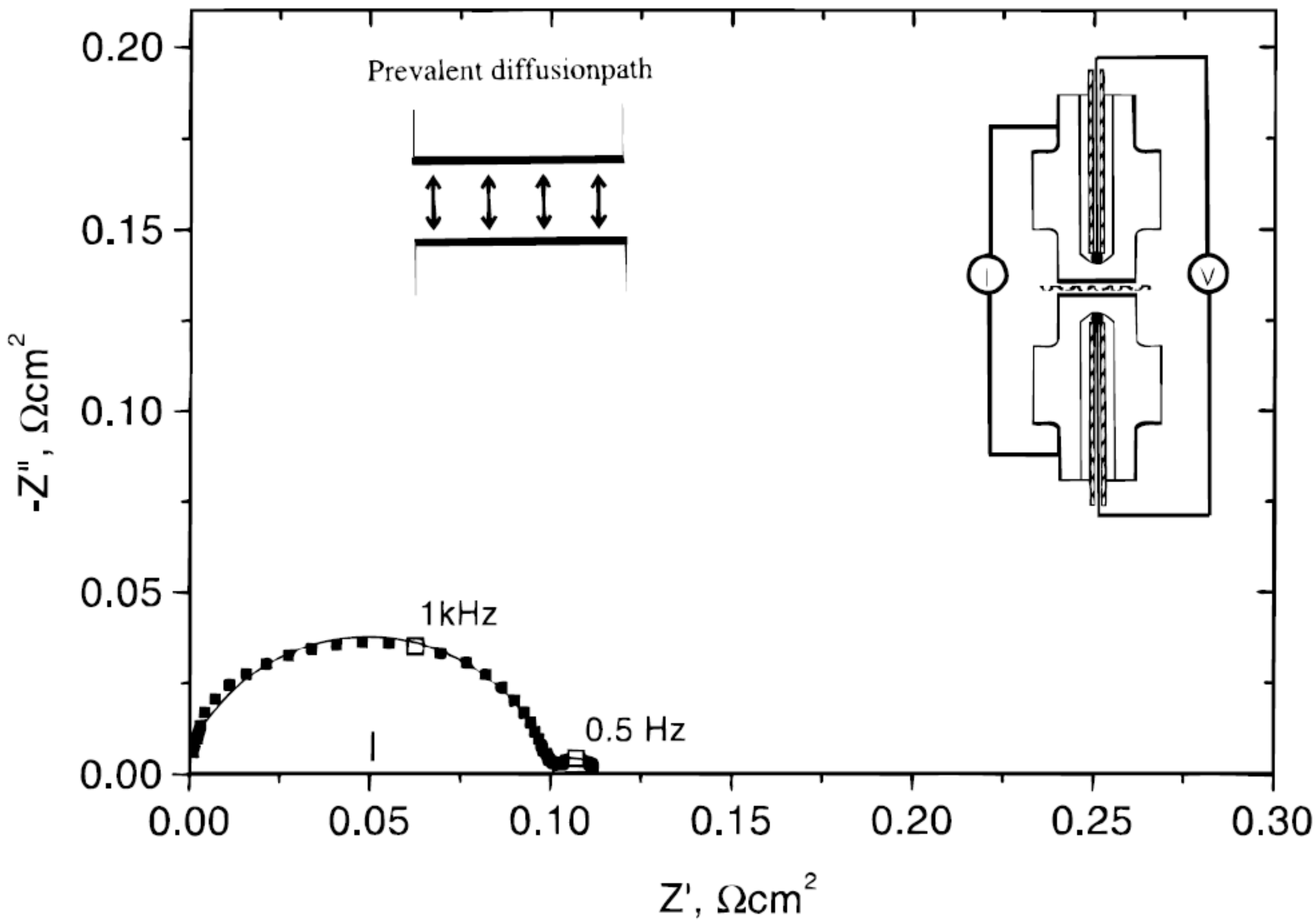
Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)



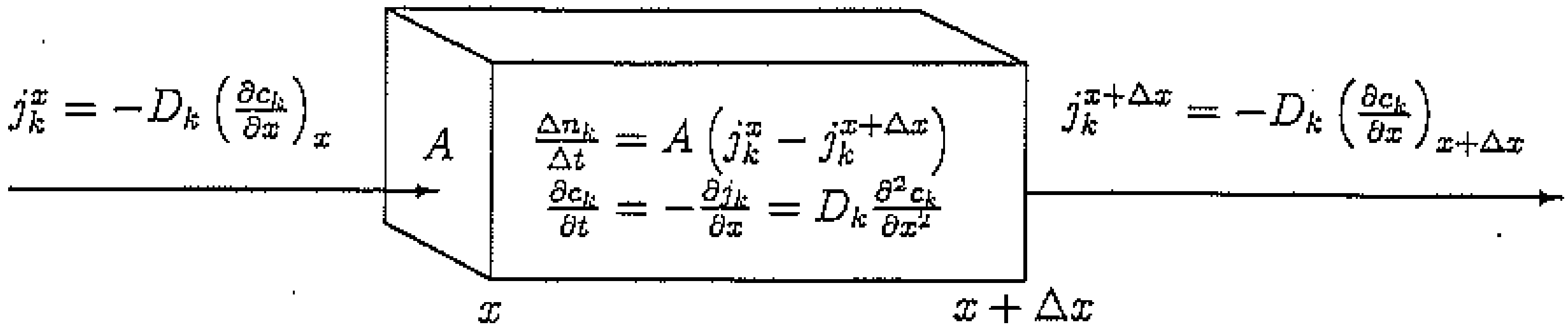
Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)



Gas Diffusion Impedance

Chapter 5.4 in: Atlung og Jacobsen. *Elektrokemi*, DTU, Lyngby DK (2005)



$$\frac{\partial c_k(t,x)}{\partial t} = D_k \frac{\partial^2 c_k(t,x)}{\partial x^2}$$

Gas Diffusion Impedance

Chapter 5.4 in: Atlung og Jacobsen. *Elektrokemi*, DTU, Lyngby DK (2005)

$$Z_d = \frac{\eta_d}{i} = \frac{RT\delta}{n^2F^2}\left(\sum \frac{\nu_j^2}{D_j c_j^o} \frac{\tanh\left[\delta\sqrt{\frac{\jmath\omega}{D_j}}\right]}{\delta\sqrt{\frac{\jmath\omega}{D_j}}}\right)$$

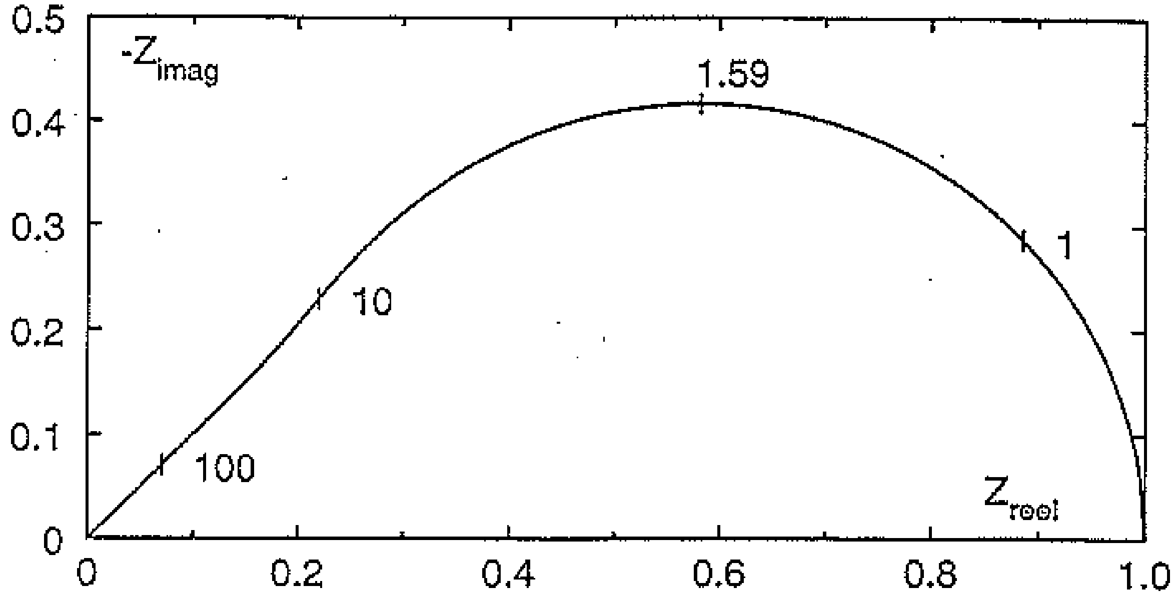
$$Z_d = \frac{RT\delta}{n^2F^2}\left(\sum \frac{\nu_j^2}{D_j c_j^o} \frac{1}{\delta\sqrt{\frac{\jmath\omega}{D_j}}}\right)$$

$$\sum \nu_k R_k \rightleftharpoons \sum \nu_l X_l + ne^-$$

$$\frac{\partial \Delta c_j}{\partial t} = D_j \frac{\partial^2 \Delta c_j}{\partial x^2}$$

Gas Diffusion Impedance

Chapter 5.4 in: Atlung og Jacobsen. *Elektrokemi*, DTU, Lyngby DK (2005)



Figur 5.12: Diffusionsimpedans, $Z_{d,j} / \frac{RT\delta\nu_j^2}{n^2F^2D_jc_j^o} = \frac{\tanh\left[\delta\sqrt{\frac{j\omega}{D_j}}\right]}{\delta\sqrt{\frac{j\omega}{D_j}}}$, afbildet i den komplekse plan. Talværdierne angiver parameteren $\delta\sqrt{\frac{\omega}{D_j}}$.

Gas Diffusion Impedance

Primdahl and Mogensen. *JES* **146**, 2827 (1999)

- Exercises
  - 1. Figure 7 (Primdahl, Diffusion, *JES*, **146**, 2827 (1999)) show a linear dependency of the gas resistance. Why is it linear?
  - 2. Read the appendix (Primdahl, Diffusion-paper)