

Lecture 5. Impedance spectroscopy

MIT Student

Last time we talked about the non-linear response to DC voltage, and today we will discuss about the AC linear response at frequency ω . A simplified model of voltage response of galvanic cell can be written as

$$V(I,Q)=V_0(Q)-\eta(I,Q)$$

If we consider small perturbations around a reference state (constant current), voltage, current and charge can be expressed as

$$\Delta V=V-V_{\text{ref}}$$

$$\Delta I=I-I_{\text{ref}}$$

$$\Delta Q=Q-Q_{\text{ref}}$$

Since we are assuming small changes (perturbation), we can use Taylor expansion to express voltage,

$$\Delta V \simeq \frac{\Delta Q}{C_{\text{ref}}} + R_{\text{ref}}\Delta I \dots(1)$$

where $\frac{1}{C_{\text{ref}}} = \left(\frac{\partial V}{\partial Q}\right)_{I_{\text{ref}},Q_{\text{ref}}} = \left(\frac{\partial V_0}{\partial Q}\right)_{I_{\text{ref}},Q_{\text{ref}}} - \left(\frac{\partial \eta}{\partial Q}\right)_{I_{\text{ref}},Q_{\text{ref}}}$, C_{ref} = differential capacitance

$$R_{\text{ref}} = \left(\frac{\partial V}{\partial I}\right)_{I_{\text{ref}},Q_{\text{ref}}} = -\left(\frac{\partial \eta}{\partial I}\right)_{I_{\text{ref}},Q_{\text{ref}}}, R_{\text{ref}} = \text{differential resistance}$$

$$\Delta I = \left(\frac{\partial \Delta Q}{\partial t}\right)$$

Consider alternating-current (AC) sinusoidal perturbations at frequency ω and introduce complex amplitudes for the perturbations (to induce phase lag):

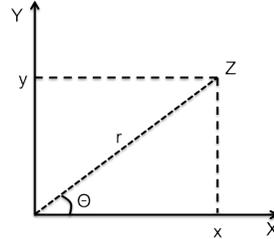
$$\Delta V = \text{Re}(\mathbf{V}e^{i\omega t}) = V\cos(\omega t); \text{ chose } t \text{ to fit real number for } \Delta V, \mathbf{V}: \text{real number}$$

$$\Delta I = \operatorname{Re}(I e^{i\omega t}) = |I| \cos(\omega t + \varphi)$$

$$\Delta Q = \operatorname{Re}(Q e^{i\omega t}), \text{ where } I = i\omega Q \text{ since } \Delta I = \left(\frac{\partial \Delta Q}{\partial t}\right)$$

Note: $z = x + iy = r e^{i\theta}$ ($e^{i\theta} = \cos\theta + i\sin\theta$),

$$r = \sqrt{x^2 + y^2} = |z|, \theta = \arg(z)$$



From equation (1), we have our series RC circuit and for the same ω , time dependence disappears:

$$V \simeq \frac{Q}{C_{\text{ref}}} + R_{\text{ref}} i\omega Q = \frac{I}{i\omega C_0} + R_0 I$$

To characterize AC linear response, we use following variables,

Impedance, $Z = \frac{V}{I} = \frac{V}{|I|} e^{-i\varphi}$, (φ = angle of phase lag of current behind voltage) this expression is complex generalization of resistance for linear AC current.

Admittance, $Y = \frac{1}{Z} = \frac{I}{V}$ this expression is the generalization of conductance.

Complex capacitance, $C = \frac{Q}{V}$

To express the total impedance of circuit, it is importance to separate the circuit into parallel part and series part. To start with simple examples, let's consider two simple extremes of circuit, parallel and series.

(1) Series RC circuit



$$\mathbf{Z} = R_{\text{ref}} + \frac{1}{i\omega C_{\text{ref}}} \quad \tilde{\mathbf{Z}} = 1 + \frac{1}{i\tilde{\omega}}$$

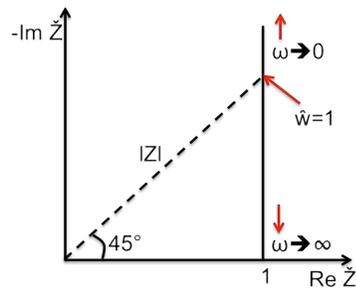
$$\mathbf{Y} = \frac{i\omega C_{\text{ref}}}{1+i\omega R_{\text{ref}}C_{\text{ref}}} \quad \tilde{\mathbf{Y}} = \frac{i\tilde{\omega}}{1+i\tilde{\omega}}$$

$$\mathbf{C} = \frac{C_{\text{ref}}}{1+i\omega R_{\text{ref}}C_{\text{ref}}} \quad \tilde{\mathbf{C}} = \frac{1}{1+i\tilde{\omega}}$$

(dimensionless form : $\tilde{\omega} = \omega R_{\text{ref}} C_{\text{ref}}$, $\tilde{\mathbf{Z}} = \frac{\mathbf{Z}}{R_{\text{ref}}}$, $\tilde{\mathbf{Y}} = \mathbf{Y} R_{\text{ref}}$, $\tilde{\mathbf{C}} = \frac{\mathbf{C}}{C_{\text{ref}}}$)

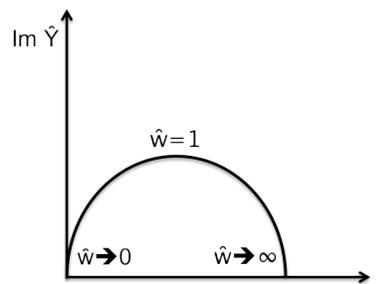
There are two ways to represent “impedance spectra”. First one is Nyquist Plot, representing $Z(\omega)$ in complex plane. Second one is Bode plot and it is beneficial to scale view.

(a) Nyquist plot (series RC circuit)



$\tilde{Z}, \tilde{\omega}$ are dimensionless forms

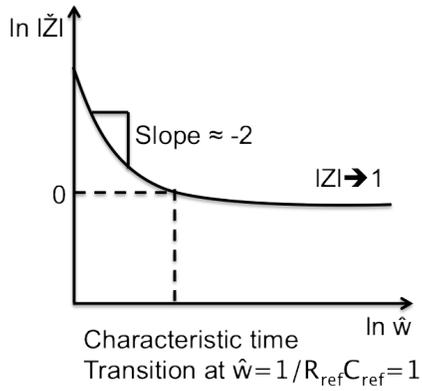
$$\mathbf{Z} = \frac{V}{|I|} e^{-i\varphi}, \quad \tilde{\mathbf{Z}} = 1 + \frac{1}{i\tilde{\omega}} = 1 - i\frac{1}{\tilde{\omega}}$$



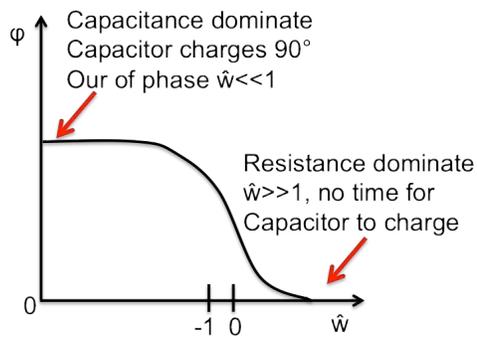
$\tilde{\mathbf{Y}}$ is dimensionless admittance

(b) Bode plot (series RC circuit)

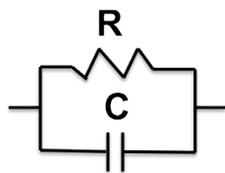
$$|\tilde{\mathbf{Z}}| = \sqrt{\tilde{\mathbf{Z}} \times \tilde{\mathbf{Z}}^*} = \sqrt{\left(1 + \frac{1}{i\tilde{\omega}}\right) \left(1 - \frac{1}{i\tilde{\omega}}\right)} = \sqrt{1 + \tilde{\omega}^{-2}}$$



$$\phi = -\arg(\tilde{Z}) = -\tan^{-1}\left(\frac{\text{Im}\tilde{Z}}{\text{Re}\tilde{Z}}\right) = \tan^{-1}\left(\frac{1}{\tilde{\omega}}\right)$$



(2) Parallel RC circuit

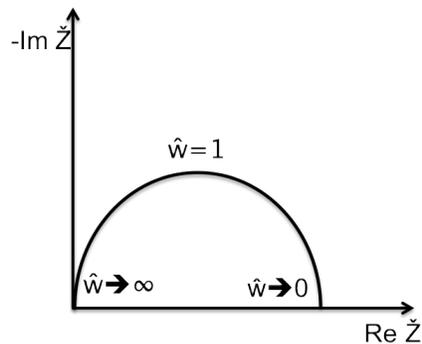


$$\tilde{Z} = \frac{1}{1+i\tilde{\omega}}$$

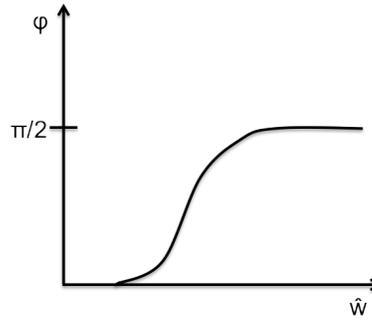
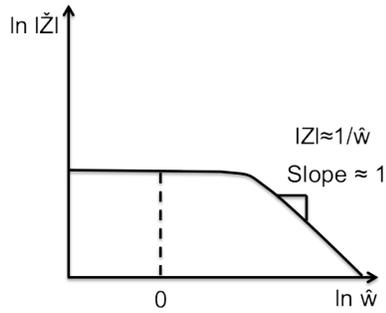
$$\tilde{Y} = 1 + i\tilde{\omega}$$

$$\tilde{C} = 1 + \frac{i}{\tilde{\omega}}$$

(a) Nyquist plot (parallel RC circuit)



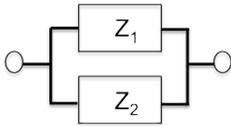
(b) Bode plot (parallel RC circuit)



Note: Using Kirchoff's circuit rules, it is easy to see that impedances can be combined just like resistances.



$$Z = Z_1 + Z_2 \text{ dominated by larger impedance}$$

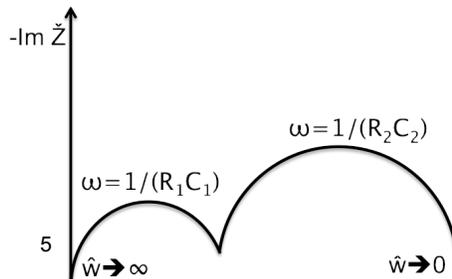
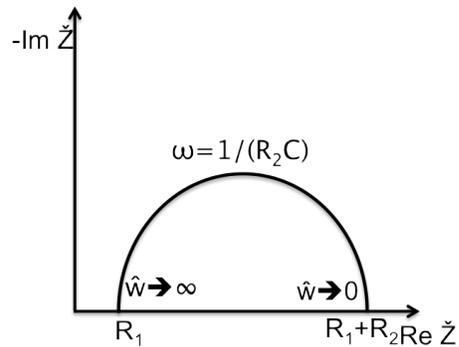
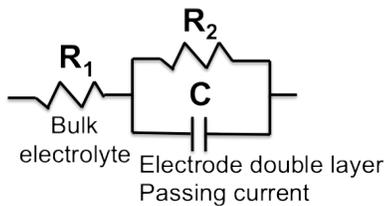


$$\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} \text{ dominated by smaller impedance}$$

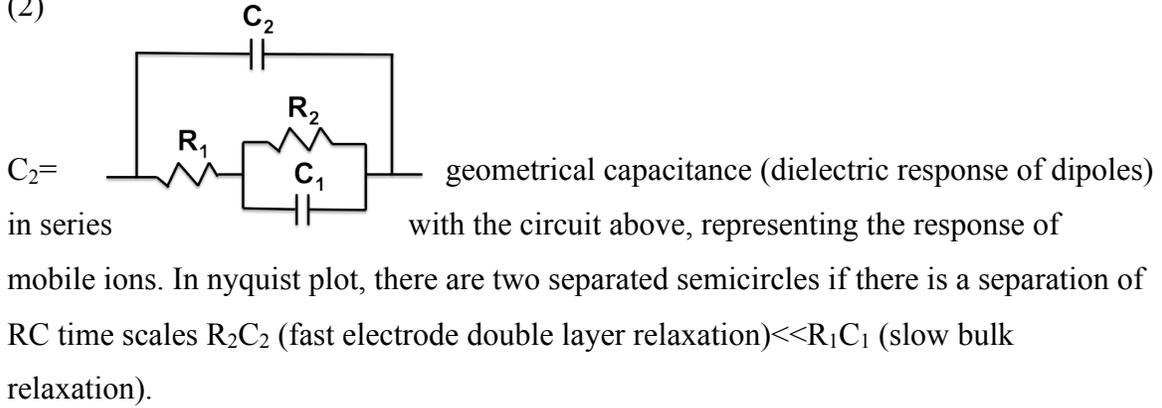
- Later, we will see that electrochemical double layers can be modeled as parallel RC circuit elements if Faradaic reactions occur.

By combining impedances in series and parallel, we can analyze more complicated circuits.

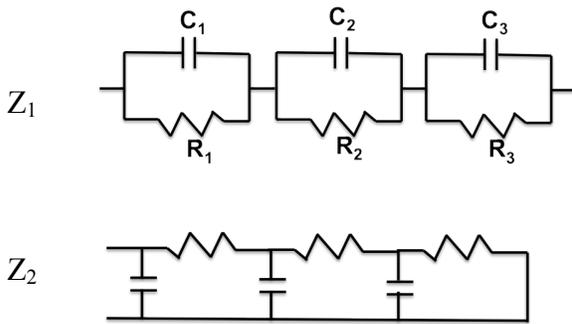
(1)



(2)

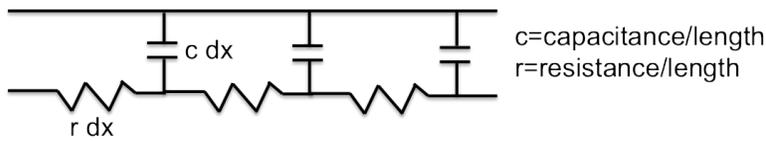


It is possible for different circuits to have the same impedance spectra $Z(\omega)$ for all frequencies (with suitable parameters). For examples,

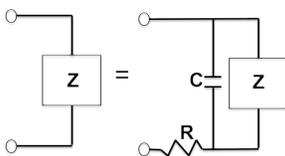


They have $Z_1(\omega) = Z_2(\omega)$. This makes it difficult to infer circuit models unambiguously from impedance data, without microscopic models or other types of measurements (e.g. nonlinear I-V response).

We have seen that blocking porous electrodes can be modeled as an RC transmission line



For an infinite transmission line, analyze this by recursion:



In the limit $dx \Rightarrow 0$, this yields the Warburg impedance, $Z_w = \frac{A}{\sqrt{i\omega}}$

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