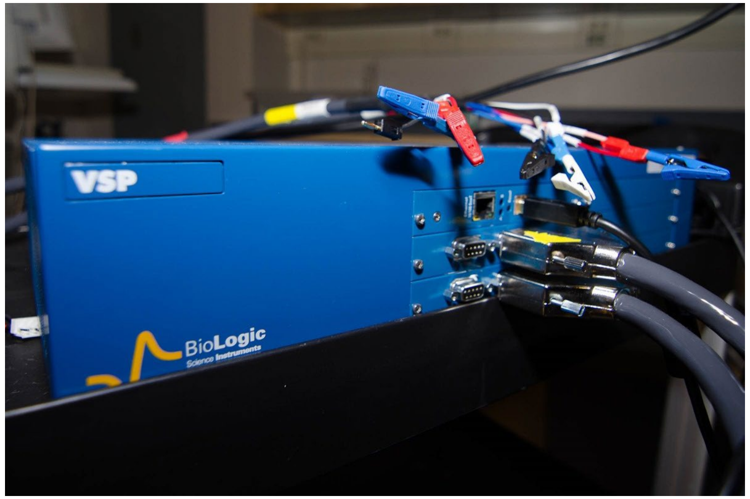
Impedance spectroscpy to extract kinetic parameters

The importance of EIS over other electrochemical techniques lies in its ability to discriminate and, thus, to provide a wealth of information for various electrical, electrochemical, and physical processes take place in a real electrochemical system. This task is very challenging as all these different processes exhibit different (from very fast to very slow) time behaviors.

Notably, EIS measurements at an electrochemical system can be simulated to an equivalent electrical circuit, which consists of common passive components (such as resistances, capacitors, and inductors) and others, more complicated (referred to as distributed) elements,

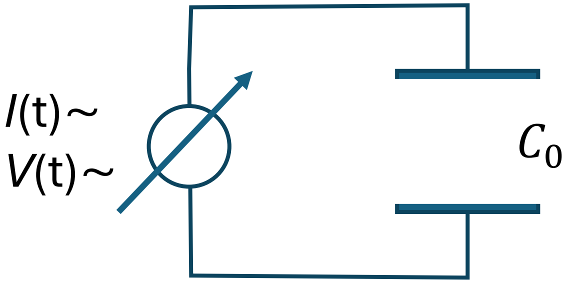


The frequency range in most of the commercially available electrochemical analyzers spans from 10 μHz to 1 MHz

<u>Applications</u>: electrochemical cells in modern applications in corrosion science, fuel cells, lithium-ion batteries, photovoltaic cells, and (bio)sensing.

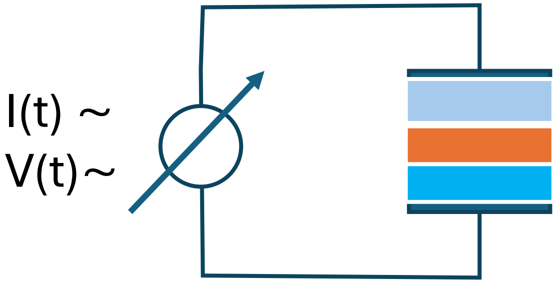
A. Lazanas et al., ACS Meas. Sci. Au 2023, 3, 162−193

Impedance spectroscpy to extract kinetic parameters



$$C_0 = \frac{\varepsilon_0 A}{d}$$

(phase lag of $^{\pi}/_{2}$)



$$\frac{1}{C_{tot}} = \sum_i \frac{1}{C_i}$$

In complex notation

$$V^*(\omega,t) = V_0\ e^{i\omega t}$$

$$I^*(\omega,t) = I_0\ e^{i(\omega t-\varphi)}$$

⇒

$$Z^*(\omega,t) = \frac{V^*(\omega,t)}{I^*(\omega,t)} = \frac{V_0}{I_0} e^{i\varphi} = Z' + iZ''$$

$$Q(\omega,t) = C^* \cdot V^*(\omega,t)$$

$$I^*(\omega,t) = \frac{dQ}{dt} = C^* i\omega V^*(\omega,t)$$

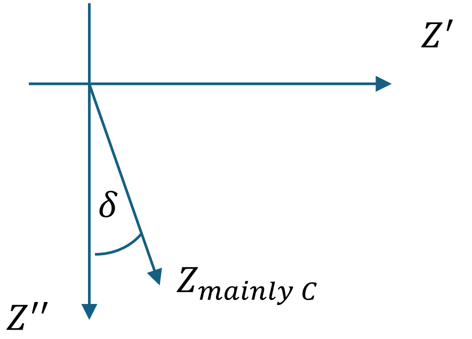
$$Z^*(\omega,t) = \frac{1}{i\omega C^*}$$

$$C^*(\omega,t) = \frac{1}{i\omega Z^*(\omega)}$$

⇒

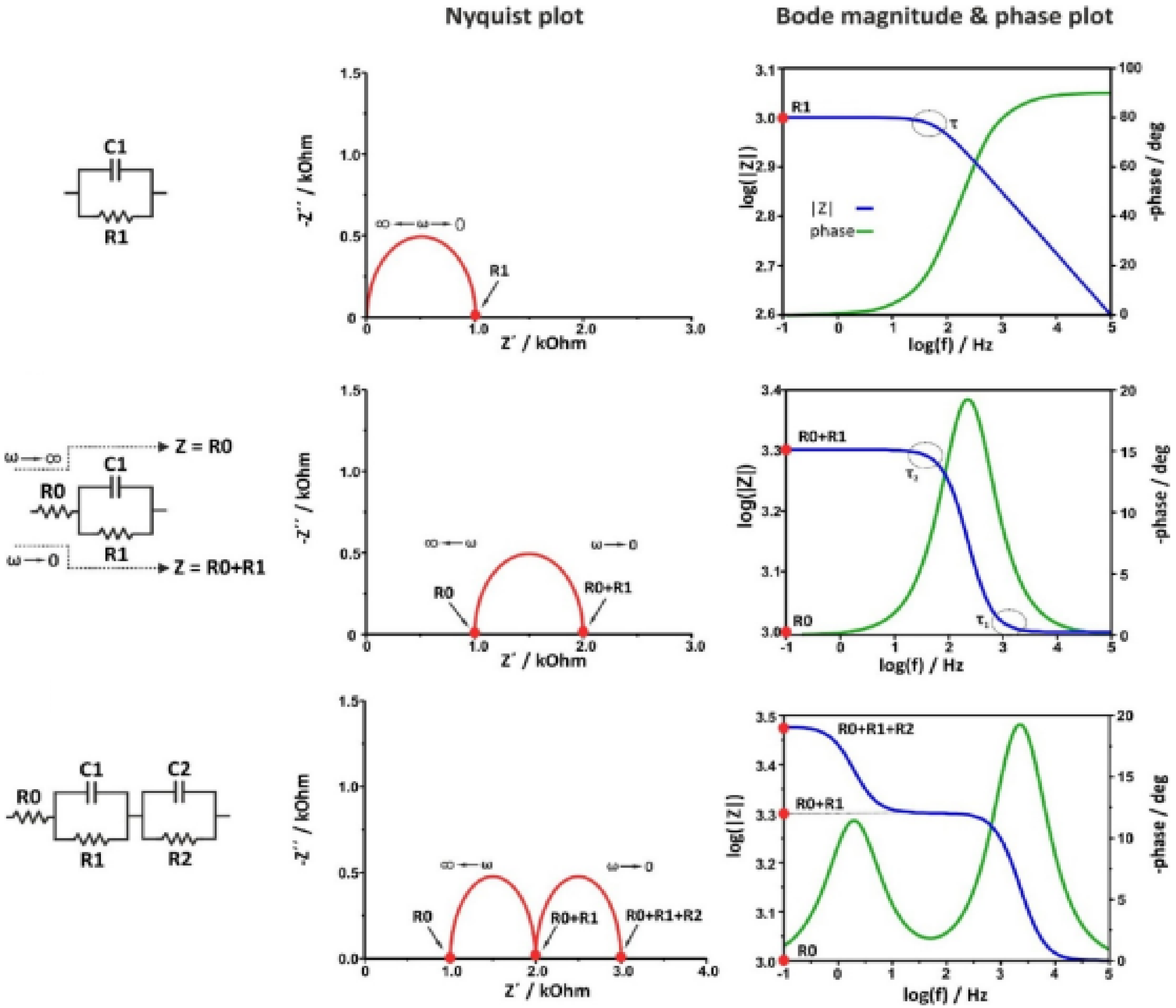
$$C'(\omega) = \frac{-Z''}{\omega|Z^*|^2}$$

$$C''(\omega) = \frac{Z'}{\omega|Z^*|^2}$$

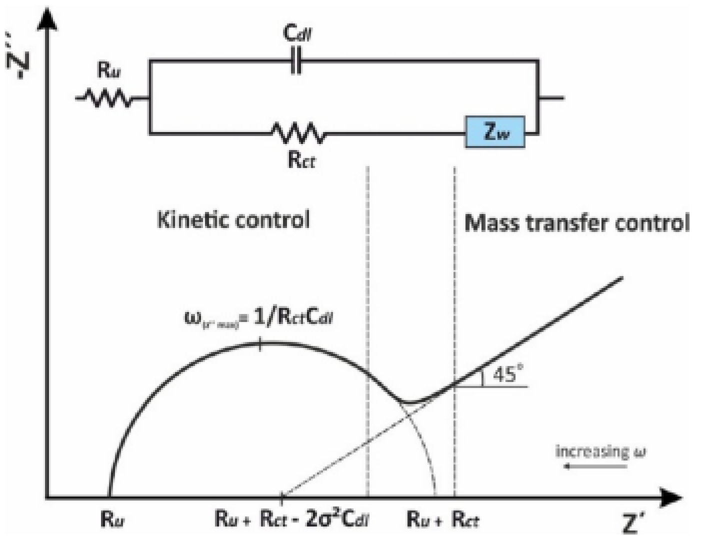


$$\boxed{\tan(\delta) = \frac{Z'}{Z''}}$$

Nyquist and Bode plots, for some typical circuit models



Warburg impedance, Z_w



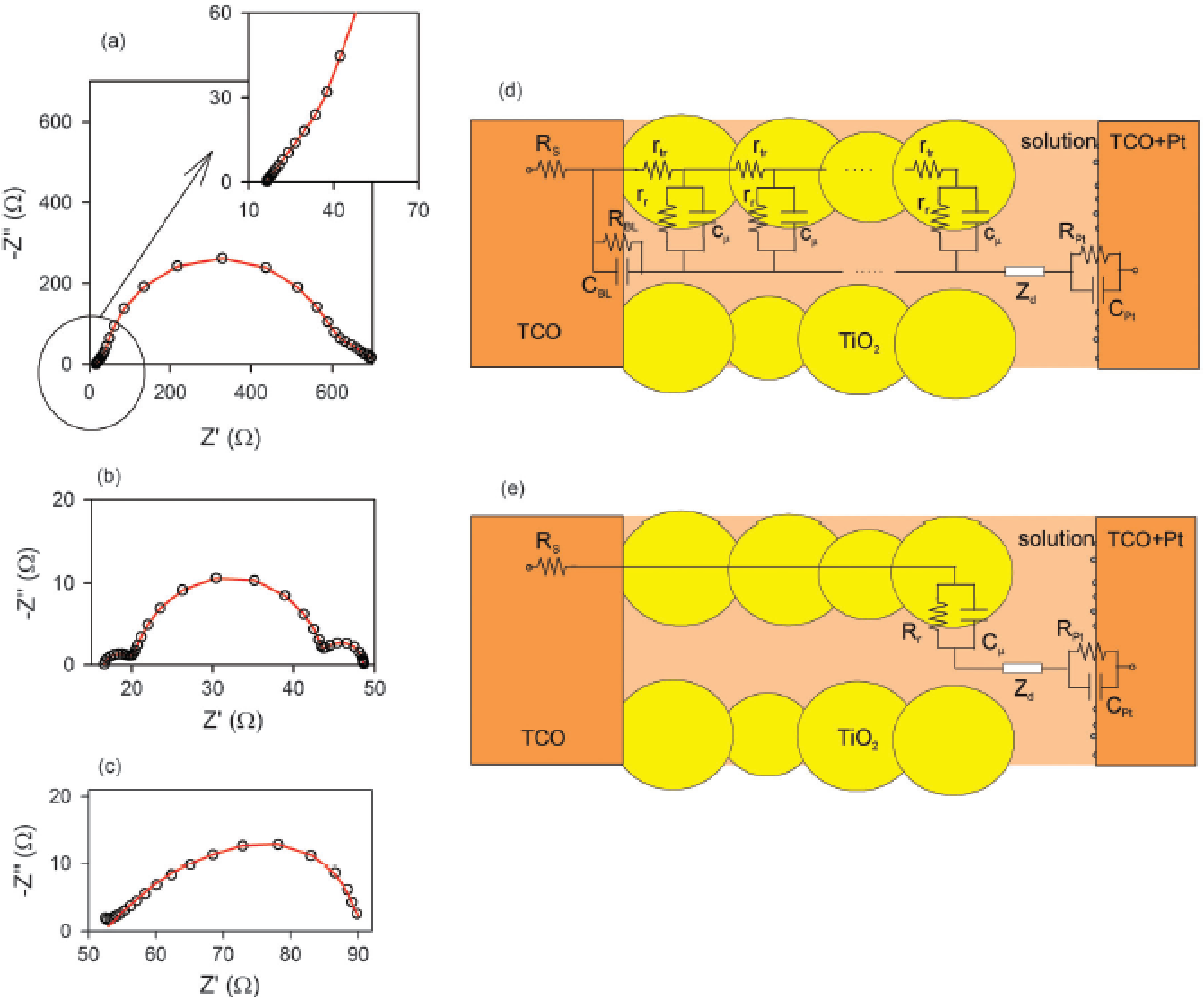
Z_W is a function of the diffusion constant

$$Z_W = \frac{RT}{n^2F^2\sqrt{2DC}}\left[\frac{1}{\sqrt{\omega}} - \frac{i}{\sqrt{\omega}}\right]$$

Time constant and maximum frequency

$$\omega_{max} = \frac{1}{RC} = \frac{1}{\tau}$$

Impedance spectra of a dye sensitized solar cell (DSSC)



F. Fabregat-Santiago et al., Phys. Chem. Chem. Phys., 2011, **13**, 9083–9118

Experimental impedance spectra of a DSC with an ionic liquid based electrolyte under illumination at

(a) At 0.40 V
(b) Open circuit conditions, 0.65 V
(c) Impedance spectra of a defective cell
(d) The complete equivalent circuit model to fit experimental data

At the open circuit voltage (Figure b) the following assignment can be made:

- High frequency arc due to the counter-electrode charge transfer resistance and the associated CPt.
- The second arc is due to the recombination resistance at the TiO2/electrolyte interface and the chemical capacitance of the TiO2.
- The low frequency arc is due to the impedance of diffusion in the electrolyte. The width of each of these arcs corresponds to RPt, Rrec and Rd, respectively, while the initial displacement of the arcs from the origin corresponds to the contribution from the FTO resistance RS.

Final Notes

The assignment of spectroscopic features in impedance spectroscopy needs to be backed by physical processes.

Kinetic rate equations allow to correlate rate constants of physical processes (recombination, transport, hopping, etc.) to the relaxation times obtained from impedance spectroscopy.

The modelling of impedance spectra by an equivalent circuit is not unique.