# 2.1 Fundamental AC impedance

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Alternating current impedance (AC impedance), also called electrochemical impedance spectroscopy (EIS), started from the prototypical experiment of faradaic impedance measurement, which is the resistance and capacitance at the surface of the electrode in an electrochemical cell. It is the measurement of the response of calculated impedance at each frequency with applied a small sinusoidal potential (or current) at fixed frequency. In Figure 1, a small sinusoidal potential signal is supplied by the waveform generator and then applied to the electrochemical cell through a potentiostat. The produced output signal of current (or potential) is converted through the i/E converter and lock-in amplifier to get the information of angular frequency ω, phase angle $\phi$, and a rotating vector (phasor).[1]

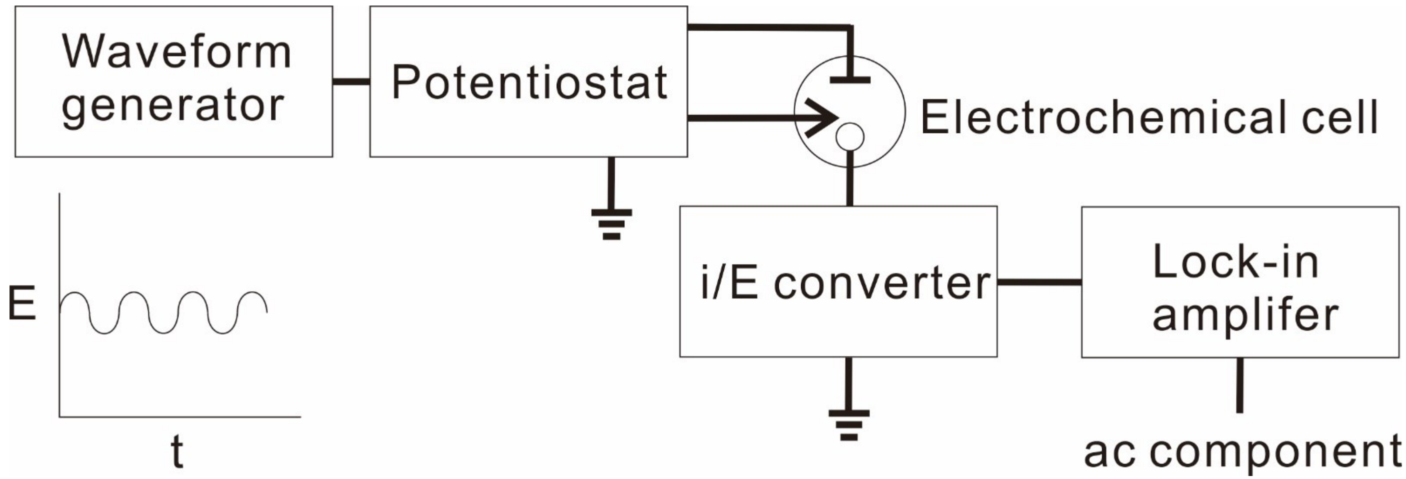



**Figure 1**. Schematic diagram of apparatus of AC impedance


References
(1)Allen J. Bard, Larry R. Faulkner, Electrochemical Methods and Applications 2nd, 2001

# 2.1.1 Fundamental AC circuits

As illustrated in electrochemical methods and applications, The electrochemical cell is considered as an equivalent circuit with applying a sinusoidal signal to measure the response. For a purely sinusoidal voltage, it can be presented as

$$e = E \sin \omega t$$

where ω is the angular frequency (2π times the conventional frequency in Hz), E is amplitude, and t is time. And resulting produced a current $\dot{I}$ which is a phasor as well as the potential $\dot{E}$, it is illustrated as

$$i = I \sin (\omega t + \phi)$$

The phasors $\dot{I}$ and $\dot{E}$, are separated by a phase angle, $\phi$. (see Figure 2) [1]

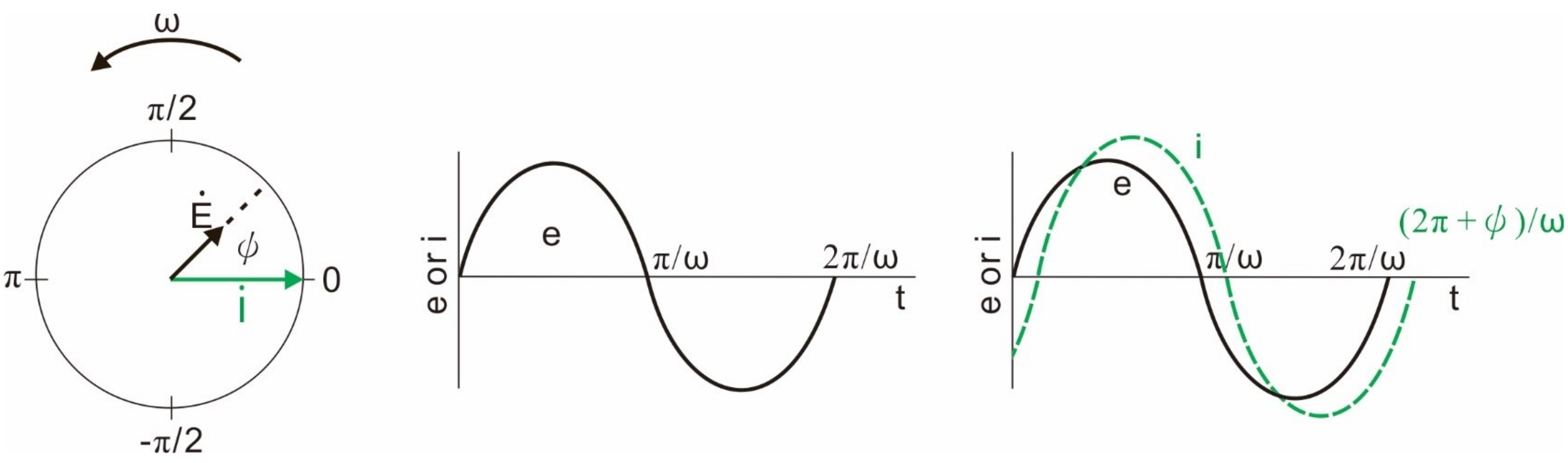



**Figure 2**. The phasor diagram of alternating voltage and alternating current.


References
(1)Allen J. Bard, Larry R. Faulkner, Electrochemical Methods and Applications 2nd, 2001

# 2.1.1 Fundamental AC circuits

As illustrated in electrochemical methods and applications, a simple circuit through a resistor with the phase angle of zero, its sinusoidal voltage is represented as $e = E \sin \omega t$, and the responded current is $(E/R) \sin \omega t$ which obeys the Ohm's law (see Figure 3(a)). While the voltage and current across the capacitor, the relation is described as $i = (E/X_c) \sin(\omega t + \pi/2)$, where Xc is the capacitive reactance, $1/\omega C$, and resulting the current leads the voltage as shown in Figure 3(b). In general, the impedance is divided into two parts, which are the real parts $Z_{Re}$ and imaginary parts $Z_{im}$ (multiplied by $j= \sqrt{-1}$) and thus is represented as $Z(\omega) = Z_{Re} - jZ_{Im.}$ [(1)]

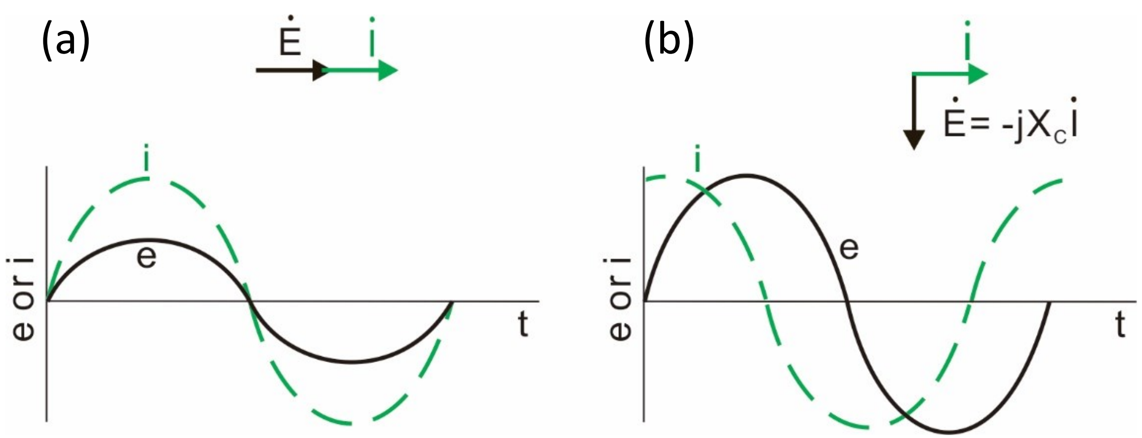
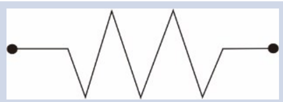
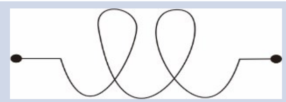
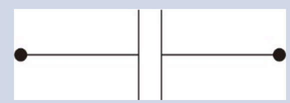



**Figure 3**. The diagram of voltage and current across through the resistor (a) and capacitor (b).


References
(1)Allen J. Bard, Larry R. Faulkner, Electrochemical Methods and Applications 2nd, 2001

## 2.1.2 Circuit Elements

The common existed in an equivalent electrical circuit are resistor, inductor, capacitor. In Table 1, it is illustrated that the circuit elements and its symbol, the impedance, and the relation between current and voltage.  The impedance of a resistor is independent of frequency with real part. The impedance of a inductor increases as frequency increases. It is with imaginary part, the through current is phase shifted $90^o$ to the voltage. The impedance of capacitor decreases as the frequency increases with an imaginary impedance component. The flowed through current is phase shifted $-90^o$ to the voltage.

| | Resistor | Inductor | Capacitor |
|---|---|---|---|
| Element |  |  |  |
| Current vs. Voltage | $E = IR$ | $E = L\frac{di}{dt}$ | $I = C\frac{dE}{dt}$ |
| Impedance | $Z = R$ | $Z = j\omega L$ | $Z = \frac{1}{j\omega C}$ |
| Phase shift | $0^o$ | $90^o$ | $-90^o$ |

References
(1)Allen J. Bard, Larry R. Faulkner, Electrochemical Methods and Applications 2nd, 2001

# 2.1.3 Nyquist plot and Bode plot for EIS

The EIS response can be represented as either a Nyquist plot, $Z_{im}$ vs. $Z_{Re}$ for different values of ω (see Figure 4 (A)), or a Bode plot, $\log|z|$ and phase angle $\phi$ are both plotted against log ω (see Figure 4(B). In Nyquist plot, it is plotted with higher frequency at left side of the plot, and it is for lower frequency on the right region. In Figure 4(A), the capacitance line in the Nyquist plot in the lower frequency region inclines constantly by an angle between 0° and 45°. $Z_{CPE} = 1/T(j\omega)\gamma$, where T represents a pure capacitor only when $\gamma = 1$, and γ is related to α by $\alpha = (1 - \gamma)90°$. So, $\alpha = 0$ and $\gamma = 1$ represents a perfect capacitor, and lower γ values directly reflect the roughness of the electrode. [1]

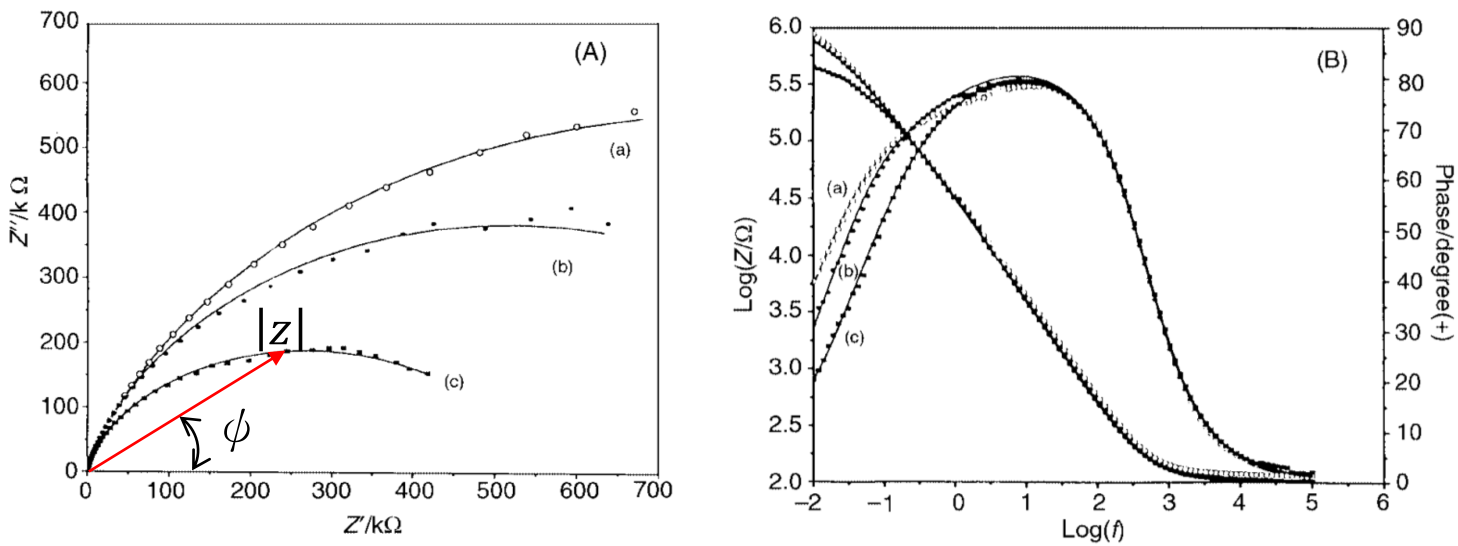



**Figure 4**. (A) Nyquist plots of impedance acquired in pH 5.5 PBS on GCE preanodized in 0.01 M $H_2SO_4$ (a), $Na_2SO_4$ (b) and HCl (c). (B) Bode's plots of the data presented in (A).

Reference
Jyh-Myng Zen,* Hsieh-Hsun Chung, Govindasamy Ilangovan and Annamalai Senthil Kumar, Analyst, 2000, 125, 1139–1146

# 2.1.4 Equivalent circuit of a cell

For the real system of the NCGCE/solution interface (see Figure 5(a)), It has been illustrated its performance by an equivalent circuit of resistors and capacitors which flowed current with the same amplitude and phase angle. The most common used model is called the Randles equivalent circuit as shown in Figure 5(b). The GCE/Nafion interface is represented by a constant phase element (CPE) in parallel connection with a charge-transfer resistance ($R_{ct}$), and pure capacitor ($C_{dl}$). The parallel combination of bulk resistance ($R_b$) and bulk capacitance ($C_b$) represents the bulk dielectric properties of Nafion. To maintain the electro neutrality within the Nafion film, the cations/anions extrude into the Nafion film. Thus, the circuit is accommodated by the inclusion of additional $R_{fs}$ and $C_{fs}$ in parallel combination. Finally, the circuit is terminated with the $R_s$ in serial connection, representing the solution resistance and uncompensated potential drop

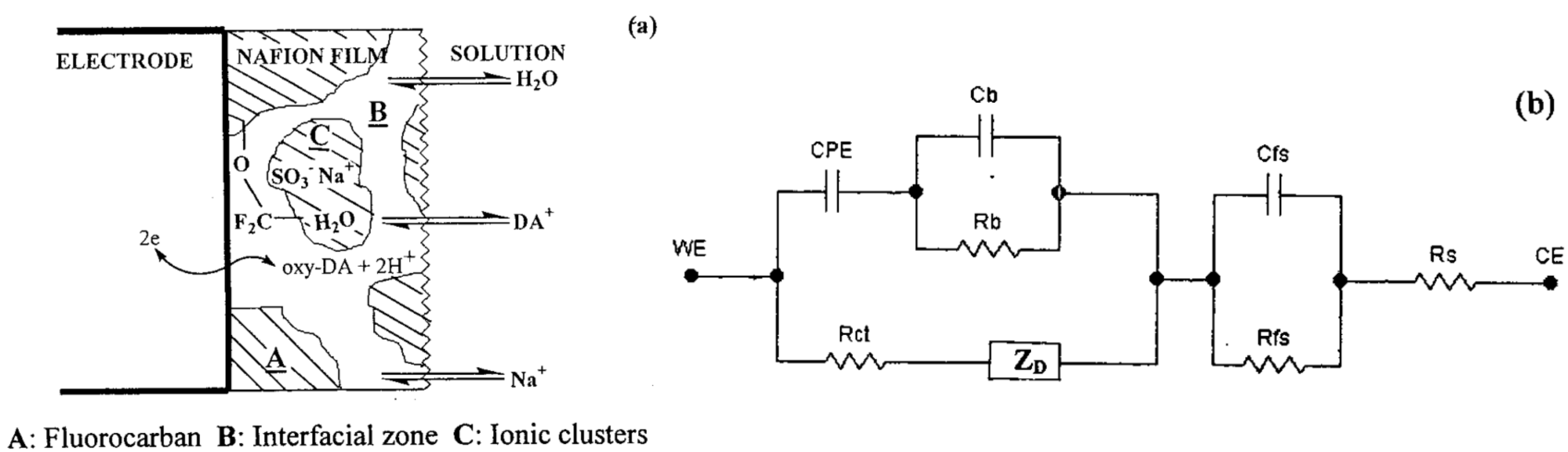



**Figure 5**. Schematic figure (a), equivalent circuit (b) of the NCGCE.

Reference
Jyh-Myng Zen,* Govindasamy Ilangovan, and Jia-Jen Jou, Anal. Chem. 1999, 71, 2797-2805

## 2.1.5 Impedance plot for an electrochemical system

As published, in the Nyquist plot (see Figure 6), the first semicircle appearing at a very high frequency domain represents the dielectric properties of Nafion while the second semicircle represents $R_{ct}$ and CPE. The straight line after these two semicircles arises due to the mass-transfer limitation of the redox that couples with a typical characteristic of 45$^{\circ}$ with respect to Z' axis. At low-frequency domain, a vertical line is observed due to the capacitance of the film. Apart from $Z_D$, all other components in the circuit are assumed independent of frequency.

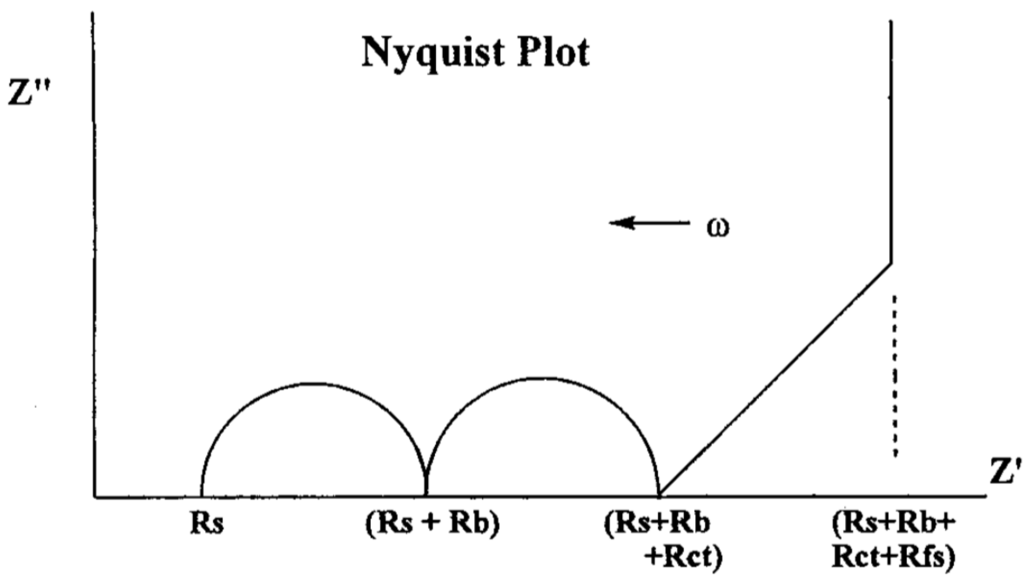



**Figure 6**. Schematic figure impedance spectrum of the NCGCE. Physicochemical characteristics modeled by different circuit components are specified in text. The value of n = 1 for CPE was used to simulate the Nyquist plot.


Reference
Jyh-Myng Zen,* Govindasamy Ilangovan, and Jia-Jen Jou, Anal. Chem. 1999, 71, 2797-2805