Lecture #11

Techniques based on concepts of impedance

By imposing potential sweeps, potential steps, or current steps, we typically drive the electrode to a condition far from equilibrium, and we observe the response, which is usually a transient signal. Another approach is to perturb the cell with an alternating signal of small magnitude and to observe the way in which the system follows the perturbation at steady state. Many advantages accrue to these techniques. Among the most important are (a) an experimental ability to make high-precision measurements because the response may be indefinitely steady and can therefore be averaged over a long term, (b) an ability to treat the response theoretically by linearized current-potential characteristics, and (c) measurement over a wide time (or frequency) range (10^4 to 10^{-6} s or 10^{-4} to 10^6 Hz). Since one usually works close to equilibrium, one often does not require detailed knowledge about the behaviours of the *i-E* response curve over great ranges of overpotential. This advantage leads to important simplifications in treating kinetics and diffusion [1].

EIS technique relies to the application of a small-amplitude stimulus (voltage or current), usually superimposed on a dc signal (voltage or current) to an electrochemical system and measurement of the resulting response (current or voltage, respectively) over a wide range of frequencies. It is essential that measurements are conducted by applying a small-amplitude perturbation in order to ensure a linear relationship between the applied signal and the response of the system.

However, as can be seen in Figure 1 A, the current−voltage relationship in real electrochemical cells is not linear.

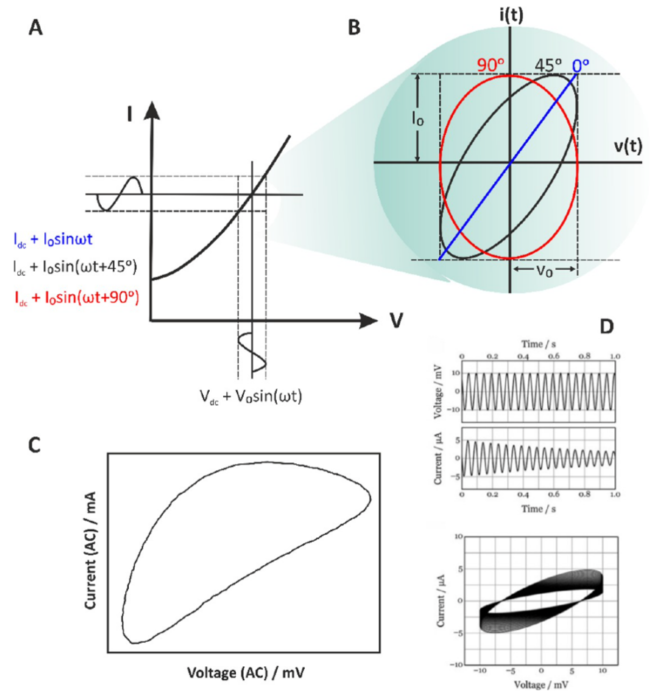

Figure 1. (A) Schematic representation of an electrochemical system's response to alow-amplitude (Vo) sinusoidal signal super imposed to a constant voltage Vdc and(B) the respective Lissajous plots if we consider that the phase shif tbetween the perturbating

and response alternating signals is 0°, 45°, or 90°. (C). A Lissajous plot showing a nonlinear response. Courtesy of Metrohm Autolab B.V. (D) Lissajous plots of a system interrogated with an ac voltage with amplitude±10mV, at 20Hz, where the amplitude of the current response decreases with time [2].

Measurements at a linear domain can sufficiently be approximated only by using a small-amplitude perturbation signal. Most of the available software in modern electrochemical analyzers provides at real time during the impedimetric measurements the so-called Lissajous plots that display the alternating voltage at the x-axis and the alternating current at the y-axis signals over time (Figure 1 B).

Depending on the magnitude of the signals and the phase difference between them, a typical oval plot is obtained. It turns out that when the phase difference is 0° or 90°, the plot appears as a diagonal or circle, respectively. The symmetry and the motion of the Lissajous plot over time indicate whether the electrochemical system conforms to the constrain of linearity (for nonlinear systems the shape of the plot is distorted) and time-invariance. To highlight the difference in the Lissajous plots. in the cases mentioned above, Figure 1C shows a nonlinear Lissajous plot with an apparent distorted shape, while Figure 1D shows an unstable Lissajous plot where the amplitude of the current response decreases over time.

In studying the stage of transfer of the electrochemical reaction charge, pulse potentiostatic and galvanostatic techniques and relaxation methods are used most often. The polarization measurements are accompanied by an electrochemical reaction which proceeds in the mixed kinetics mode; hence, this requires elimination of diffusion limitations. The method of impedance spectroscopy allows finding. the exchange current density (i_0) without introducing any corrections for concentration polarization [3].

From the results of impedance measurements, it is evident (Figure 2) that in the high-frequency range from 100 kHz to 49.4 Hz, this dependence represents a semi circumference, while in the low-frequency range from 5.2 to 0.1 Hz, a linear dependence corresponding to the Warburg impedance can be seen. The equivalent circuit contains the electric-double-layer capacitance (C_{EDL}- CPE), the solution resistance (R_s), the charge-transfer resistance (R_{ct}), the Gerischer impedance (G), and the Warburg impedance (W) (Figure 2, insert).

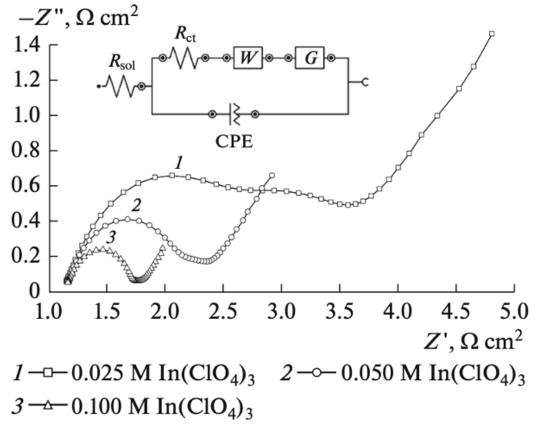

Figure 2. Experimental impedance diagrams at 25°C on In electrode in 2.0 M NaCl solution with different content of $In(ClO_4)_3$. Insert: equivalent circuit of electrochemical cell.

References

1. Bard, Allen J., Larry R. Faulkner, and Henry S. White. Electrochemical methods: fundamentals and applications. John Wiley & Sons, 2022.
2. Lazanas, Alexandros Ch, and Mamas I. Prodromidis. "Electrochemical impedance spectroscopy─ a tutorial." *ACS measurement science au* 3.3 (2023): 162-193.
3. Avchukir, Kh, et al. "The kinetics of indium electroreduction from chloride solutions." Russian Journal of Electrochemistry 54.12 (2018): 1096-1103.