Fundamentals of the Electrode–Solution Interface

Lecture 2 | Charge transfer and the electrical double layer

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Discipline: Modern research methods in electrochemistry

Educational program: 7M05301 Chemistry

Lecturer: Khaisa Avchukir, PhD, Acting Associate Professor

Avchukir Khaisa © 2025

Purpose and learning outcomes

PURPOSE

Explain how charge is stored and transferred at electrode–electrolyte interfaces, and how these processes influence electrochemical measurements.

BY THE END, STUDENTS CAN

- Distinguish faradaic and nonfaradaic currents
- Describe the electrical double layer
- Interpret charge-transfer driving forces
- Estimate capacitive currents and charge
- Identify interfacial contributions in CV and EIS

Avchukir Khaisa © 2025

Lecture trajectory: from interface to measurement

01

Interfacial structure

Surface charge, ions, solvent

02

Nonfaradaic response

Double-layer charging

03

Faradaic response

Electron transfer and kinetics

04

Measurement signatures

CV, transients and EIS

APPLICATION: separate charging artefacts from reaction kinetics to design more reliable experiments.

Avchukir Khaisa © 2025

Two pathways for current at an electrode

NONFARADAIC

No net electron transfer across the interface.

Double-layer charging, ion rearrangement, adsorption/desorption.

Transient current may flow after a potential change.

FARADAIC

Electrons cross the electrode–solution interface and drive oxidation or reduction.

Example: $Fc^{+} + e^{-} \rightleftharpoons Fc$

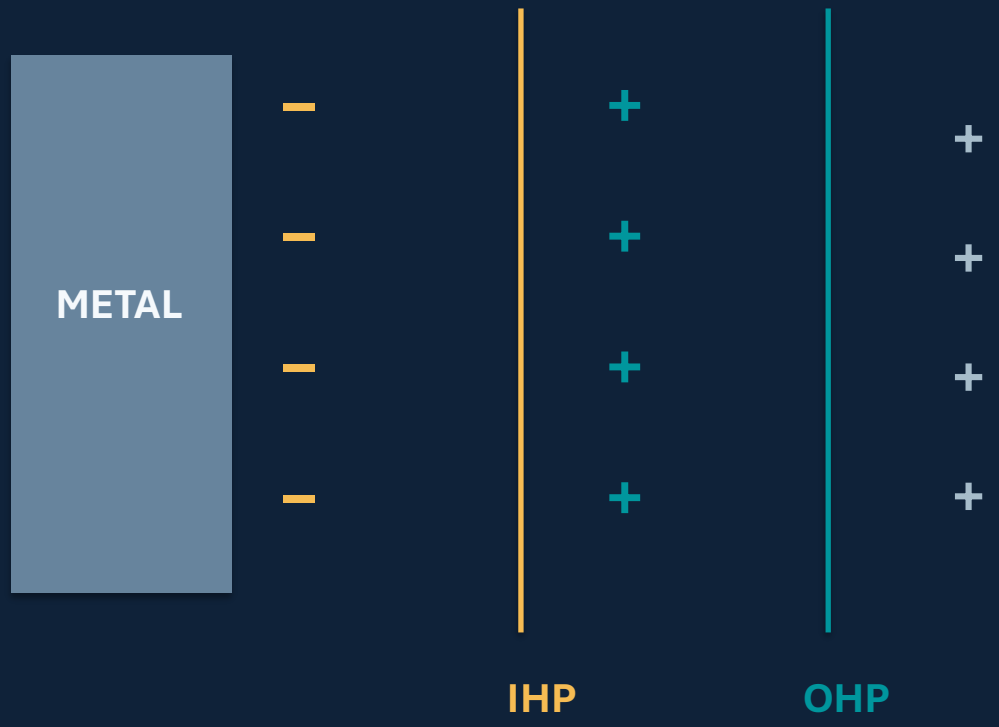
Current depends on kinetics and mass transport.

Measured current: $i_{total} = i_F + i_C$ (plus possible other interfacial contributions)

Avchukir Khaisa © 2025

Electrical double layer: structure and charge

At equilibrium, excess metal charge is balanced by opposite charge in the electrolyte: $q_M + q_S = 0$.



INTERPRETATION

IHP: specifically adsorbed species / oriented solvent.

OHP: closest approach of solvated ions.

Beyond OHP: diffuse ionic layer.

Layer structure depends on electrolyte, potential and adsorption.

Avchukir Khaisa © 2025

Capacitance and nonfaradaic charging

CORE RELATIONSHIPS

For constant capacitance: $Q = C_{dl}\,\Delta E$

General differential definition:

$C_{dl} = dQ/dE$

Charging current: $i_C = dQ/dt$

If C_{dl} is constant: $i_C = C_{dl}\,v$

where $v = dE/dt$ (scan rate).

EXAMPLE

Electrode area: 0.20 cm^2

Specific capacitance: 20 µF cm^{-2}

Scan rate: 0.10 V s^{-1}

C = 4.0 µF

i_C = 0.40 µA

Typical aqueous C_{dl}: ~10–40 µF cm^{-2}; strongly system-dependent.

Avchukir Khaisa © 2025

Faradaic charge transfer: Fc^+/Fc example

Homogeneous electron transfer

$$Fc^+ + Co(Cp^*)_2 \rightleftharpoons Fc + [Co(Cp^*)_2]^+$$

Heterogeneous electron transfer at an electrode

$$\mathbf{Fc^+ + e^- \rightleftharpoons Fc}$$

DRIVING FORCE

The applied electrode potential changes electron electrochemical potential and hence the driving force for oxidation or reduction. The observed rate also depends on interfacial kinetics and transport.

Avchukir Khaisa © 2025

Kinetics: equilibrium, overpotential and exchange current

BUTLER–VOLMER MODEL

$\eta = E - E_{eq}$

$i = i_0 [\exp(\alpha_a nF\eta/RT) - \exp(-\alpha_c nF\eta/RT)]$

i_0 is exchange current; α_a, α_c is transfer coefficients.

Valid under the model's kinetic assumptions; measured current can also be mass-transport limited.

READ THE EXPERIMENT

- $\eta = 0$: net faradaic current is zero at equilibrium.
- Positive / negative η favors opposing reaction directions.
- Larger i_0 generally indicates faster interfacial electron-transfer kinetics.
- Correct for iR drop before interpreting kinetic parameters.

Avchukir Khaisa © 2025

How the interface appears in CV and EIS

CYCLIC VOLTAMMETRY

Capacitive background scales approximately with scan rate: $i_C \propto v$.

A reversible diffusion-controlled redox peak typically scales as $i_p \propto v^{1/2}$.

Compare blank electrolyte and redox-containing solution; vary scan rate to distinguish contributions.

IMPEDANCE SPECTROSCOPY

Ideal Randles-type model:

$R_s + (C_{dl} \parallel R_{ct})$, optionally with diffusion impedance.

R_{ct} is charge-transfer resistance; C_{dl} is double-layer capacitance.

Real interfaces may require CPEs, adsorption or more complex models.

Avchukir Khaisa © 2025

Conclusions: key concepts to retain

01 The electrode interface stores charge in an electrical double layer.

02 Nonfaradaic currents can occur without net electron transfer.

03 Faradaic currents reflect redox reactions and are governed by kinetics and transport.

04 Potential controls driving force; electrolyte structure affects measured responses.

05 Combining CV, transients and EIS helps separate interfacial mechanisms.

Avchukir Khaisa © 2025

Homework and quantitative problems

1. Calculate charging current for $A = 0.50\ cm^2$, $C_{dl} = 25\ \mu F\ cm^{-2}$, and $v = 0.20\ V\ s^{-1}$.

2. An interface has $C = 8\ \mu F$. Estimate ΔQ for a 0.30 V potential step, assuming constant C.

3. Explain the physical meaning of IHP and OHP and how specific adsorption changes the double layer.

4. Design a CV experiment to distinguish double-layer charging from Fc^+/Fc electron transfer.

5. Discuss why an ideal capacitor may fail to represent a rough or heterogeneous electrode.

Reading: Bard, Faulkner & White, Electrochemical Methods (2022); Elgrishi et al., J. Chem. Educ. 95 (2018), 197–206.

Avchukir Khaisa © 2025