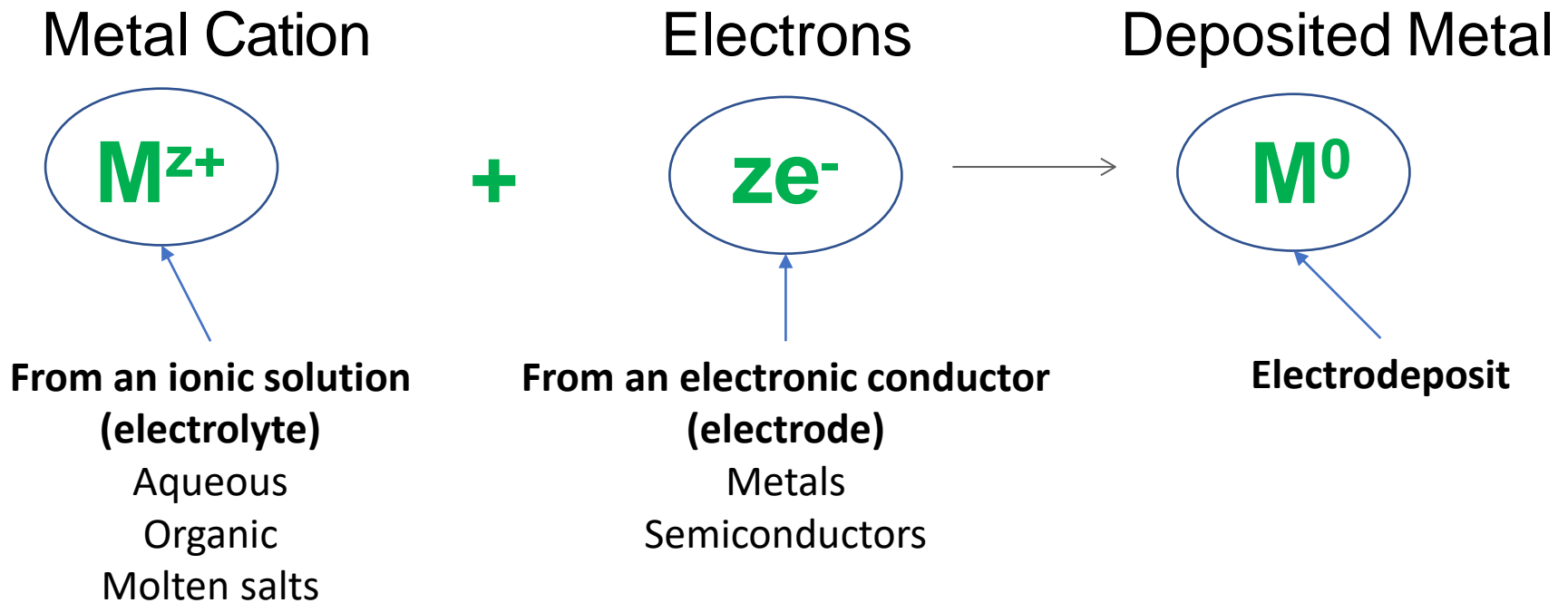


# 3 – Mechanistics and kinetics of electroplating

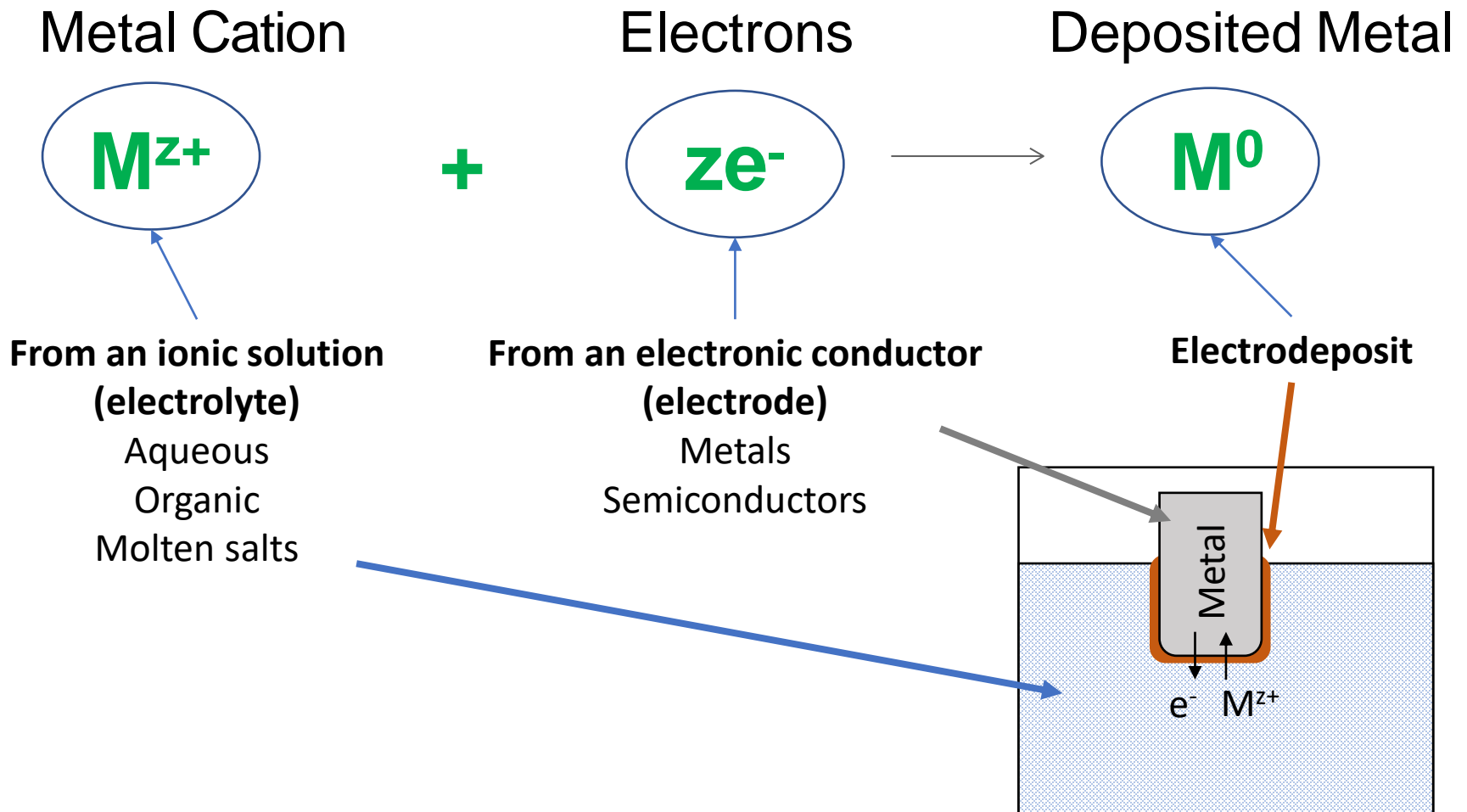
# 1) Electrodeposition process: an overview

## Reduction of metal ions from a solution



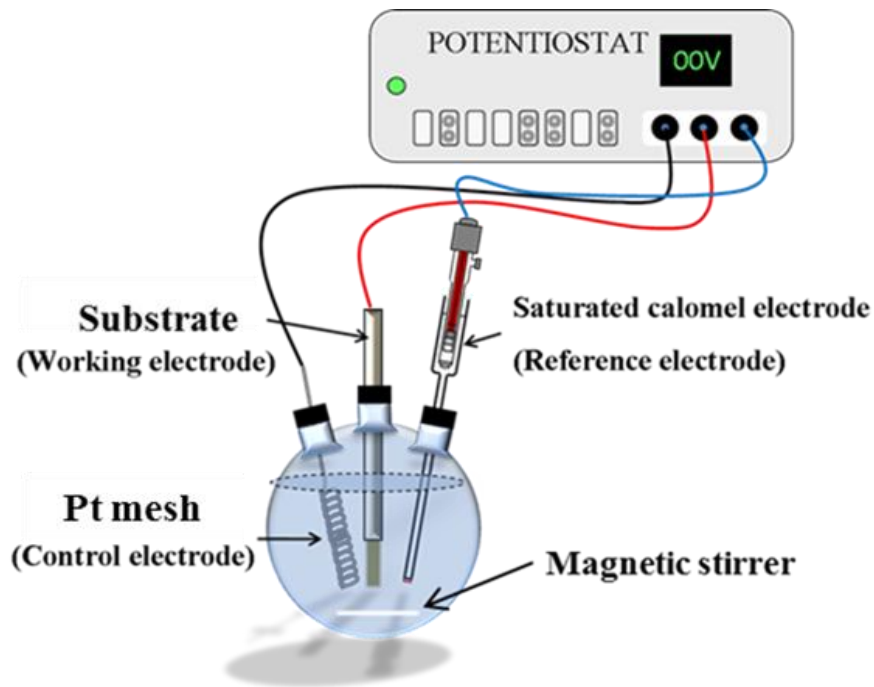
# 1) Electrodeposition process: an overview

## Reduction of metal ions from a solution



# 1) Electrodeposition process: an overview

## Typical 3-electrodes setup



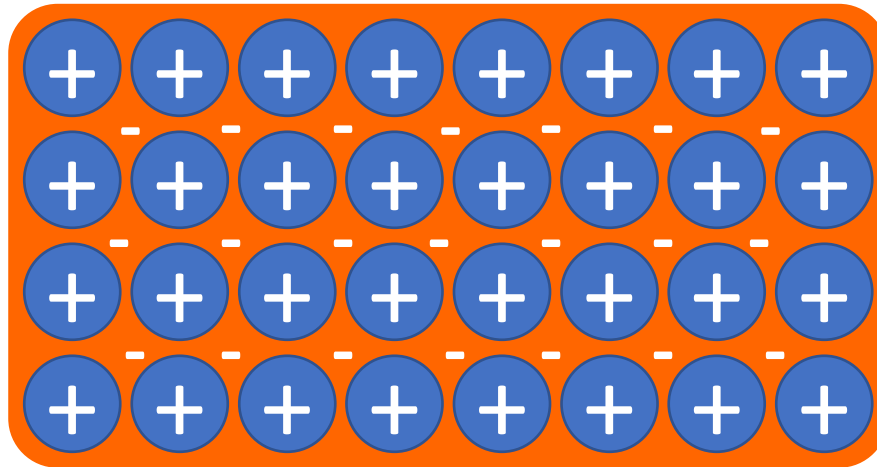
The current passes between the **working electrode** (cathode) and the **counter electrode** (anode)

The reference electrode measures the **substrate potential**

## II) Metals and metallic surfaces

### Metal M: Defects

A lattice of cations  $M^{z+}$  in a cloud of free electrons



About  $10^{22}$  atoms in  $1 \text{ cm}^3$  of metal  $\rightarrow$  large number  $\rightarrow$  unavoidable defects

Point defects (0D): vacancy defects, interstitial defects

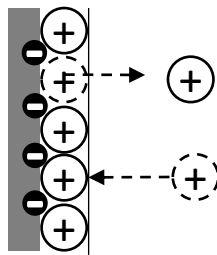
Line and planar defects: dislocations, grain and twin boundaries, stacking faults

### III) Metal-electrolyte interface

## Surface charge development

When immersed in an electrolyte, ions and dipoles will reorganize at the interface

1) There can be spontaneous exchanges of  $M^{z+}$  between the electrode and the electrolyte



If  $M^{z+}$  leaving the lattice  $>$   $M^{z+}$  bonding to the lattice

Metal develops an excess of negative charges

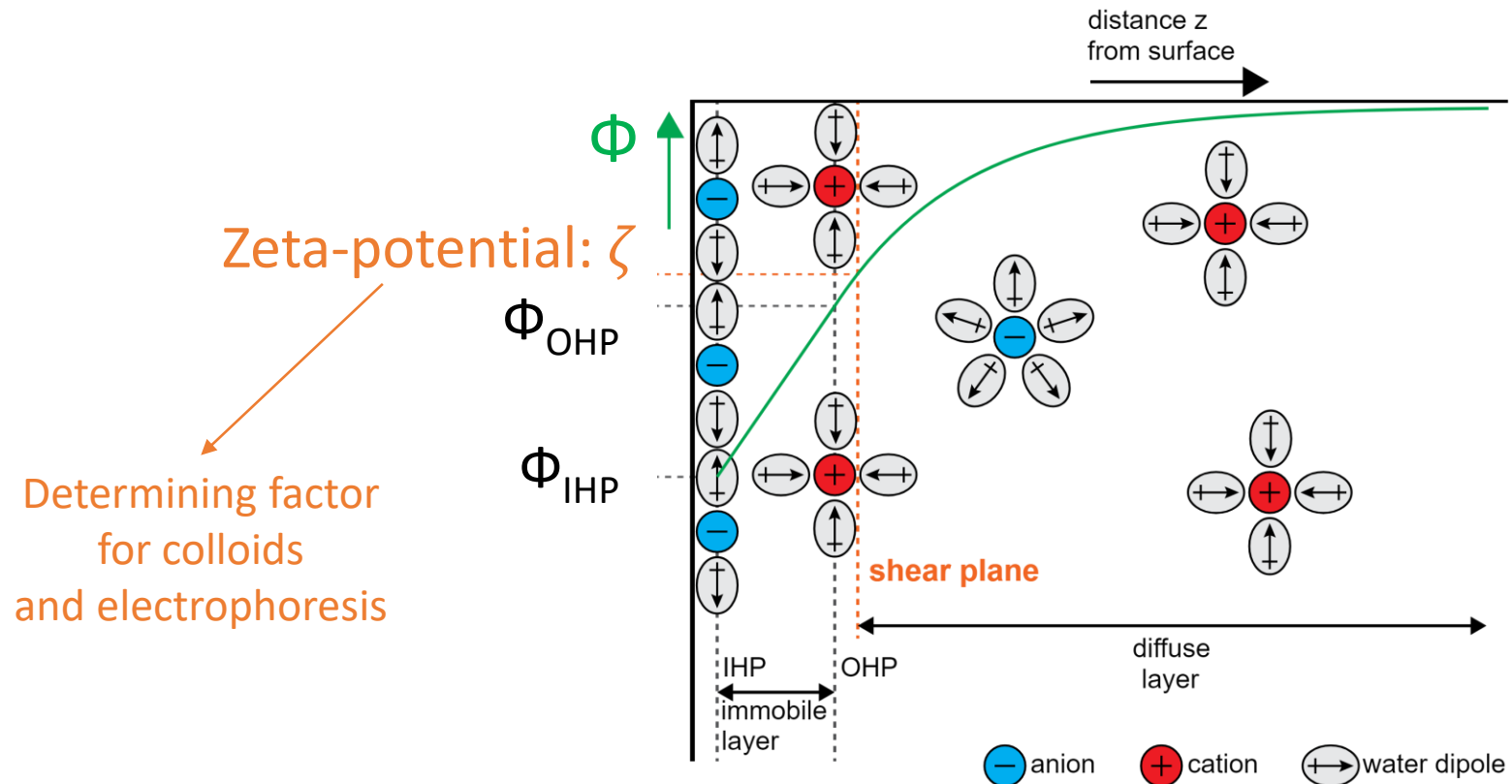
2) Reorientation of dipoles and redistribution of ions:

→ formation of an electrochemical double layer

# III) Metal-electrolyte interface

## Grahame model (1947):

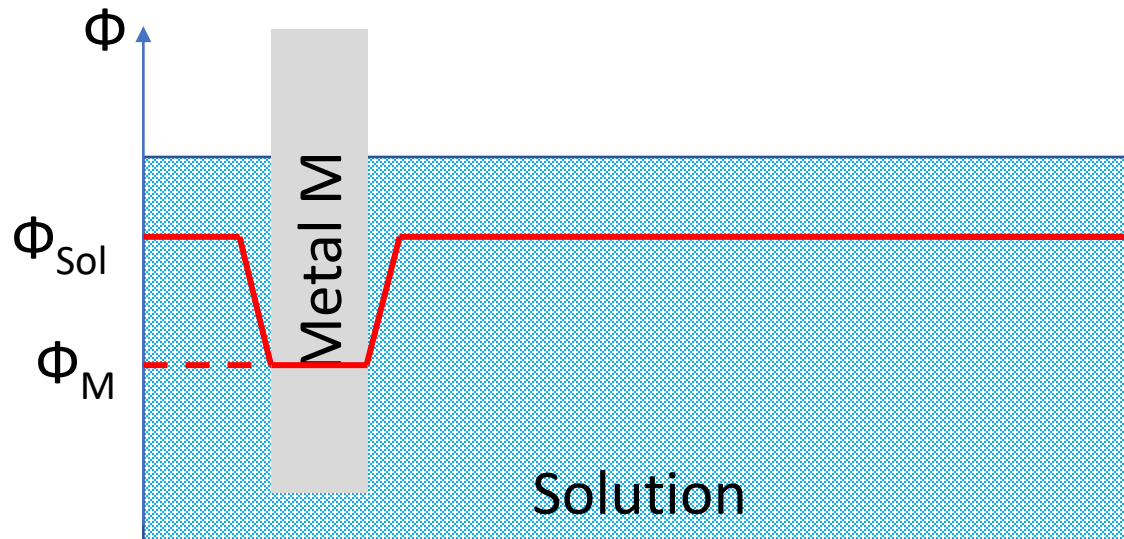
Some ions can lose their solvation sphere and specifically interact with the electrode surface: existence of immobile inner and outer Helmholtz planes



# IV) Electrode potential

## Electrode, solution, and cell potential

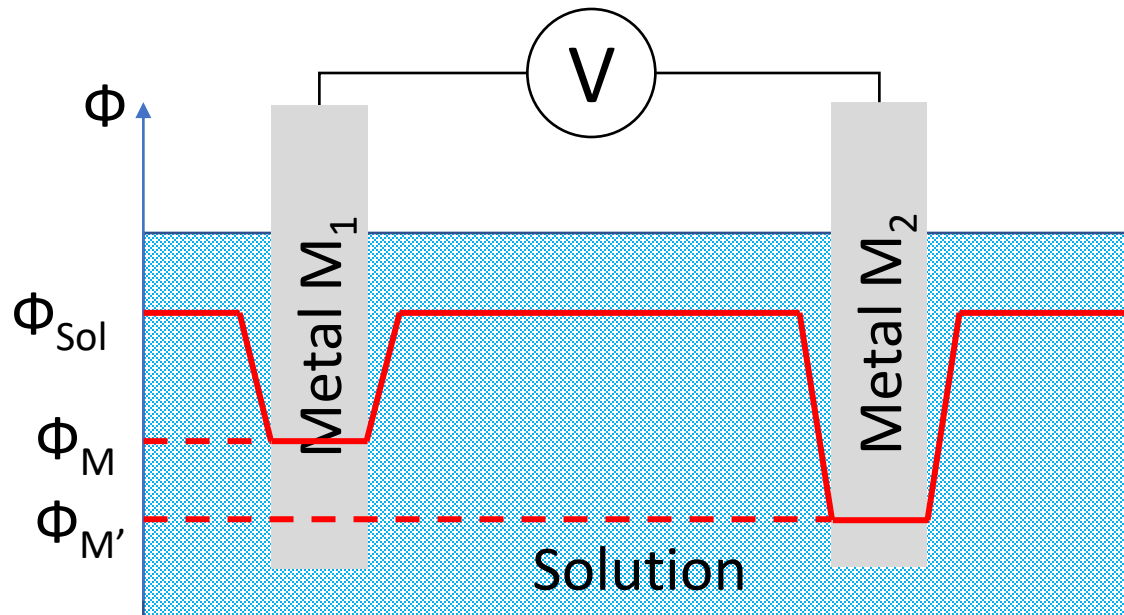
Direct measurements of  $\Phi_M$  and  $\Phi_S$  are not possible



# IV) Electrode potential

## Electrode, solution, and cell potential

Need an additional electrode



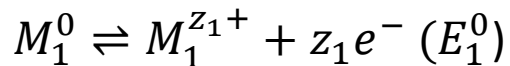
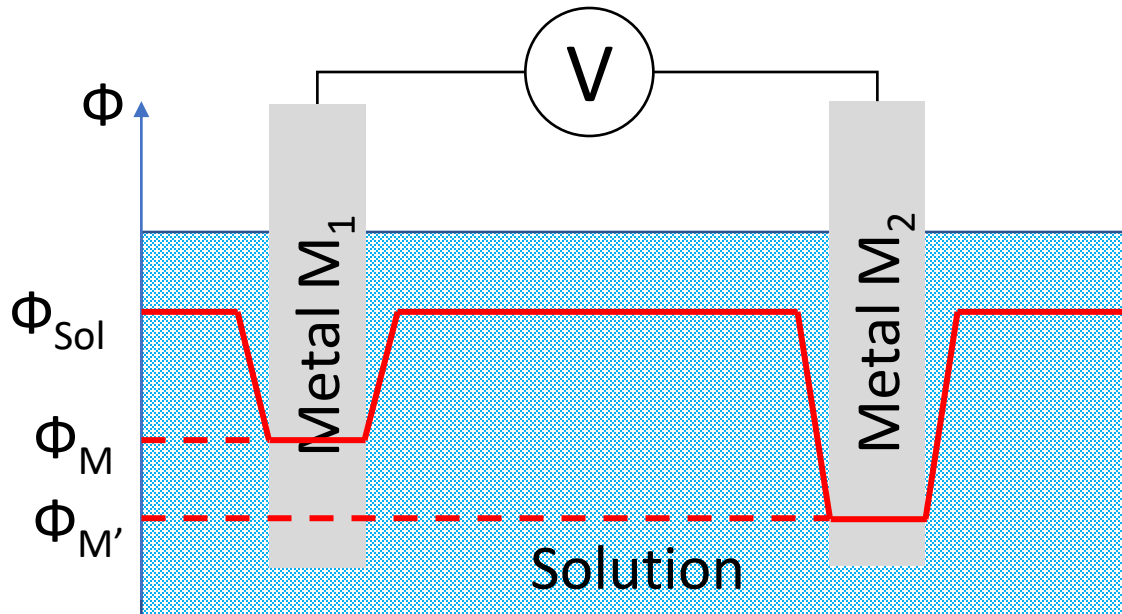
$$\Delta E = \sum \Delta \phi = \phi_M - \phi_{M'} = E_M^{eq} - E_{M'}^{eq}$$

$\Delta E$  is the difference of Nernst potentials

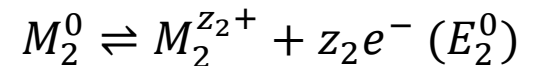
# IV) Electrode potential

## Electrode, solution, and cell potential

Need an additional electrode



$$E_1^{eq} = E_1^0 + \frac{RT}{z_1 F} \ln[M_1^{z_1^+}]$$

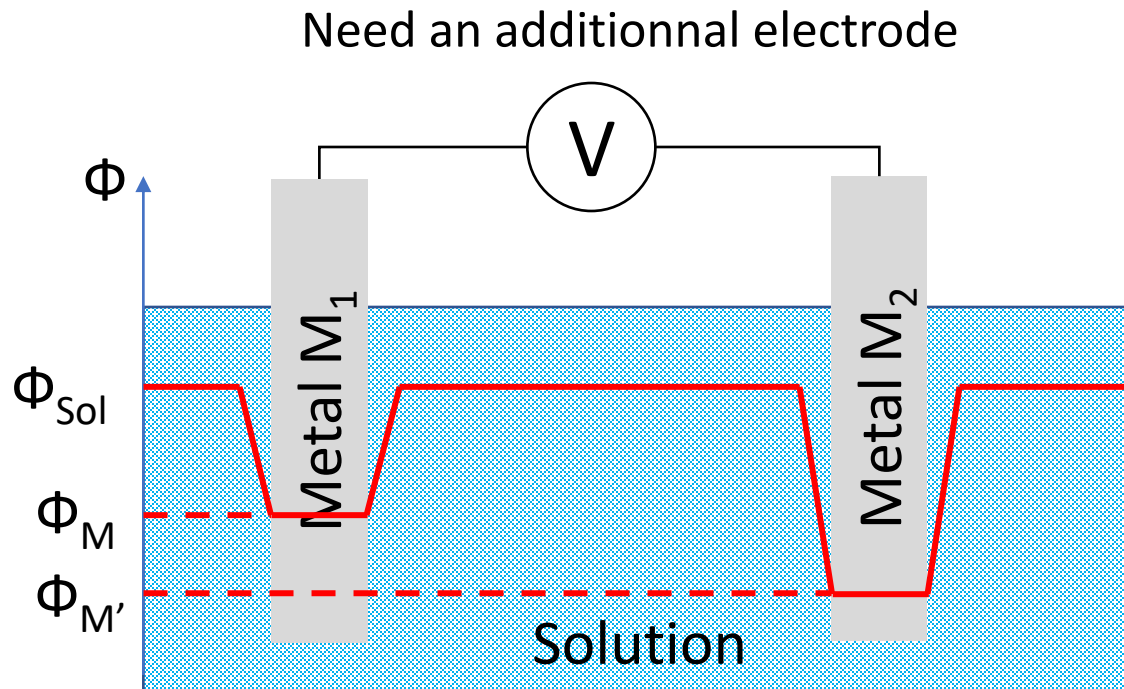


$$E_2^{eq} = E_2^0 + \frac{RT}{z_2 F} \ln[M_2^{z_2^+}]$$

$$\Delta E = \Delta E^0 + \frac{RT}{z_1 F} \ln[M_1^{z_1^+}] - \frac{RT}{z_2 F} \ln[M_2^{z_2^+}]$$

# V) Electrodeposition mechanism and kinetics

## Overview



Let us use an electrolyte that contains solvated  $M_1^{z_1+}$  cations

And let us apply a  $\Delta E > \Delta E^0 \Leftrightarrow E_1 < E_1^{eq}$  and  $E_2 > E_2^{eq}$

Overpotential:  $\eta_i = E_i - E_i^{eq} \Leftrightarrow i \neq 0 \text{ A}$  (*electrical current*)

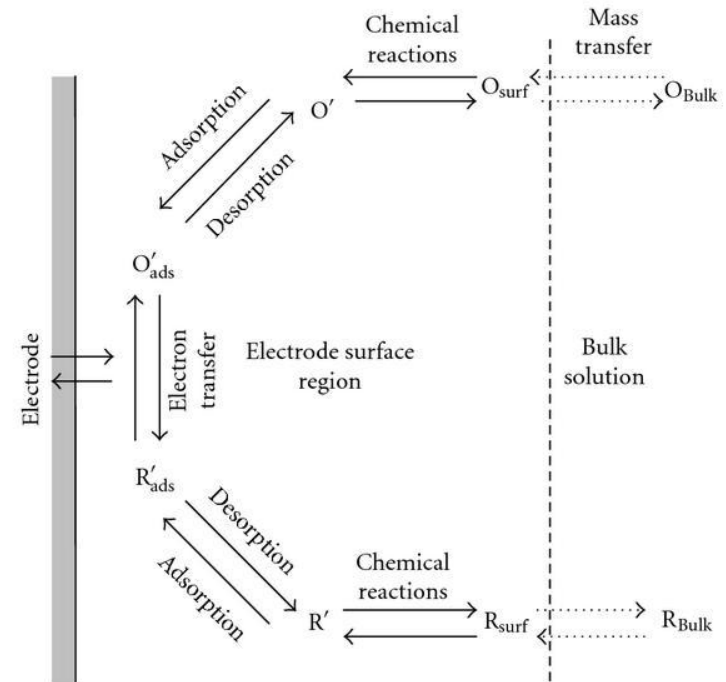
Electrodeposition at the cathode:  $M_1^{z_1+} + z_1 e^- \rightleftharpoons M_1^0$

# V) Electrodeposition mechanism and kinetics

## Overview

Electrodeposition is governed by 5 fundamental processes

- 1) Mass transfer from the bulk solution to the interphase  $\eta_{mt}$
- 2) Chemical reactions in the electrode region  $\eta_r$
- 3) Adsorption and diffusion of adions  $\eta_a$
- 4) Charge transfer  $\eta_{ct}$
- 5) Crystallisation  $\eta_c$



$$\eta = \underbrace{\eta_{mt} + \eta_r + \eta_a + \eta_c}_{\text{Current independent}} + \eta_{ct} = \boxed{a + b \cdot \log i}$$

**Tafel law**