Nano-materials for Energy conversion and storage

NAC 2401: Lecture 6

Electrocatalysis using nanomaterials

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Rate of electrochemical reaction

Current density (A cm^{-2}):

is a measure for the rate of redox processes running at the anode and cathode of the electrolytic cell.

$$Ox + n\,e^{-} \rightarrow Red$$

$$Rate = -\frac{dN_{ox}}{dt} = \frac{dN_{Red}}{dt}$$

$$mol\ cm^{-2}s^{-1}$$

Inspect the unit

$$\frac{i}{nF} = \frac{Acm^{-2}}{\left(\frac{mol\ e^{-}}{mol\ Ox}\right)\left(\frac{C}{mol\ e^{-}}\right)} = \frac{\frac{C}{s}cm^{-2}}{\left(\frac{C}{mol\ Ox}\right)} = mol\ cm^{-2}s^{-1}$$

Rate of electrochemical reaction

$$Ox + n\,e^{-} \rightarrow Red$$

$$Rate = \frac{i}{nF}$$

Current density (A cm^{-2}):

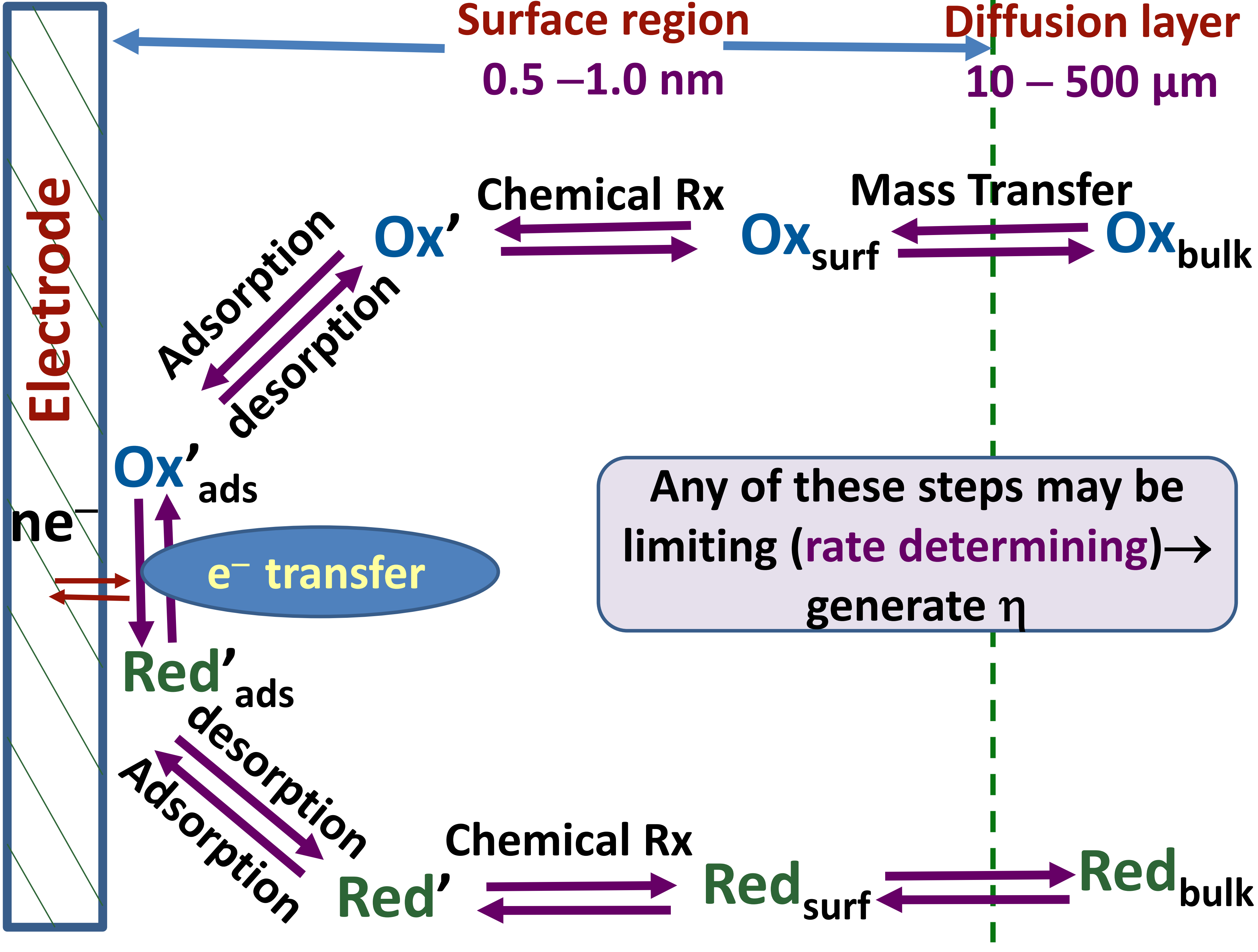
can easily probe the rate of electrochemical reactions.

- As electrochemical reactions concern with the material change and charge transfer at the Electrode/electrolyte interface, equations concern with surface area of the electrode not the volume of the electrolyte in the rate’s calculations.

Steps of an electrochemical reaction

$$Ox + n\,e^- \rightarrow Red$$

- **Mass transfer** (diffusion, migration, convection) of reactants from the bulk solution to the double layer.
- **Possible chemical reaction** (dissociation of a molecule, dehydration of an ion, structural change, crystallization of a metal or a salt, …etc).
- **Adsorption** of reactants onto the electrode surface.
- **Charge transfer** (Electrode/reactants) across the double layer.
- **Desorption** of the product off the electrode surface.
- **Possible chemical reaction** (hydration of an ion, association of a molecule, …etc).
- **Mass transfer** (diffusion, migration, convection) of Products from electrode surface to the bulk solution.



Surface region

0.5 –1.0 nm

Diffusion layer

10 – 500 µm

Electrode

Mass Transfer

$\mathrm{Ox}_{bulk} \rightleftarrows \mathrm{Ox}_{surf}$

Chemical Rx

$\mathrm{Ox}_{surf} \rightleftarrows \mathrm{Ox}'$

Adsorption / **desorption**

$\mathrm{Ox}' \rightleftarrows \mathrm{Ox}'_{ads}$

ne^- ⇄ **e⁻ transfer**

$\mathrm{Ox}'_{ads} \rightleftarrows \mathrm{Red}'_{ads}$

desorption / **Adsorption**

$\mathrm{Red}'_{ads} \rightleftarrows \mathrm{Red}'$

Chemical Rx

$\mathrm{Red}' \rightleftarrows \mathrm{Red}_{surf}$

$\mathrm{Red}_{surf} \rightleftarrows \mathrm{Red}_{bulk}$

Any of these steps may be limiting (rate determining)→ generate η

Polarization (p)/Overpotential (η)

$E_{I=0}$: is called also the open circuit potential

For a single redox process

$E_{I=0}$: is **equilibrium potential** calculated using Nernst equation

$$p = E_i - E_{rev}$$

$$\eta = E_i - E_{I=0}$$

Overpotential or Overvoltage, η

is the extra potential over the equilibrium potential that drives the process in a specific direction at a given rate

Concentration Polarization (η_c)

- results when the concentrations of reactants/products at the electrode surface are different under non-equilibrium conditions from their values under equilibrium (bulk) values.
- grows and decays **slowly** on application and interruption of current, respectively, at a rate characteristic of the diffusion coefficients of the species involved.
- is the only form of η affected by stirring and is unaffected by the nature of electrode surface.

Activation Polarization (η_a)

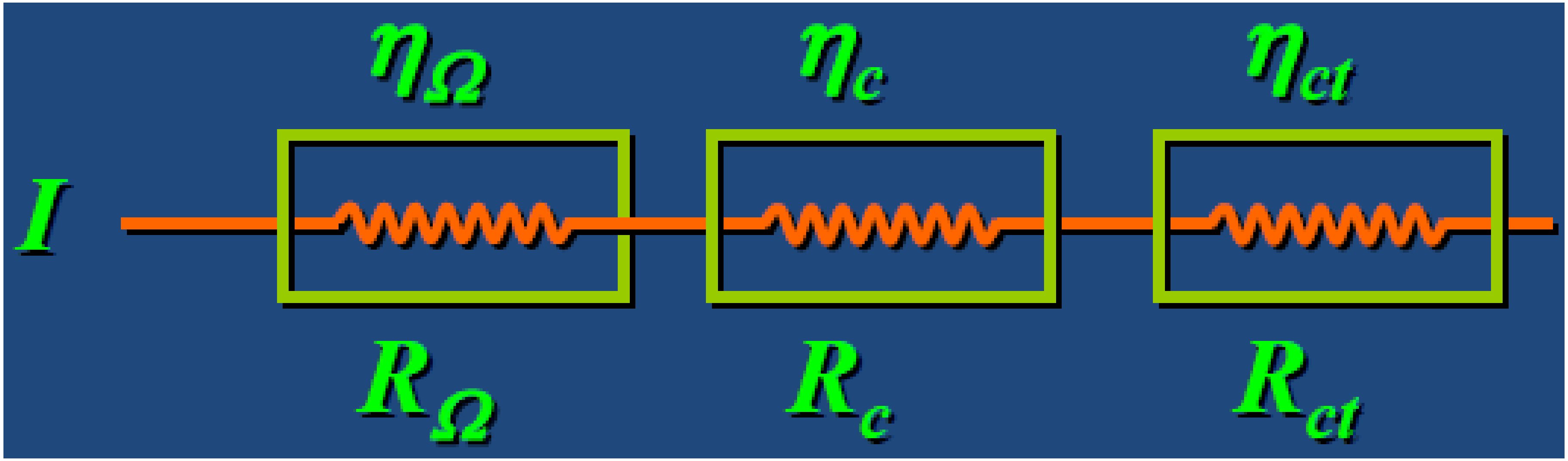
- is also called **charge transfer** polarization, η_{ct}
- is the polarization needed to promote the ECR in one direction and retard it in the opposite direction.
- appears as a change in the value of potential difference across the electrical double layer between non-equilibrium and equilibrium.

Ohmic (Resistance) polarization, η_Ω

- results from the current flow in resistive electrolytes (R_{sol}), and/or electrodes (R_{e}: oxide films or salts, gas bubbles, grease, dirt, ..etc). **Heating effect**.
- Even with using electrodes of very low resistance and with using electrolytes of very high ionic conductivity and with using Luggin capillary, there remains a sort of uncompensated (unavoidable) resistance, R_{u}.
- It appears and disappears instantaneously when the polarizing current is imposed or disconnected

$$\eta_{\Omega} = I \times R = I \times (R_{\mathrm{e}} + R_{\mathrm{sol}} + R_{\mathrm{u}})$$

Generally,



$$\eta = \eta_\Omega + \eta_c + \eta_{ct}$$

The degree of reversibility in each ECR depends on the rates of mass and charges transfers involved

Reversible **Quasi-reversible** **Irreversible**

Reversible processes

Rate of charge transfer >>> Rate of mass transfer

Mass transfer controlled

- stays close to equilibrium (Nernst equation applies) regardless of the passing current.

$$E = E^0 + \frac{RT}{nF} \ln \frac{(Ox)}{(Red)}$$

- $\eta_{ct} = 0$.
- in absence of η_{Ω} , $\eta = \eta_c$

Quasi-reversible processes

Rate of charge transfer <<< Rate of mass transfer

Charge transfer controlled

- $\eta_c = 0$.
- In absence of η_Ω , $\eta = \eta_{ct}$

Irreversible processes

Rates of charge and mass transfers are comparable

- In absence of η_Ω , $\eta = \eta_c + \eta_{ct}$

Activation overpotential, η_a or η_{ct}

Reflects the energy (nF η_a) required to speed up the heterogeneous charge transfer (of η_{ct}) and the preceding and/or following chemical reactions.

Assumptions

$$\mathbf{Ox} + \mathbf{ne^-} \rightleftharpoons \mathbf{Red}$$

1) The concentrations at the surface and in the bulk solution for reactants and products are the same. To eliminate the concentration polarization, η_c.
2) Solution is so large around the electrode.
3) A large amount of a supporting electrolyte is added. To eliminate the migration polarization, η_m.
4) Solution and electrode are stagnant (no convection).
5) Only η_a is limiting.

Effect of η_a on the reaction Kinetics

$$\mathbf{Ox} + \mathbf{ne^-} \rightleftharpoons \mathbf{Red}$$

- For electrochemical Rxs at equilibrium, the potential difference across the double layer will have its equilibrium value, ΔE_r.

$$\frac{d\emptyset}{dx} \approx \frac{1\,V}{5\times10^{-8}\,cm} \approx 2 \times 10^7\,V cm^{-1}$$

- If the equilibrium is disturbed, net flow of current will occur and the potential difference changes to ΔE_i.

$$\eta_a = \Delta E_i - \Delta E_r$$

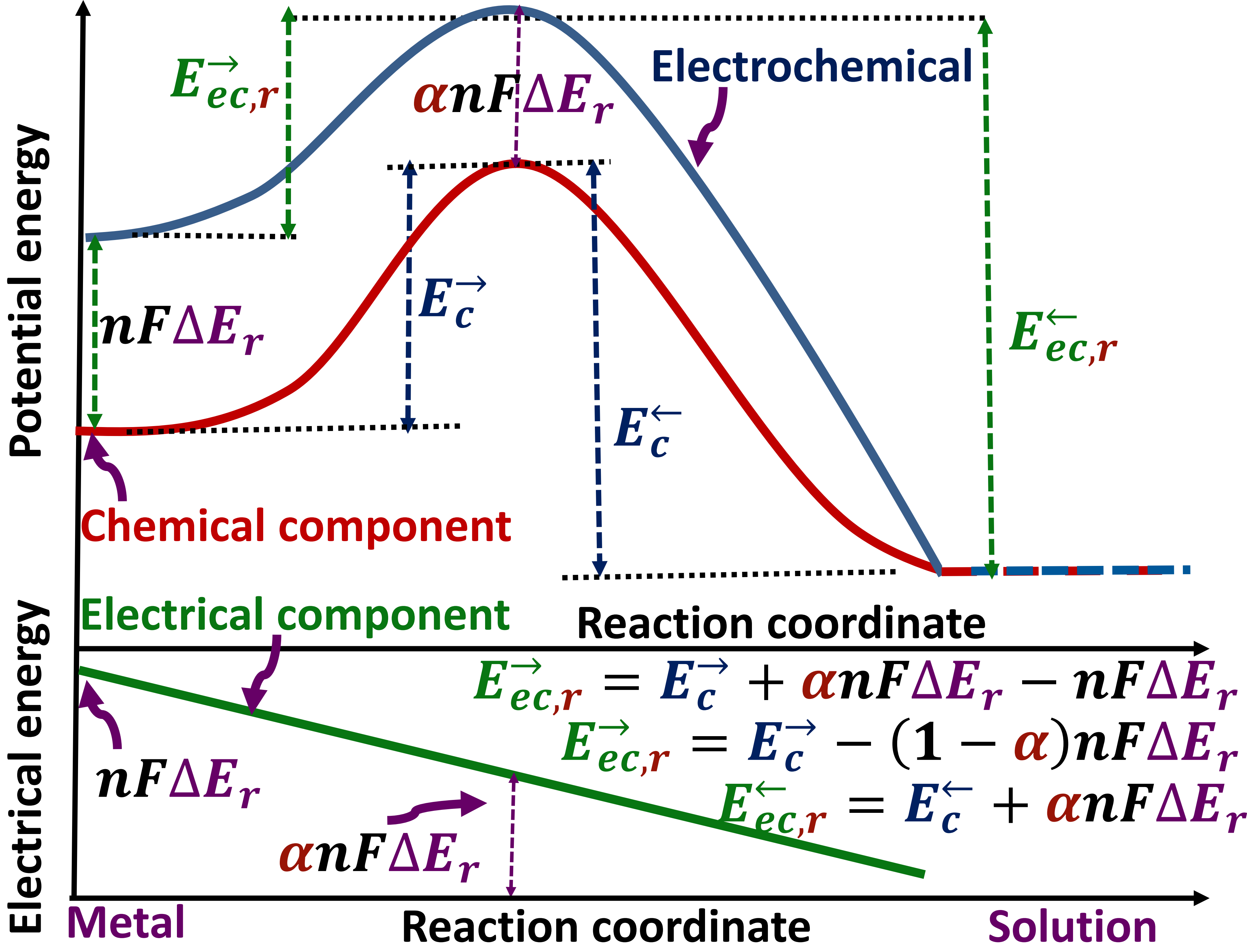
- If η_a was positive, the activation energy (E_a) of the anodic Rx will decrease while E_a of the cathodic Rx will simultaneously increase. This change may or may not be equal.

- This, in turn, increases the rate of anodic RX and decreases the rate of cathodic Rx

$$k = Ae^{\left(\frac{-E_a}{RT}\right)}$$

Arrhenius Equation

- E_a is best described by potential energy profiles.
- These profiles should consider the chemical and electrical components of the electrochemical potential.
- The potential in solution is taking to be zero while the potential at the electrode surface is E_r where equilibrium is assumed.
- On the solution side, the contribution of the electrical component is zero while at the electrode surface is maximum ($nF\Delta E_r$).
- At the point where the activated complex occurs, the contribution of the electrical component is midway ($\alpha nF\Delta E_r$)



Potential energy
$E_{ec,r}^{\rightarrow}$
$\alpha nF\Delta E_r$
Electrochemical
$E_c^{\rightarrow}$
$nF\Delta E_r$
$E_{ec,r}^{\leftarrow}$
$E_c^{\leftarrow}$
Chemical component
Electrical energy
Electrical component
Reaction coordinate
$E_{ec,r}^{\rightarrow} = E_c^{\rightarrow} + \alpha nF\Delta E_r - nF\Delta E_r$
$E_{ec,r}^{\rightarrow} = E_c^{\rightarrow} - (1-\alpha)nF\Delta E_r$
$E_{ec,r}^{\leftarrow} = E_c^{\leftarrow} + \alpha nF\Delta E_r$
$nF\Delta E_r$
$\alpha nF\Delta E_r$
Metal
Reaction coordinate
Solution

$$E^{\rightarrow}_{ec,r} = E^{\rightarrow}_{c} + \alpha nF\Delta E_r - nF\Delta E_r$$

$$E^{\rightarrow}_{ec,r} = E^{\rightarrow}_{c} - (1-\alpha)nF\Delta E_r$$

$$\beta = (1-\alpha)$$

$$E^{\rightarrow}_{ec,r} = E^{\rightarrow}_{c} - \beta\, nF\Delta E_r$$

$$E^{\leftarrow}_{ec,r} = E^{\leftarrow}_{c} + \alpha nF\Delta E_r$$

- The activation energy of the forward direction decreases by $(1-\alpha)nF\Delta E_r$ while that of the backward Rx increases by $\alpha nF\Delta E_r$, i.e., the potential difference across the double layer ΔE_r promotes the forward Rx and retards the backward Rx based on the fraction α which is known as the transfer coefficient or symmetry factor $(0 < \alpha < 1)$.

- α may be considered as the fraction of ΔE_r that retards the backward Rx while $\beta = (1-\alpha)$ is the fraction of ΔE_r that promotes the forward Rx .

- ☐ In simple one electron transfer RXs, α is often close to 0.5. $\boldsymbol{\beta = (1 - \alpha) \approx 0.5}$
- ☐ Normally, α ranges from 0.3 to 0.7

Effect of η_a on activation energy

- ☐ Under conditions of electrochemical equilibrium, the rates of anodic and cathodic RXs are equal and no net flow of electrons occurs.

- ☐ Under conditions of polarization, this dynamic equilibrium is disturbed and electrons flow either to the electrode (in case of cathodic polarization, $\eta_a < 0$) or from the electrode (in case of anodic polarization, $\eta_a > 0$) .

Under non-equilibrium conditions, ΔE_r will be replaced by ΔE_i

$$E_{ec,i}^{\rightarrow} = E_c^{\rightarrow} - \beta\, nF\Delta E_i$$

However, ⇨ $\Delta E_i = \Delta E_r + \eta$

$$E_{ec}^{\rightarrow} = E_c^{\rightarrow} - \beta\, nF\Delta E_r - \beta\, nF\eta$$

Since $E_{ec,r}^{\rightarrow} = E_c^{\rightarrow} - \beta\, nF\Delta E_r$

⇨ $E_{ec,i}^{\rightarrow} = E_{ec,r}^{\rightarrow} - \beta\, nF\eta$

Similarly,

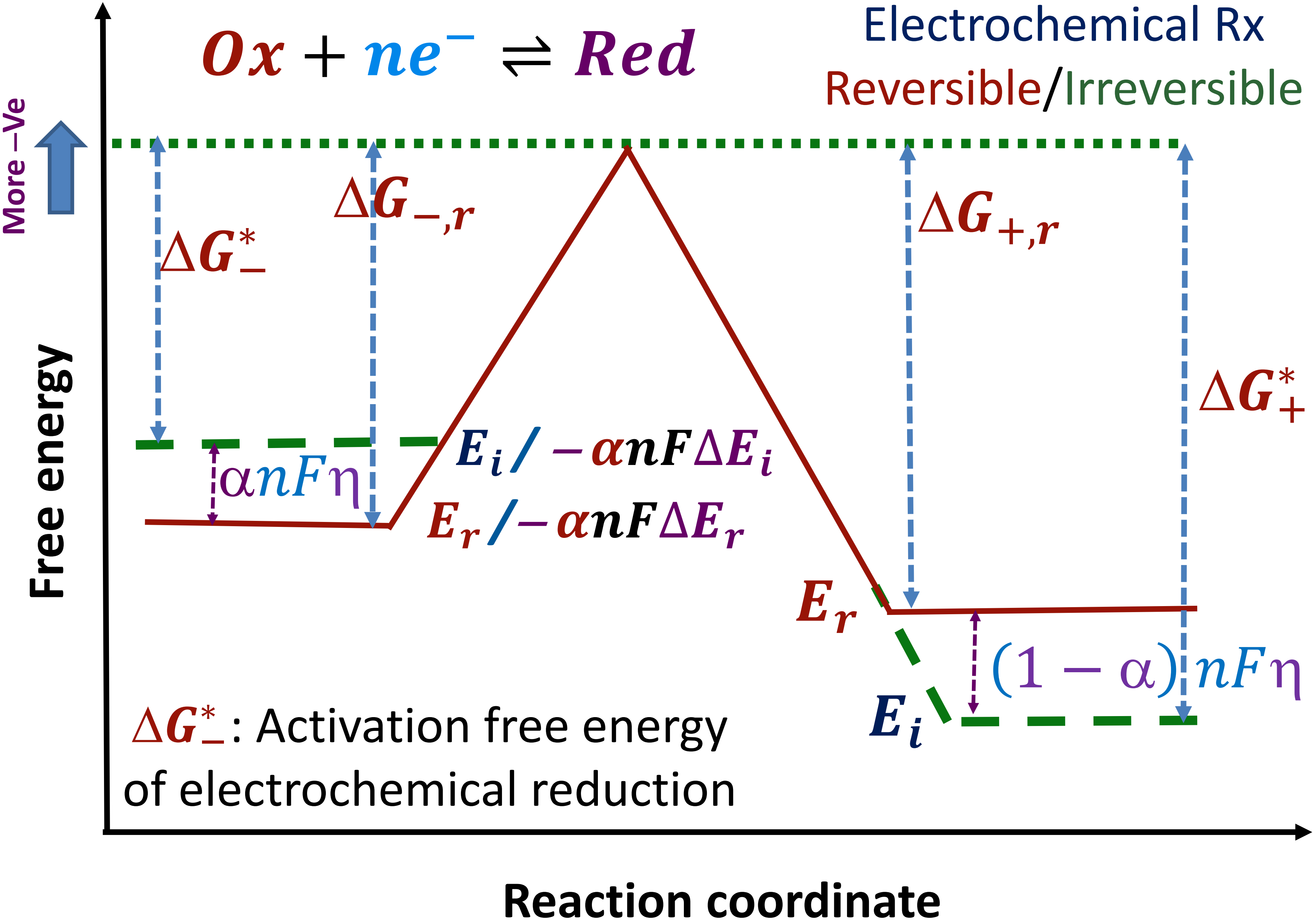
$$E_{ec,i}^{\leftarrow} = E_c^{\leftarrow} + \alpha nF\Delta E_i$$

$$E_{ec,i}^{\leftarrow} = E_c^{\leftarrow} + \alpha nF\Delta E_r + \alpha nF\eta$$

⇨ $E_{ec,i}^{\leftarrow} = E_{ec,r}^{\leftarrow} + \alpha nF\eta$

Electrochemical Rx
Reversible/Irreversible

$$Ox + ne^{-} \rightleftharpoons Red$$



ΔG^{*}_{-}: Activation free energy of electrochemical reduction

For the forward cathodic direction, at E_{rev}

$$\Delta G_{-}^{*} = \Delta G_{-} + \alpha nFE_{i}$$

$$\Delta G_{-}^{*} = \Delta G_{-} + \alpha nFE_{r} + \alpha nF\eta$$

ΔG_{-} : free energy change of activation for the chemical component of cathodic Rx

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$$\Delta G_{+}^{*} = \Delta G_{+} - (1-\alpha)nFE_{r} - (1-\alpha)\,nF\eta$$

$$Ox + ne^{-} \rightleftharpoons Red$$

- ☐ α may be considered as the fraction of electrical energy promoting the reduction process and $(1-\alpha)$ is the fraction slowing down the oxidation process.
- ☐ η is supposed to be –Ve in the cathodic polarization.

Electrocatalysis

- takes place when, in an electrochemical reaction, the electrode acts as electron donor or acceptor, and as a (**heterogeneous**) catalyst.
- The electrode is present in both catalyzed and noncatalyzed "pure" electrochemical reactions, facilitating the reaction and not suffering any chemical change in the process.
- In an electrocatalytic process, in addition to transferring charge to an electroactive species in the electrolyte, the electrode must interact **specifically** and **intimately** with that species (commonly referred to as "**inner sphere**" electron transfer), altering the reaction pathway and changing the activation energy and reaction rate.

Inner/Outer Sphere

- electron transfers occur much more quickly in the presence of certain ligands.

$$Co(NH_3)_6^{3+} + Cr^{2+} \longrightarrow Co^{2+} + Cr^{3+} + 6NH_3, \quad k = 10^{-4}\ mol^{-1} L\ s^{-1}$$

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \longrightarrow Co^{2+} + CrCl^{2+} + 6NH_3, \quad k = 6 \times 10^{5}\ mol^{-1} L\ s^{-1}$$

Presence of chloride boosted the reaction

Inner Sphere Electron Transfer

- Electron transfers that occur via ligands shared by the two metals undergoing oxidation and reduction are termed "**inner sphere**" electron transfers.

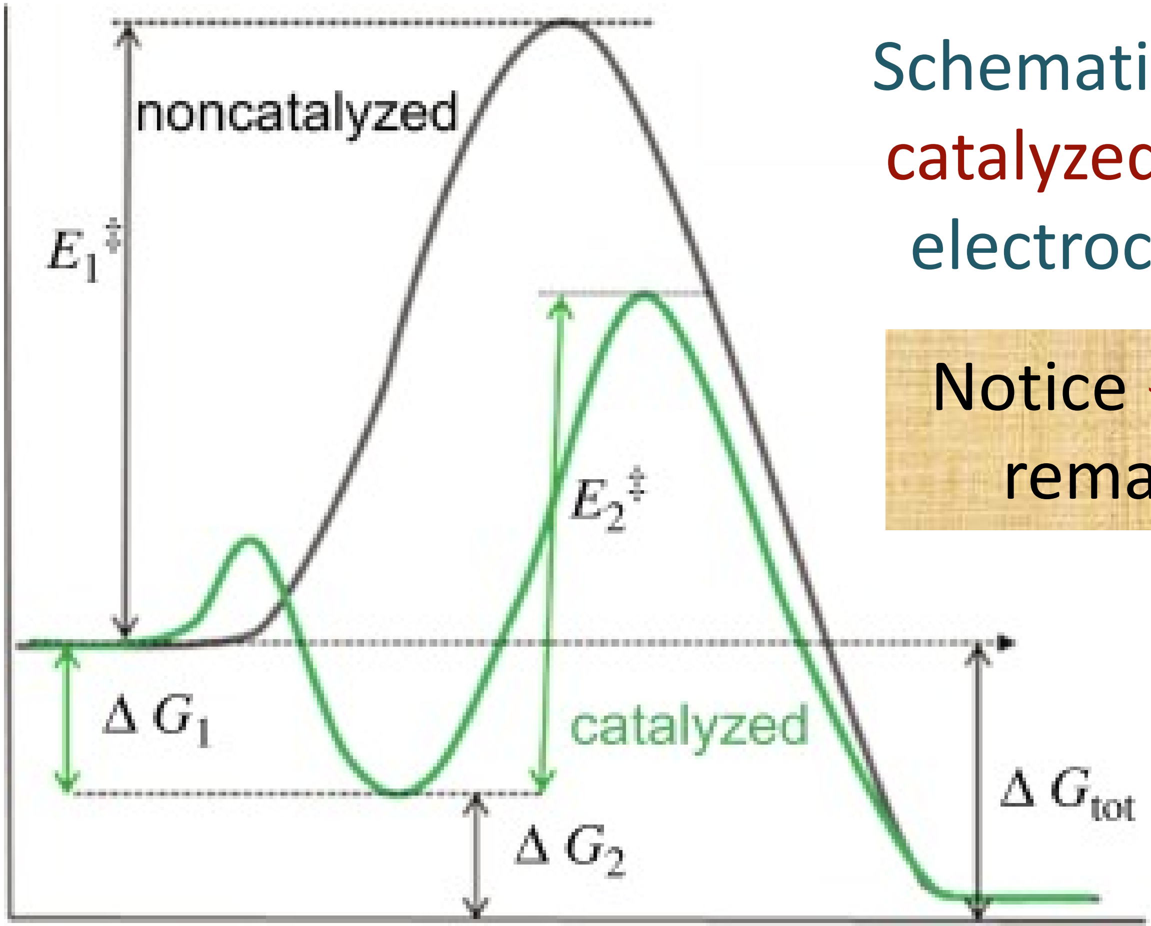
- Inner sphere electron transfer occurs between complexes via a bridging ligand. At least one of the complexes needs to be labile to allow the bridge to form.

- Bonds are broken and formed.

Outer sphere electron transfer

- **Outer sphere** electron transfer occurs between two species that do not undergo substitution and do not involve the incursion of significant covalent bond formation.
- None of the ligands can function as a bridge. It is **faster** than inner sphere because the energetic demands are less. No new bonds are broken or formed.
- Interaction between the two coordination spheres exist but is not as pronounced as for the bridge complex in the inner sphere.
- Outer Adduct is held together by one of the following: Electrostatic interactions, Vander Waals forces, or Hydrogen bonding.

- In electrocatalysis, for a given reaction, under a given set of reaction conditions, such as defined concentration and temperature, different reaction rates will be observed for different electrode materials due to the highly specific nature of this interaction.



Schematic energy profile for catalyzed and noncatalyzed electrochemical reactions

Notice ↓ in E_a while ΔG_{tot} remains unchanged.

Adsorption

- The primary origin of the electrocatalyst-specific interactions with any chemical species is **adsorption**.
- Consider a simple electrochemical reaction: A + e^{-} → B, in which A is the only species adsorbed on the electrode surface (S). A simple reaction mechanism would be:

Pre-equilibrium $S + A \rightleftharpoons S - A$ **Eq. 1**

e^{-} transfer $S - A + e^{-} \rightarrow S - B$ **Eq. 2**

Product Desorption $S - B \rightleftharpoons S + B$ **Eq. 3**

- If Eq. 3 is assumed fast (B is weakly adsorbed), and the reactant adsorption (Eq. 1) is treated as a pre-equilibrium, the rate of the reaction can be correlated with the adsorption properties of the surface according to this generic eqn. (Eq. 4):

Eq. 4

$$J = k_0 \frac{\exp\left(-\frac{(1-\alpha)\Delta G_{\mathrm{ads,A}}}{RT}\right)}{1+\left(\frac{c_{\mathrm{A}}}{c_{\mathrm{ref}}}\right)\exp\left(-\frac{\Delta G_{\mathrm{ads,A}}}{RT}\right)} \exp\left(-\frac{\alpha F(E-E_0)}{RT}\right) c_{\mathrm{A}}$$

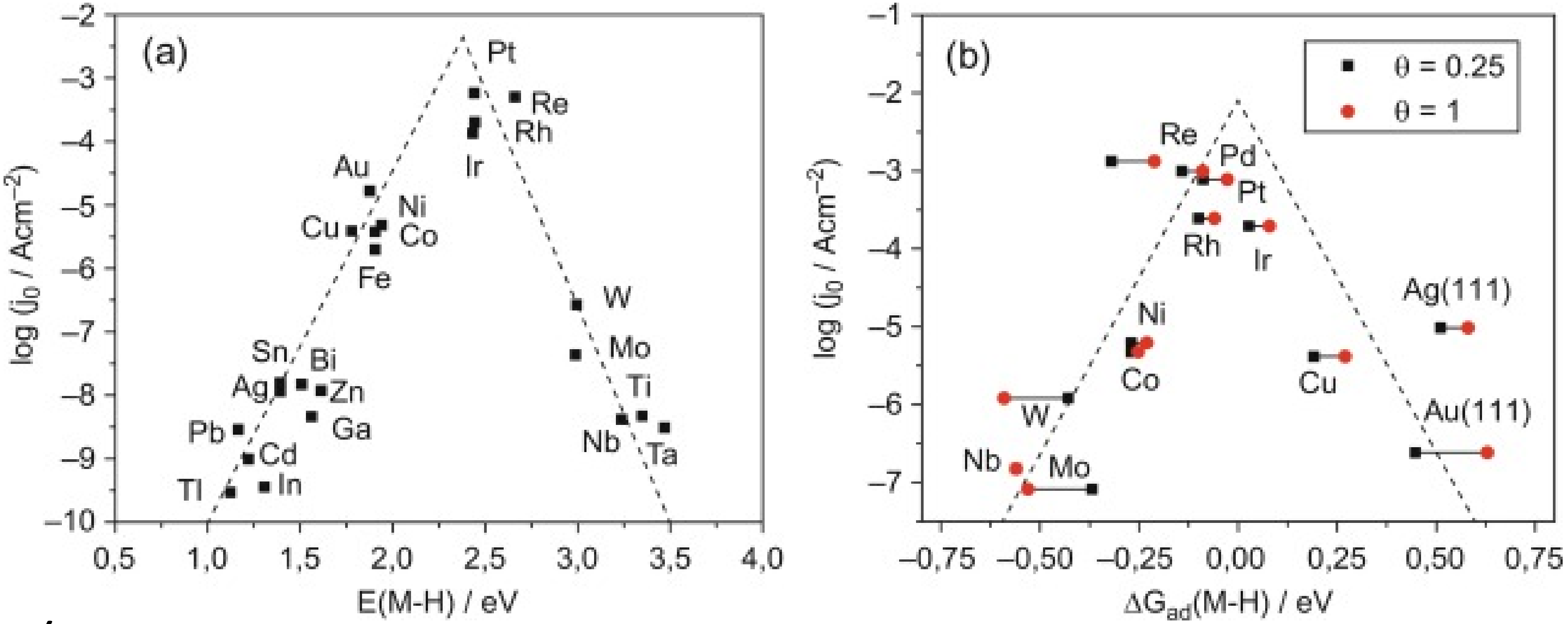
J: surface reaction flux (mol m^{-2} s^{-1}), α (≈ 0.5) is the reductive-direction transfer coefficient for the one-electron reduction (Eq. 2), k_0 is the heterogeneous rate constant of the electron transfer (m s^{-1}), E is the electrode potential, E_0 is the standard potential for the overall reaction of A to B, $\Delta G_{\mathrm{ads,A}}$ is the Gibbs energy of adsorption of species A (Eq. 1), and c_{A} is the concentration of A. R and T are the gas constant and temperature, respectively; c_{ref} is a reference concentration corresponding to unit activity of A.

- J depends principally on: $\Delta G_{\text{ads,A}}$ (depends on the electrode material), E and c_{A}
- If the catalytic activity of several surfaces is compared at constant E, assuming similar values of α, J will depend only on $\Delta G_{\text{ads,A}}$ and c_{A}.
- an increase in $\Delta G_{\text{ads,A}}$ increases J as long as $\Delta G_{\text{ads,A}}$ is **not** too negative (strongly adsorbing).
- More negative values of $\Delta G_{\text{ads,A}}$ (stronger adsorption) lower the overall rate as they correlate to an increased activation energy for Eq. 2 (assuming $\alpha < 1$).
- If the intermediate $S - B$ is too strongly adsorbing, it can form rapidly but then effectively **poison** the electrocatalyst itself.

Sabatier Principle

high electrocatalytic rates require the interaction between the reactant and the electrode surface to be **neither** too weak nor too strong

- “**volcano plots**” of the reaction rate vs. the free energy of the intermediate adsorption result in curves with peaked shapes.



(a) Experimental and (b) DFT-derived volcano plots for the HER (exchange current density notated j_0)

On the left side, the electrocatalysts adsorb the key reactants too weakly, and the reaction rate increases with more favorable adsorption energy until it passes through a maximum near $\Delta G_{\mathrm{ads,A}} = 0$. After the maximum, the rate decreases again as the adsorption becomes too strong, and product desorption becomes rate limiting.

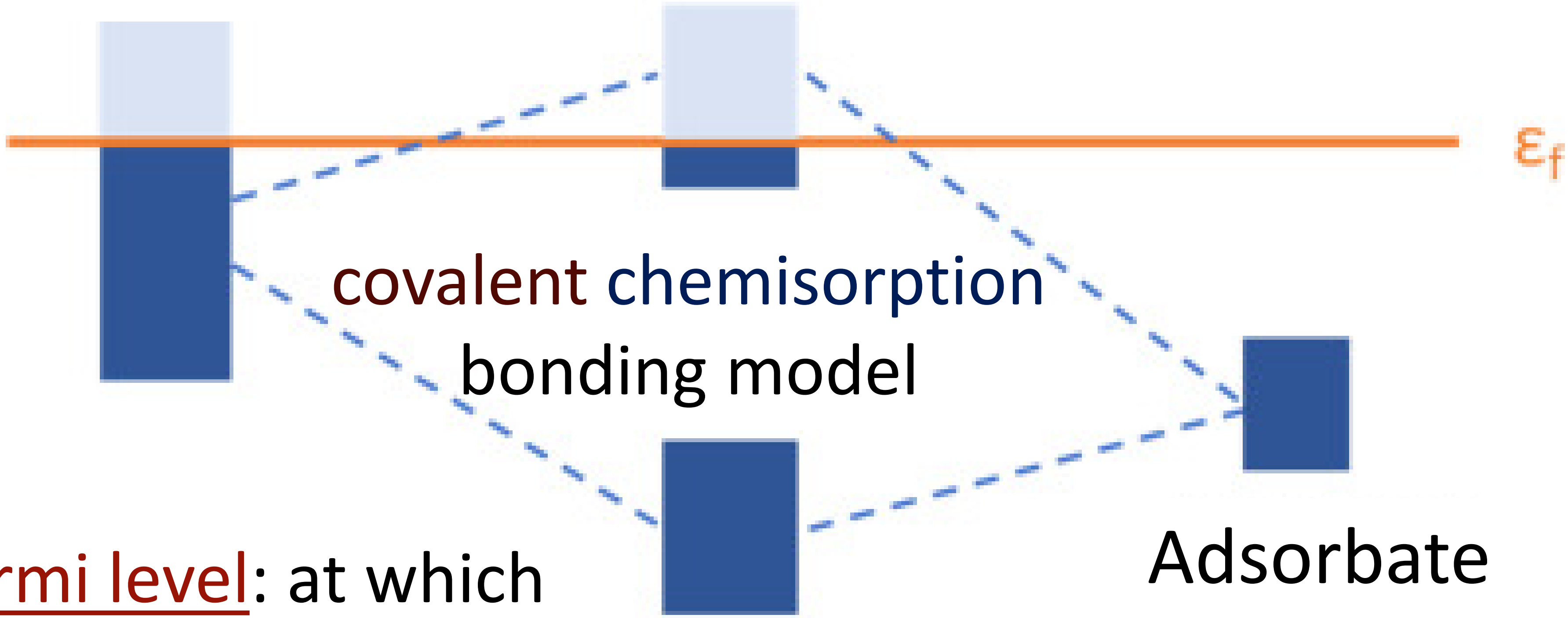
Catalytic Activity of Electrode Materials

- is affected largely by the adsorption/desorption of species at the surface.
- Consider a transition metal with an energetically sharp, partially filled d-band and a molecule with a partially filled molecular σ orbital.
- When the molecule interacts with the metal surface, the orbital overlap between σ and d will lead to chemisorption with rehybridization and the formation of new d–σ orbitals.
- In the adsorbate system, bonding (d–σ) and antibonding (d–σ)* states are formed.

Fermi level: highest energy level that an electron can occupy at 0K

Metal d–band

(d–σ)*



covalent chemisorption bonding model

Adsorbate σ orbital

(d–σ)

Fermi level: at which the probability of occupancy of state by an electron is 0.5

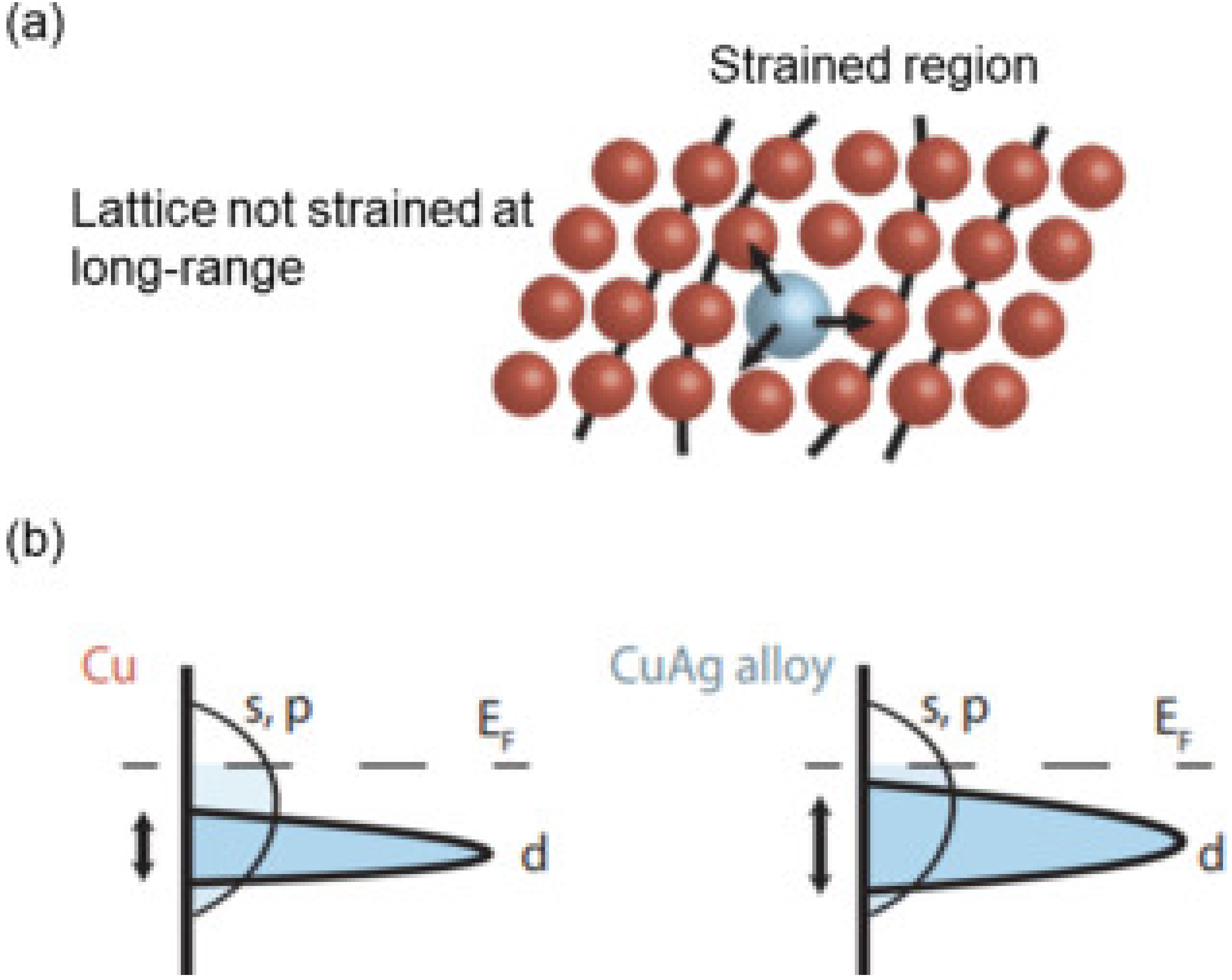
- The strength of the adsorption will depend on the d-band occupancy.

- The lower the d-band filling, the less occupancy in the antibonding (d–σ)* and the more strongly the molecule will adsorb on the electrocatalyst surface.

- To modify the catalytic activity of a specific material, one can tune properties that will influence its d-band filling, such as electronic structure, surface geometry, surface composition, or electrode potential.

Electronic Structure

- Engineering electronic properties of an electrocatalyst can be carried out by **mixing different metals**, such as in alloys, intermetallic compounds, and bimetallic compounds.
- This changes the adsorption energy and intramolecular bond energy in the adsorbed reactants and intermediates through changes in the lattice, interatomic distance, etc.
- In addition, some strain effects can also occur when either the second or the host metal atoms are forced to adopt positions different from their equilibrium position in the bulk materials.


(a)
Strained region
Lattice not strained at long-range
(b)
Cu
s, p
E_F
d
CuAg alloy
s, p
E_F
d

Strain and Ligand Effects

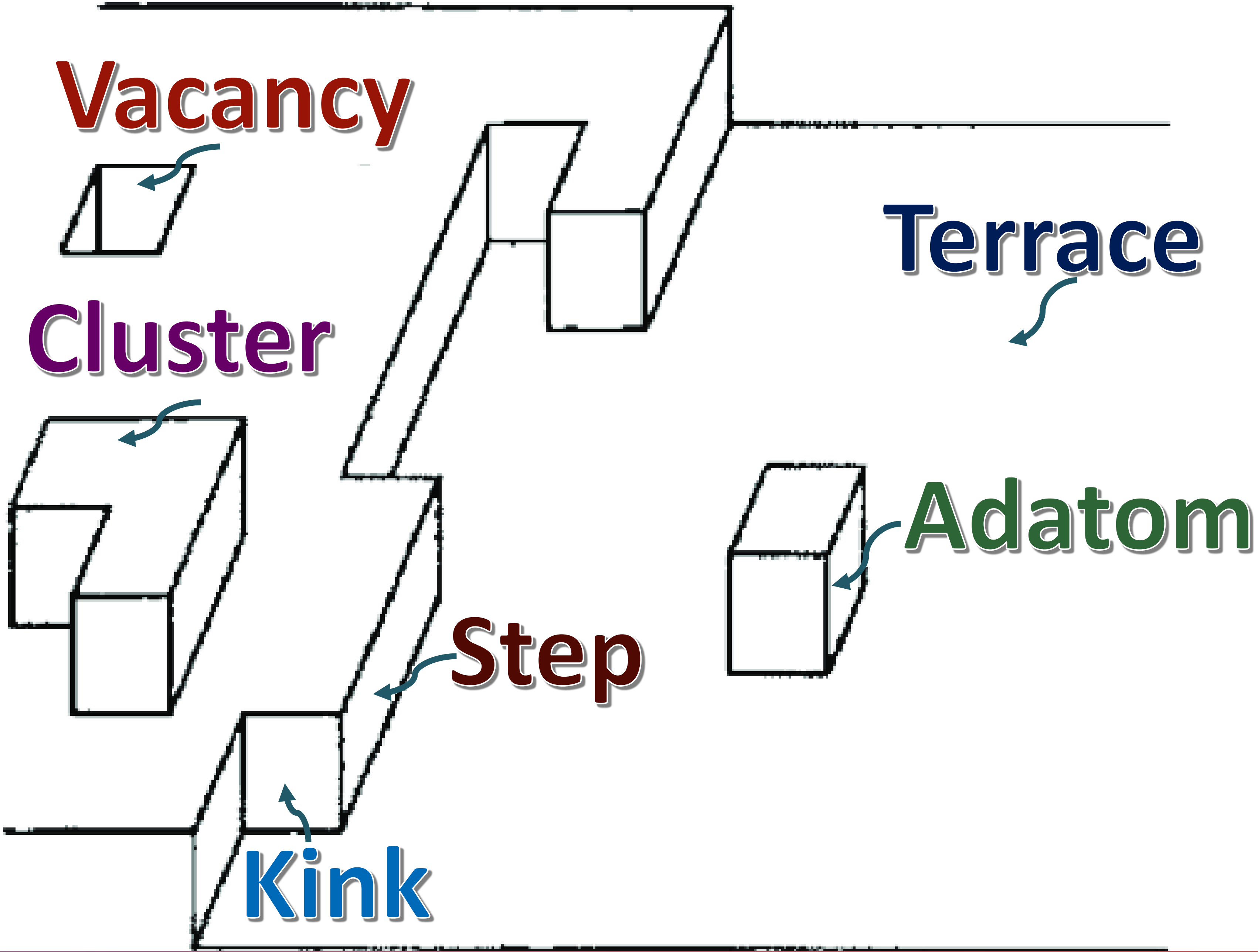
- The average bond lengths between the metal atoms in the supported monolayer surface are typically different from those in the bulk metal, resulting in **strain**-derived changes.

- Also, heterometallic bonding interactions, called “ligand effects,” between the surface atoms and the substrate can result in modification of the surface electronic structure.

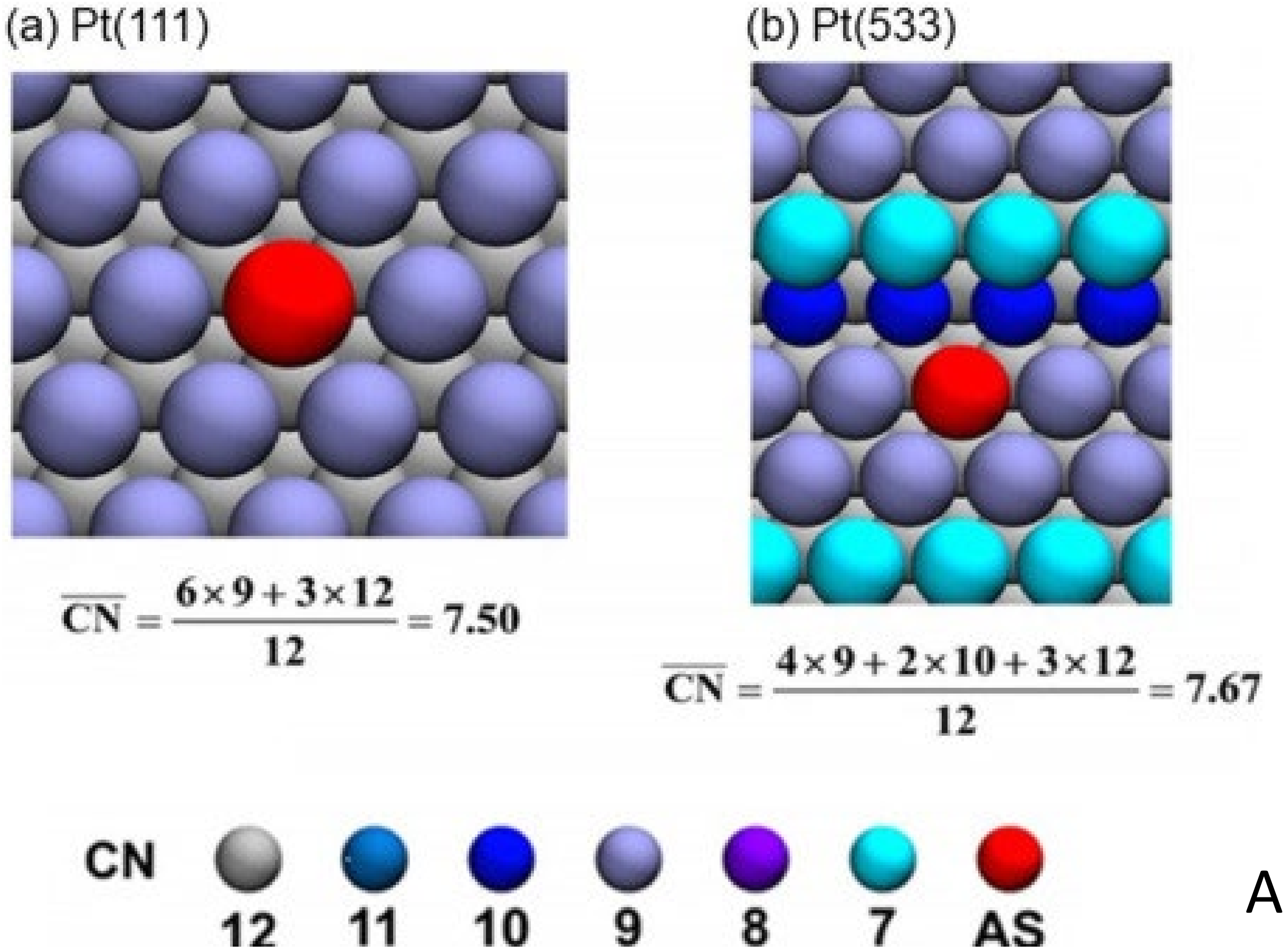
- The combination of these strain and ligand effects in the formation of a bimetallic surface leads to changes in the surface d-band width.

Surface Geometry

- Spatial arrangement of atoms in surface active sites influences adsorption, and thus catalytic activity.
- A very common and straightforward geometric descriptor is the coordination number (CN), which for metals is the number of atoms located in the proximity of a given atom, taking as a reference the interatomic distance observed in bulk.
- Typically, adsorption energies (↓) linearly with (↑) CN.
- CNs can be tuned in some metals by the introduction of different surface atomic facets, steps, and kinks.
  - knowing which surface sites are favorable (catalytic **activity** and/or **selectivity**) for a given electrocatalytic material.


Vacancy
Terrace
Cluster
Adatom
Step
Kink

Generalized CN ($\overline{\mathrm{CN}}$)



$$\overline{\mathrm{CN}} = \frac{6\times9+3\times12}{12} = 7.50$$

$$\overline{\mathrm{CN}} = \frac{4\times9+2\times10+3\times12}{12} = 7.67$$

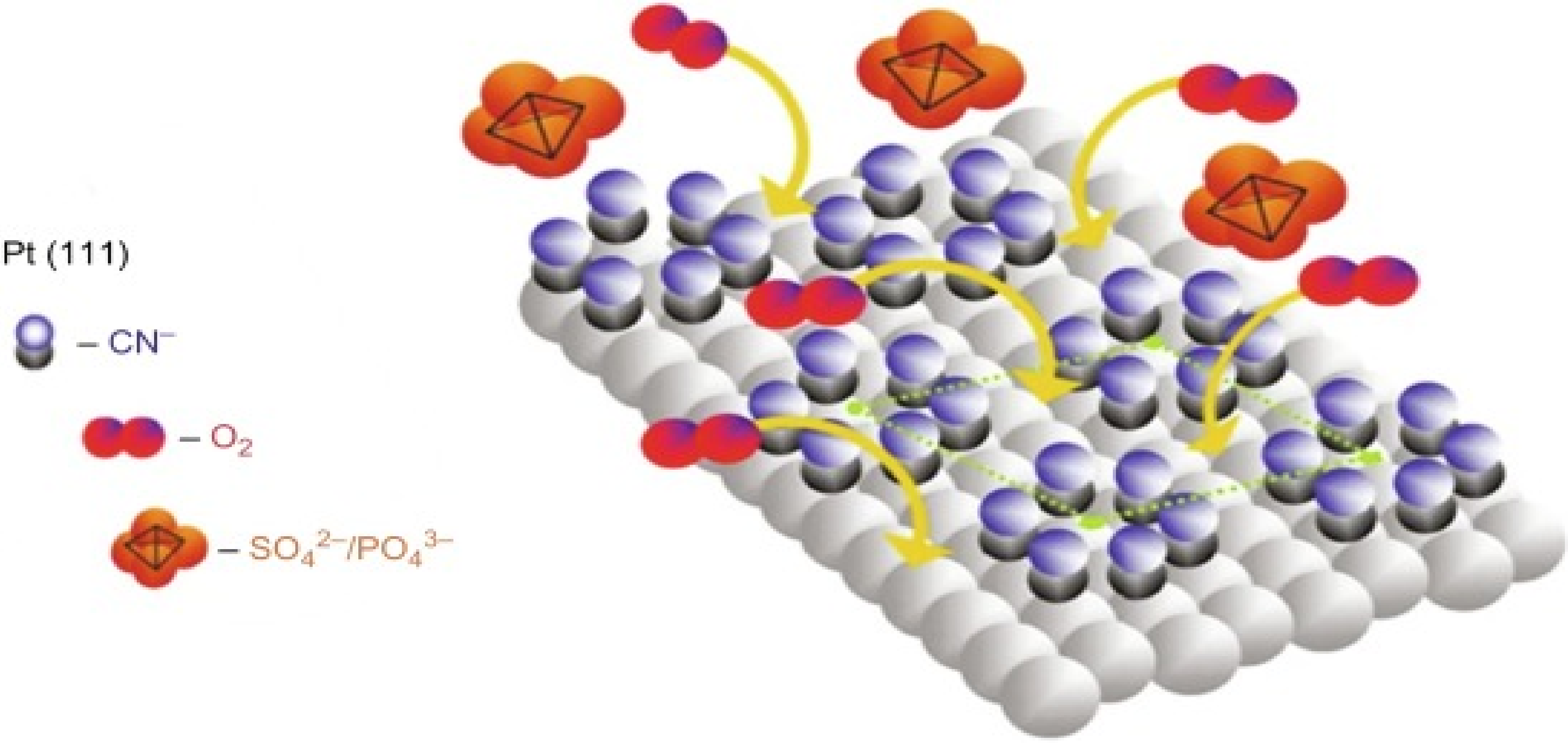
AS:
Active sites

Coordination number for atoms in different surface sites (a) Pt (111) and (b) Pt (533). **Generalized CN ($\overline{\mathrm{CN}}$) (**extends to 2nd coordination shell**)** can be calculated by taking the sum and normalizing by the bulk coordination (CN_{max}= 12).

ChemSusChem 11 (2018) 1824–1828.

Surface Composition

- influences the adsorption properties of metals.
- is tuned by using surface alloys or adatoms of a foreign metal.
- This modification can lead to enhanced activity by 2 main effects: bifunctional catalysis (BFC) and third body effects (TBE).
- BFC occurs when the second metal provides a suitable secondary adsorption site (*that did not exist before*) for a co-adsorbate that is necessary for the reaction to proceed, while the primary reactant still adsorbs on the free sites of the substrate.
- TBE arise from selective blockage of a particular adsorption site by deposited adatoms or molecular adsorbate.



TBE for Pt(111) surfaces modified with CN^- moieties. The presence of CN^- blocks specific sites on the surface to impede the adsorption of sulfate and phosphate, leaving free adsorption sites for O_2 and thus enhancing the O_2 electroreduction

Nat. Chem. 2 (2010) 880–885

Electrode Potential, EP

- It is a huge advantage of electrochemical reactions that their driving force can be varied with EP. ($\Delta \boldsymbol{G} = -nFE$)
- EP may influence the reaction rate and determine the **sequences** of elementary bond-breaking and bond-forming processes.
- The rate-determining step of an electrocatalytic reaction may be potential-independent (e.g., a chemical step),
  - EP is less important.
  - the effect of EP originates from the differences in charge donation from the metal to the adsorbate that occur when the electrode potential is changed.
  - The change in EP will affect filling the antibonding orbitals and, consequently, strengthen or weaken the adsorption energies.

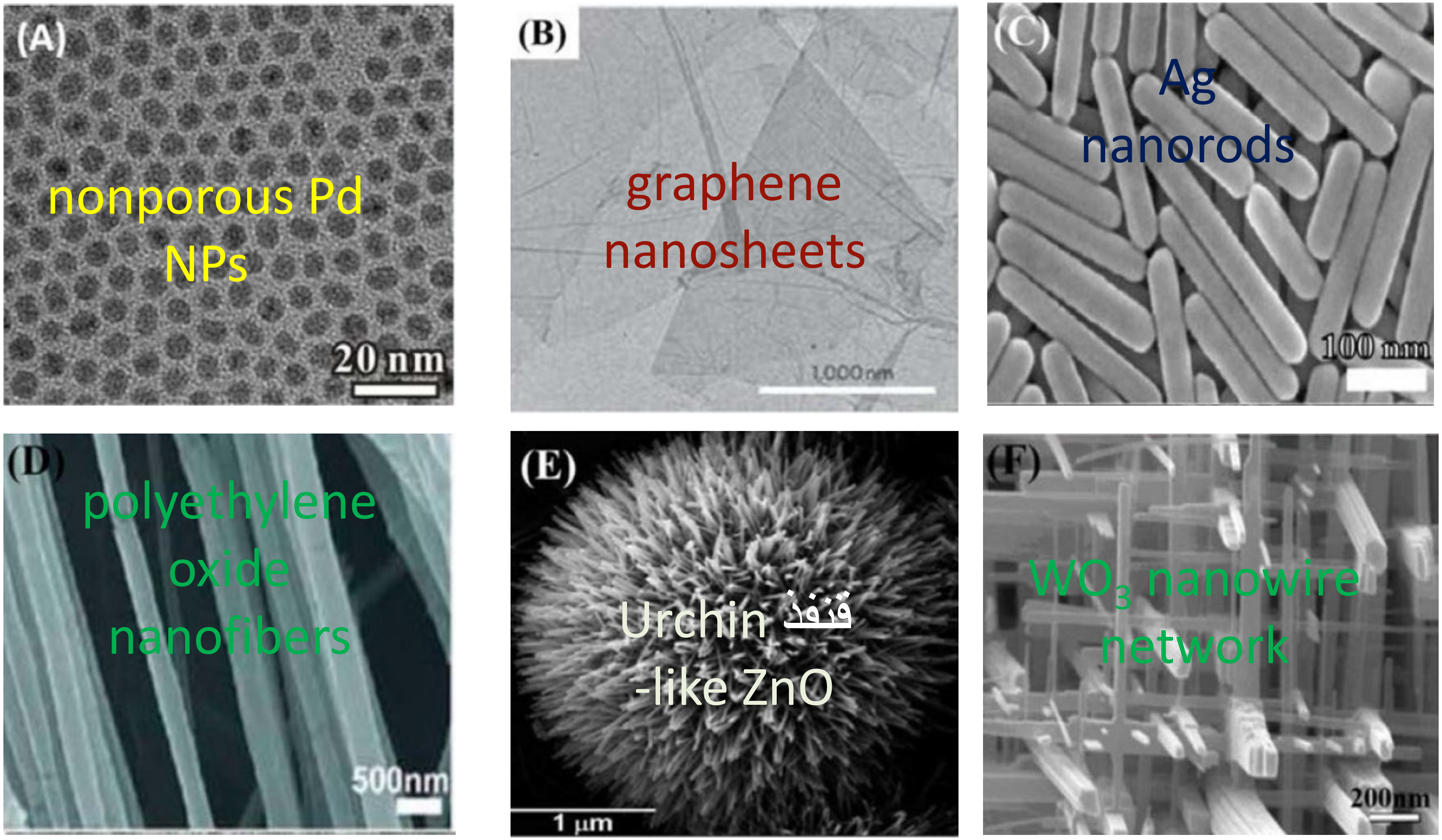
Nanoscale Effects in Electrocatalysis

Nanoparticles, NP

- gained importance due to their tunable physicochemical characteristics (melting point, wettability, electrical and thermal conductivity, catalytic activity, and light absorption and scattering).
- In practical electrochemical applications, electrocatalysts are usually nanostructured, NPs being the most common.
- Nanoscale materials allow one to maximize the surface-to volume ratio and control (structurally and electronically) the exposed surface sites, thereby increasing the mass-specific utilization and efficiency of the electrocatalyst material.

NP Reactivity

- Particle shape, size, and composition are crucial parameters in determining NP reactivity



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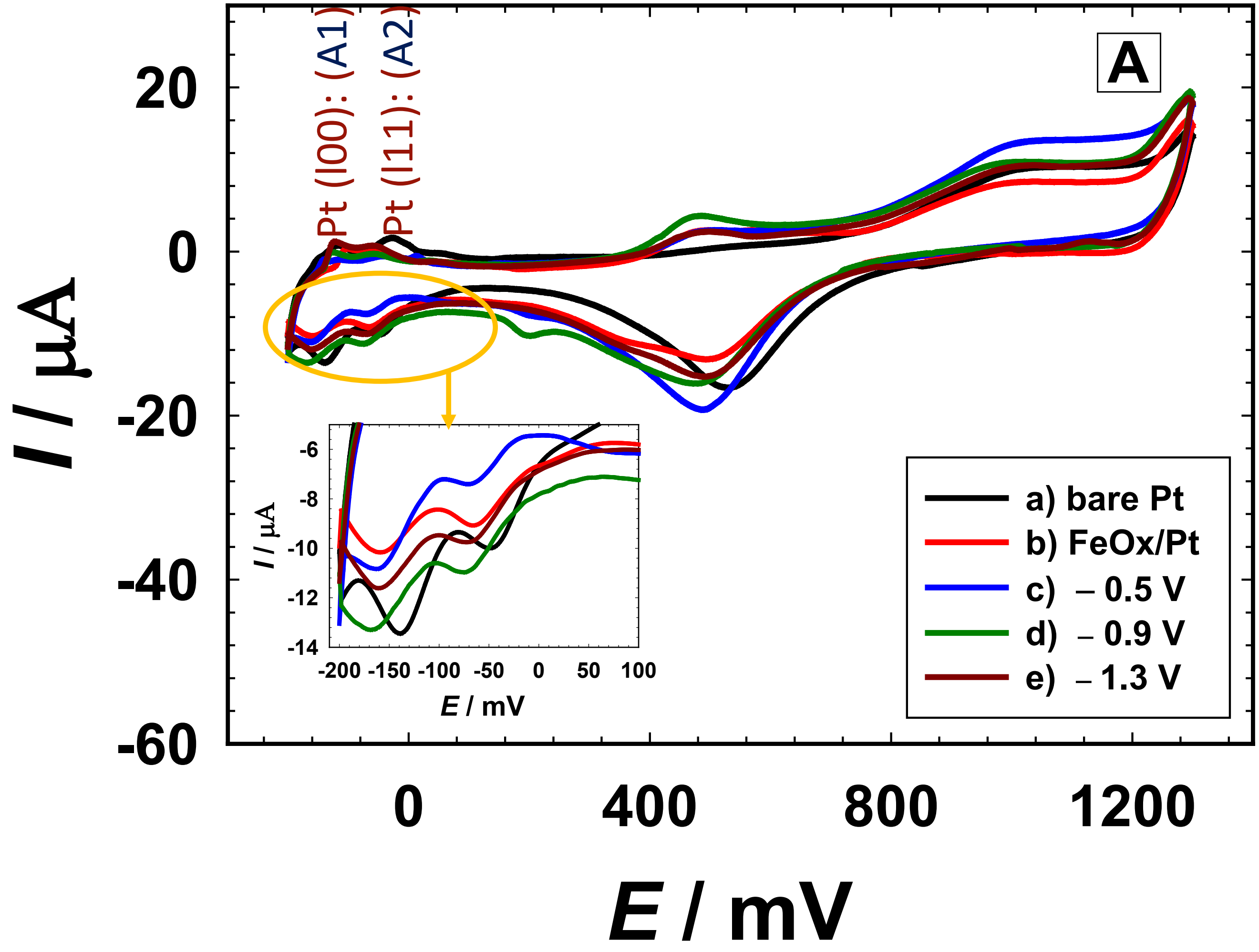
Nanoparticles Shape

- Electrochemical reactions are surface structure-sensitive reactions where the NP shape and resulting arrangement of surface atoms will strongly control their overall reactivity.
- The shape of the particles usually dictates the crystallographic facets that are exposed: e.g., octahedra and tetrahedra expose (111) facets, and cubes expose (100) facets, whereas truncated octahedra and cuboctahedra expose a combination of (111) and (100) facets.
- During crystal growth, the crystal facets evolve to achieve the lowest surface energy (γ).

Face-centered cubic (fcc) metals

- On fcc metals surface energy increases in the order $\gamma\{111\} < \gamma\{100\} < \gamma\{110\} < \gamma\{hkl\}$, where {hkl} represents high-index planes with at least one Miller index larger than 1.
- For metal oxides, the surface energy increases with increasing density of **dangling** bonds (or immobilized free radical, i.e., unsatisfied valence on atoms due to undercoordination).
- For several reactions, Pt high index planes with open surface structure typically exhibit higher reactivity than that of (111) or (100) low-index planes due to their large density of low-coordinated atoms situated on steps and kinks, with high reactivity.

Bifunctional Tailoring of Platinum Surfaces with Earth Abundant Iron Oxide Nanowires for Boosted Formic Acid Electro-Oxidation

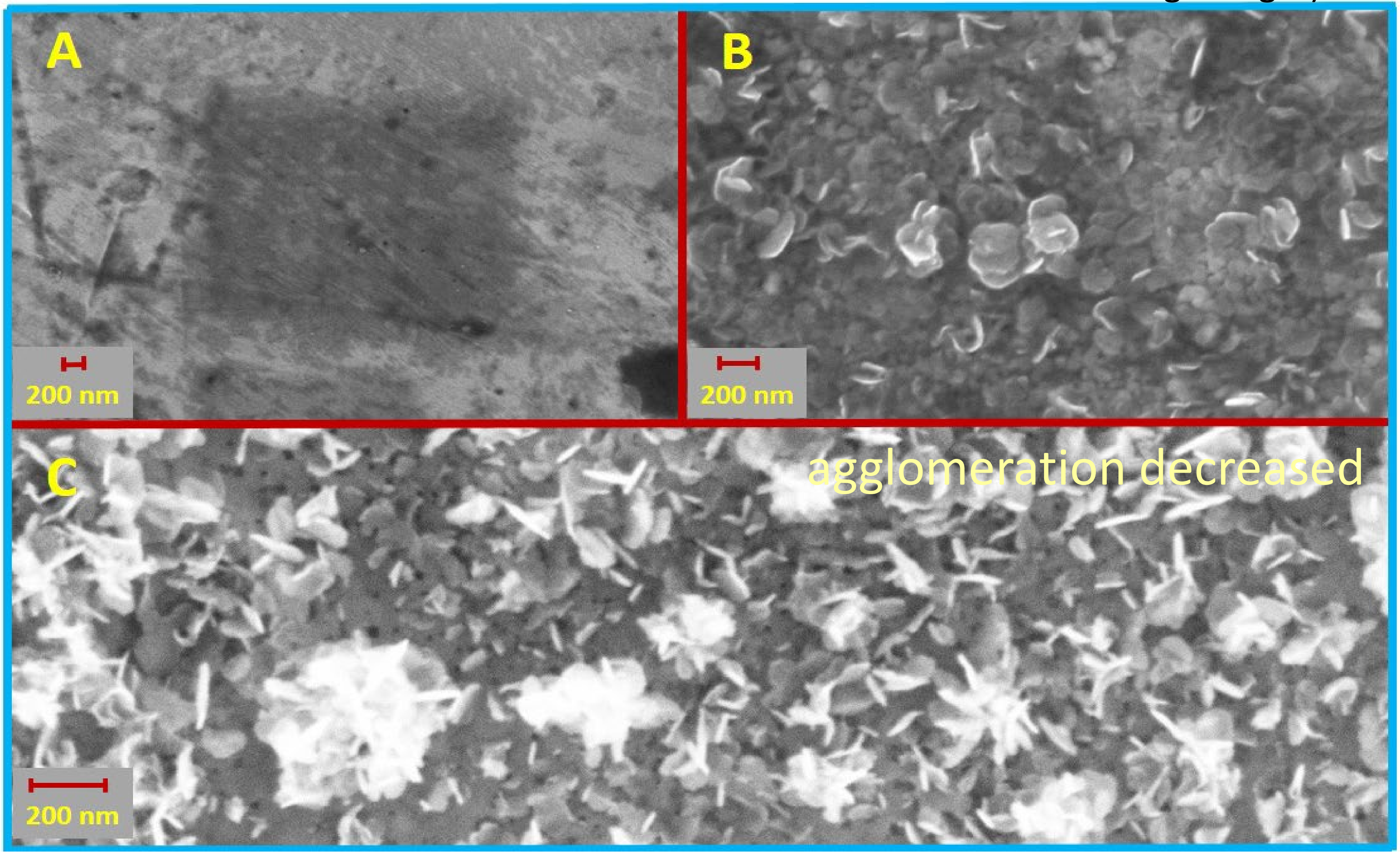


https://onlinelibrary.wiley.com/doi/10.1155/2018/4657040

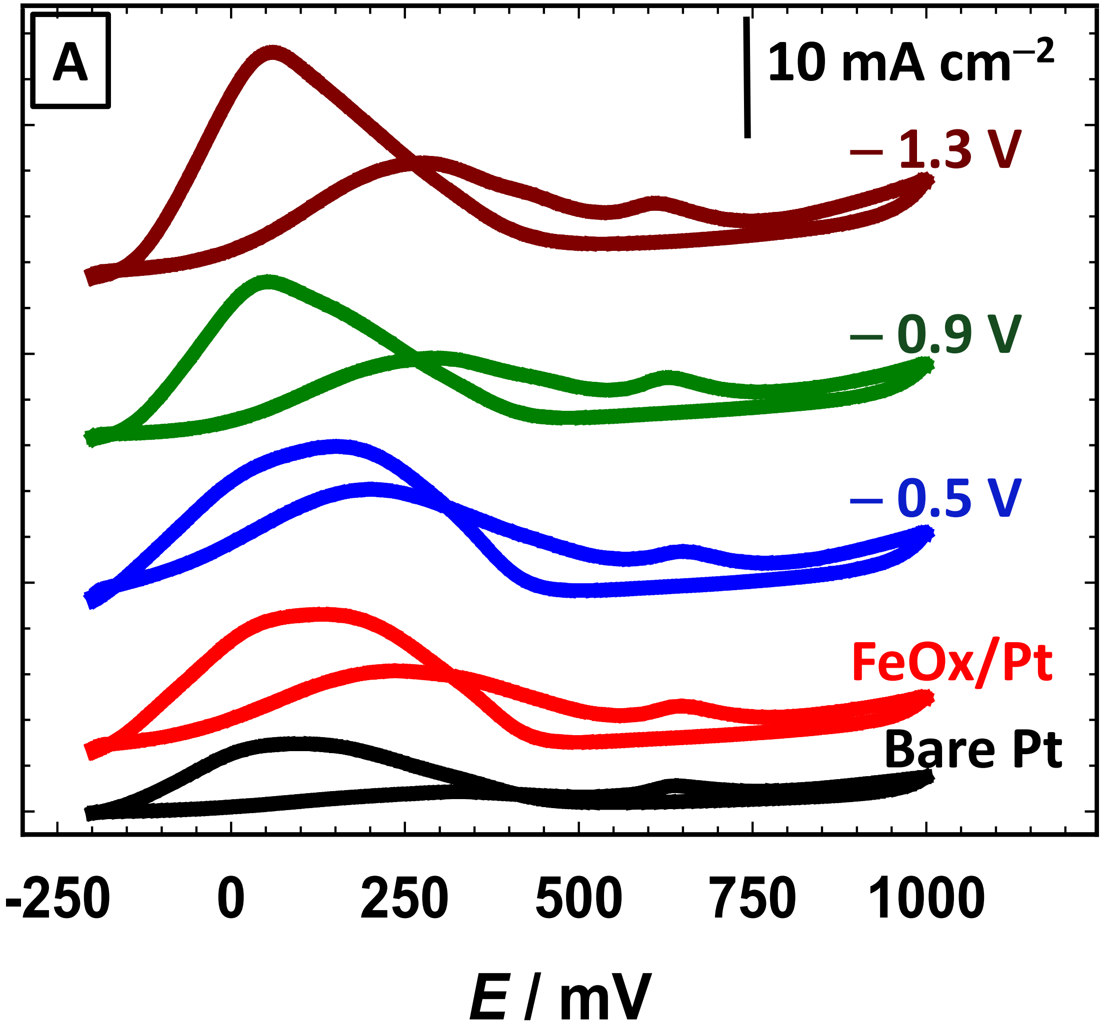
The real Pt surface areas calculated based on the ($H_{ads}/_{des}$) peaks (A1 and A2) utilizing a reference value of 210 μC cm^{-2} and based on the PtO→Pt reduction peak (A) utilizing a reference value of 420 μC cm^{-2}.

Electrode	A1(100) cm^2	A2 (111) cm^2	A1+A2 cm^2	A1:A2	A (PtO reduction) cm^2
Bare Pt	0.032	0.020	0.052	1.60	**0.064**
FeOx/Pt	0.025	0.016	0.041	1.56	**0.057**
a-FeOx/Pt (– 0.5 V)	**0.026**	**0.013**	**0.039**	**2.00**	**0.073**
a-FeOx/Pt (– 0.9 V)	0.032	0.028	0.060	1.14	**0.077**
a-FeOx/Pt (– 1.3 V)	0.030	0.028	0.058	1.07	**0.066**

agglomerated sponge-like structure nano-FeOx with few nanowires (ca. 20 nm in average diameter and 77 nm in average length).



FE-SEM images of the bare Pt (A), FeOx/Pt (B), and a-FeOx/Pt (−0.5 V) (C) catalysts



CVs in 0.3 mol/L FA (pH = 3.5)

Table 2: Electrochemical measurements obtained for FAO

Electrodes	**I_d mA cm^{-2}**	**I_{ind} mA cm^{-2}**	**I_b mA cm^{-2}**	**I_d/I_{ind}**	**I_d/I_b**	**Eonset (mV)**	**R_{ct} (kΩ)**
Bare Pt	1.6	0.7	5.1	2.3	0.31	–140	**82**
FeOx/Pt	6.4	0.7	11.1	9.1	0.58	–170	**80**
a-FeOx/Pt (– 0.5 V)	**8.7**	**0.5**	**12.6**	**17.4**	**0.7**	**–170**	**64**
a-FeOx/Pt (– 0.9 V)	6.6	1	11.8	6.6	0.56	–166	**-**
a-FeOx/Pt (– 1.3 V)	9.5	0.9	16.5	10.6	0.58	–153	**-**

Nanoparticles size

- is critical in governing its mass-activity, since this determines the **proportion** of surface atoms with respect to the total number of atoms (commonly referred to as the electrocatalyst "dispersion").
- The **smaller** the particle becomes, the **more** surface atoms there are relative to bulk.
- For fcc metals, in particles with diameters (d) < 10 nm, the proportion of surface atoms is large (≈ 20% for d = 5 nm with a total number of 6000 atoms, and 50% for d = 2 nm with a total number of 300 atoms).
- With a diameter of 1 nm, all atoms of the particles can be considered as surface atoms.

- For ideal geometric structures, such as octahedra and truncated octahedra, the proportion of edge and corner atoms with respect to the total surface atoms also increases with decreasing particle size.
- For some reactions, smaller particles are not desirable, such as when large surface site domains are required.
- Smaller particle sizes may decrease stability and durability as they have a high surface energy so are more prone to grow (e.g., via Ostwald ripening: small crystals or sol particles first dissolve and then redeposit onto larger crystals) or aggregate, with consequent loss in surface area.

Thank You