Electrodes prepared by surface modification to produce an electrode suited for a particular function – different properties from those of the unmodified substrate.

Interest in surface modification:

• Protection from corrosion.
• Electrocatalysis.
• Electrochromic devices (change color with redox state).
• Sensing.

Relevant pages = 580-589.
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- Substrate or platform (electrode to be modified)

- Monolayer (one molecular layer thick)

  a. **Irreversible adsorption** = many species spontaneously adsorb on a substrate surface from solution because the substrate environment is energetically more favorable than the solution environment.

  1. \[ R-SH + Au \rightarrow R-S-Au \]
  2. aromatics, olefins and long chain aliphatics adsorb on carbon and metal electrodes.
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b. **Covalent attachment** = attachment of the admolecule via a strong covalent bond.

![Diagram](image)

**Figure 14.2.1** Examples of specific adsorption on electrodes. (a) Adsorption of (1) a disulfide or protein on Hg; (2) an olefin on Pt; (3) an organized Langmuir-Blodgett film on Au. (b) Adsorption of a metal ion or complex through an anionic ligand bridge. [From A. J. Bard, “Integrated Chemical Systems,” Wiley, New York, 1994, with permission.]
c. **Organized layers** = sometimes spontaneous processes lead to an adlayer structure with some degree of order imposed by lateral interactions between the component molecules – *self-assembly*.

Hydrophobic interactions between component molecules. Strong covalent bond with Au. Tilted adlayer.

Alkanethiols on Au
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• Multilayers (thick films)

a. Polymers

1. Electroactive polymers with redox groups covalently attached (poly(vinylferrocene)).
2. Ion exchange polymers (Nafion, poly(styrene sulfonate)).
3. Electrically conducting polymers – accompanied by ion incorporation (polyaniline, polypyrrole).

Polymer (insulator) ↔ Polymer$^+$ (conductor) + A$^-$
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• Inorganic Films
  a. metal oxides (e.g., Al$_2$O$_3$) – adsorption and electrocatalysis.
  b. clays and zeolites (e.g., aluminosilicates) – high surface area with ion exchange capabilities.

• Biologically Important Materials (usually for chemical sensing)
  a. Enzymes
  b. Antibodies
  c. DNA

All interact with some target.
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O + ne\(^-\) \leftrightarrow R

O and or R adsorbed can significantly affect the electrode reaction kinetics and mechanism.

1. Adsorption isotherm must be selected.
2. Degree to which adsorption equilibrium is attained before the start of the electrochemical experiment.
3. Rate of ET to adsorbed species relative to that of the dissolved species.

Adsorption can be both friend and foe!
1. Electrode fouling and deactivation.
2. Pre-requisite to rapid ET
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\[
i/nFA = D_o \left( \frac{\partial C_o(x,t)}{\partial x} \right)_{x=0} - \frac{\partial \Gamma_o(t)}{\partial t} = -D_R \left( \frac{\partial C_R(x,t)}{\partial x} \right)_{x=0} - \frac{\partial \Gamma_R(t)}{\partial t}
\]

\[\Gamma = \text{surface excess, mol/cm}^2\]

\[
\Gamma_o(t) = \beta_o \Gamma_{o,s} C_o(x,t) / [1 + \beta_o C_o(0,t) + \beta_R C_R(0,t)]
\]

\[
\Gamma_R(t) = \beta_R \Gamma_{R,s} C_R(x,t) / [1 + \beta_o C_o(0,t) + \beta_R C_R(0,t)]
\]

\[\beta = \exp(-\Delta G^o_i/RT)\quad \Delta G^o_i = \text{standard free energy of adsorption}\]
When one chemically modifies an electrode surface, there are several important questions to answer.

- What is the surface coverage?
- What is the admolecule or molecular layer orientation on the surface?
- What is the spatial uniformity of the admolecule or molecular layer over the surface?
- What kind of “electrical connection” exists between the admolecule or molecular layer and the electrode surface? Through-molecule charge transport?
Case 1: Only Adsorbed O and R Electroactive - Nernstian

\[-\partial \Gamma_o(t)/\partial t = \partial \Gamma_R(t)/\partial t = i/nFA\]  {no adsorption of desorption during scan}

\[\Gamma_o + \Gamma_R = \Gamma_o^*\]

\[i_p = (n^2F^2/4RT)\nu A\Gamma_o^*\]

\[E_p = E^{o'} - (RT/nF)\ln(b_o/b_R) = E^{o'}_a\]

\[\Delta E_{p,1/2} = 3.53 \frac{RT}{nF} = 90.6/n \text{ mV (25 °C)}\]

Sweep rate fast enough that O does not have time to diffuse to or from the electrode. Electrolysis done without mass-transfer limitations.
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• $i_p$ proportional to $v$
• Area under the peak (the charge), after correcting for the residual current, is equal to $nF\Gamma^*$.
• $E_p^a = E_p^c$ or $\Delta E_p = 0$

The location of $E_p$ with respect to $E_o^*$ depends on the relative strength of adsorption of O and R.

- If $b_o = b_R$ then $E_p = E_o^*$
- If $b_o > b_R$ then $E_p < E_o^*$
- If $b_o < b_R$ then $E_p > E_o^*$

b is a measure of the adsorption strength.

$b_o = \beta_o \Gamma_o,s = \exp(-\Delta G_i^o/RT)\Gamma_o,s$

$b_R = \beta_R \Gamma_R,s = \exp(-\Delta G_i^o/RT)\Gamma_R,s$
Case 2: Only Adsorbed O Electroactive – Irreversible Rxn

- Deviations from the bell shape occur with factors such as the inhomogeneity of the adlayer, charge transport through the film, structural and resistive changes in the adlayer during changes in redox state.

\[
i_p = \alpha nF^2 A \nu \Gamma_o^*/2.7RT
\]

\[
E_p = E^{o'} + RT/\alpha nF \ln(RTk^o/\alpha F\nu)
\]

\[
\Delta E_{p,1/2} = 2.44(RT/\alpha nF) = 62.5/\alpha n \text{ mV (25 °C)}
\]
Case 3: Both Dissolved and Adsorbed Species Electroactive

Product R Strongly Adsorbed

- $\beta_0 \rightarrow 0$ and $\beta_R \rightarrow$ large number.
- Pre- and post-waves observed.
- $i_p$ (ads) proportional to $\nu$ and $\Gamma$.
- $i_p$ (dissolved) proportional to $\nu^{1/2}$ and $C^*$.
- $E_p$ shifts with $\Gamma$.

Figure 14.3.7  Effect of scan rate and $\Gamma_R$ on linear scan voltammograms when the product is strongly adsorbed. Calculated for $\alpha_F/RT = 0.05$ mV$^{-1}$, $\beta_R \beta_0 (D_R D_0)^{1/2} = 2.5 \times 10^5$ and values of $44_F \beta_R \beta_0 (n(F/RT))^{1/2}(C^*_R (\pi D_0)^{1/2}$ of: curve A, 1.6; curve B, 0.8; curve C, 0.2. Note that with all parameters constant except $\alpha$, relative scan rates are 64:16: 1. [Reprinted with permission from R. H. Wop schall and I. Shain, Anal. Chem., 39, 1514 (1967). Copyright 1967, American Chemical Society.]

Figure 14.3.8  Effect of $C^*_R$ on linear scan voltammograms when the product is strongly adsorbed. Calculated for $\alpha_F/RT = 0.05$ mV$^{-1}$, $44_F \beta_R \beta_0 (n(F/RT))^{1/2}(\pi D_0)^{1/2}$ = 1.0 $\times 10^6$, and $C^*_R (\pi D_0)^{1/2}(44_F \beta_R \beta_0 (n(F/RT))^{1/2}$ values of: curve A, 0.5; curve B, 2.0; curve C, 8.0. [Reprinted with permission from R. H. Wop schall and I. Shain, Anal. Chem., 39, 1514 (1967). Copyright 1967, American Chemical Society.]
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**Chronoamperometry**

- **E1**
- **E2**

**Time**

**i(t) = nFAD^{1/2}C^*/(πt)^{1/2}**

**Cumulative charge passed**

**Q = nFN**

**Q(t) = 2nFAD^{1/2}C^*t^{1/2}/π^{1/2}**

**Least distorted by potential rise**

**Chronocoulometry**

- **E1**
- **E2**

**Time**
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\[ \int i \, dt = nFAD^{1/2}C^*/\pi^{1/2} \int t^{-1/2} \, dt \]
(integrate from \( t = 0 \) to \( t \))

\[ Q(t) = 2nFAD^{1/2}C^*t^{1/2}/\pi^{1/2} \]

**Measurement Advantages**

- Signal grows with time, better S/N
- Integration smooths random noise
- Contribution from \( Q_{dl} \) and \( Q_{ads} \) meas.

Excellent technique for examining electroactive adlayers!

\[ Q_{total} = Q_f + Q_{dl} + Q_{ads} \]

\[ Q = 2nFAD^{1/2}C^*t^{1/2}/\pi^{1/2} + Q_{dl} + nfA\Gamma \]

Be aware that adlayer can affect \( Q_{dl} \)
Chapter 14 – Chemically Modified Electrodes

Coulometry

$O + e^- \leftrightarrow R \text{ (with } O \text{ both ads and dissolved)}$

\[
Q_f = 2nFAC_o^* (D_o t/\pi)^{1/2} + Q_{dl} + nF\Gamma_o
\]

Once $Q_{dl}$ is determined, then $nF\Gamma_o$ can be obtained.