Kinetics and Catalysis
with a nod toward water oxidation

- Daniel Strongin
- 1/22/2016
Brief Introduction Surface Catalysis

$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$
Terms

Adsorbed Phase - Atoms or molecules that are bound to a surface

Molecular Adsorption – Adsorbing molecule remains intact

Dissociative Adsorption – Bond breaks in adsorbed molecule

Surface Sites – Places on the surface where reactions occur
Types of Adsorption for Various Molecules

Solar to fuel conversion

Sunlight → Light capture → Charge separation → Electrocatalysis → Fuels (H₂ or CₓHᵧOᶻ)

- High absorption
- Long diffusion lengths
- Minimal overpotential

- Solar farms - tethering PV device with electrolyzers (inefficient)
  (solar energy → electricity → fuels)
- Advance technologies (with single energy transformation)

Photo-anodes with electrocatalysts

Catalysis may be very sensitive to surface structure

Haber Reaction: $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

Different Crystallographic Planes of BCC Iron

Langmuir-Hinshelwood

Eley-Rideal
Langmuir-Hinshelwood
Rate = $k\theta_A \theta_B$

Eley-Rideal
Rate = $k\theta_A P_B$

$\theta = \frac{\# \text{ of sites occupied}}{\text{total \# surface sites}}$
Langmuir Isotherm

At equilibrium: \( r_{\text{ad}} = r_{\text{des}} \)

\[
\frac{P}{\sqrt{2\pi n k T}} \cdot S_0 (1 - \theta) \cdot e^{-\Delta E_{\text{ad}} / kT} = v_{\text{des}} \cdot \theta \cdot e^{-\Delta E_{\text{des}} / kT}
\]

\[
\theta = \frac{bP}{1 + bP} ; \quad b = \frac{S_0 \exp(-\{\Delta E_{\text{ad}} - \Delta E_{\text{des}}\} / kT)}{v_{\text{des}} \sqrt{2\pi n k T}}
\]

coverage

Non dissociative adsorption

Dissociative adsorption
Catalysis on surfaces

Unimolecular decomposition

\[ A_g = A_{ad} \rightarrow \text{Products} \]

\[ r_a = k_a P_a(1 - \theta) \]
\[ r_d = k_d \theta \]
\[ r_a = r_d \text{ at equilibrium} \]

\[ \theta = \frac{bP}{1 + bP}; \quad b = \frac{k_a}{k_d} \]

\[ \text{Rate} = k \theta \]
\[ \text{Rate} = k \frac{bP}{1 + bP} \]

\[ \theta = \frac{\text{# of sites occupied}}{\text{total # surface sites}} \]

http://www.chem.qmul.ac.uk/surfaces/scc/
Eley-Rideal

Rate = $kP_B \theta_A$

\[
\theta_A = \frac{bP_A}{1 + bP_A}
\]

\[
R = \frac{kbP_A P_B}{1 + bP_A}
\]
Langmuir-Hinshelwood

Rate = $k\theta_A \theta_B$

\[
\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B}; K_A = \frac{k_A}{k_{A,\text{des}}}
\]

\[
\theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B}; K_B = \frac{k_B}{k_{B,\text{des}}}
\]

\[
R = \frac{k K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2}
\]

$P_A$ is constant

$P_B$ is constant
Catalysis on surfaces

Bimolecular: Langmuir-Hinshelwood Reaction

\[ \text{CO}_g = \text{CO}_{ad} \]

\[ \text{O}_2g = 2\text{O}_{ads} \]

\[ \text{CO}_{ad} + \text{O}_{ad} \rightarrow \text{CO}_2_{ads} \rightarrow \text{CO}_2g \]

\[ \theta_O = \frac{\sqrt{b_0P_{O2}}}{1 + \sqrt{b_0P_{O2} + b_{CO}P_{CO}}} ; \quad \theta_{CO} = \frac{b_{CO}P_{CO}}{1 + \sqrt{b_0P_{O2} + b_{CO}P_{CO}}} \]

\[ \text{Rate} = k\theta_{CO}\theta_O = \frac{kb_{CO}P_{CO}\sqrt{b_0P_{O2}}}{(1 - \sqrt{b_0P_{O2} + b_{CO}P_{CO}})^2} \]

\[ \text{Rate} = \frac{k\sqrt{b_0P_{O2}}}{b_{CO}P_{CO}} = k' \frac{P_{O2}^5}{P_{CO}} \]

CO strongly adsorbed

\[ b_{CO}P_{CO} >> (1 + \sqrt{b_0P_{O2}}) \]
Brief Introduction to electrochemistry for electrocatalysts

Analysis adapted from
Consider the following reaction where A is in equilibrium with B

\[
\begin{array}{c}
\text{A} \rightleftharpoons \text{B} \\
\frac{k_f}{k_r}
\end{array}
\]

Where \( K_f \) and \( k_r \) are the forward and reverse rate constants.
Reaction rate of forward and reverse reaction

- Rate of forward reaction is given by
  \[ R_f = k_f \cdot C_A \]

- Rate of reverse reaction is given by
  \[ R_r = k_r \cdot C_B \]
What is the net reaction rate?

- \( R_{\text{net}} = R_f - R_r \)
- \( R_{\text{net}} = k_f \cdot C_A - R_r = k_r \cdot C_B \)
Equilibrium

Equilibrium is defined as the point at which the net reaction rate is zero

\[ \frac{k_f}{k_b} = K = \frac{C_B}{C_A} \]

Equilibrium constant
Rates of reactions

\[ O + ne^- = R \]

\[ R_{for} = k_{for}[O] = \frac{i_c}{nF} \]

\[ R_{rev} = k_{rev}[R] = \frac{i_a}{nF} \]

\[ R_{net} = R_{for} - R_{rev} = (i_c - i_a) / nF \]

\[ = (k_{for}[O] - k_{rev}[R]) \]
Nernst Equation at Equilibrium

\[ E_{eq} = E^0 - \frac{RT}{nF} \ln \left( \frac{[R]}{[O]} \right) \]

Where \( E^0 \) is standard potential, \( F \) is Faraday’s constant, and \( n \)=#electrons transferred in equation
At Equilibrium

\[ R_{\text{for}} = R_{\text{rev}} ; \quad i_c = i_a \]

\[ k_{\text{for}} [O] = k_{\text{rev}} [R] \]

\[ \ln k_{\text{rev}} - \ln k_{\text{for}} = \ln \frac{[O]}{[R]} = \frac{F}{RT} (E - E^0) \]

\[ \frac{RT}{F} \left[ \frac{d}{dE} \ln k_{\text{rev}} + \frac{d}{dE} \ln \left( \frac{1}{k_{\text{for}}} \right) \right] = 1 \]

Oxidative Symmetry factor: \( 1-\alpha \)

Reductive Symmetry factor: \( \alpha \)
Symmetry Factor

O + e curve shifts as a potential becomes more positive

$\alpha$ is the symmetry of the energy barrier for reaction. If both sides of barrier are same, $\alpha = 0.5$

Rate constants

\[
\ln \frac{1}{k_{\text{for}}} = \frac{\alpha F E}{RT} + c
\]

\[
k_{\text{for}} = k_{\text{for}}^0 \exp \left\{ - \left[ \frac{\alpha F}{RT} \right] (E - E^0) \right\}
\]

\[
k_{\text{rev}} = k_{\text{rev}}^0 \exp \left\{ \left[ (1 - \alpha) F / RT \right] (E - E^0) \right\}
\]

Where \( k_f = k_f^0 \) and \( k_r = k_r^0 \) when \( E = E^0 \)

\( K_f^0 \) and \( k_r^0 \) are standard rate constants

When \([O] = [R]\) and \( E = E^0 \) then \( K_f^0 = k_r^0 \)
Rate constants

\[ k_{for} = k^0 \exp \left\{ -\frac{\alpha F}{RT} (E - E^0) \right\} \]

\[ k_{rev} = k^0 \exp \left\{ -\frac{(1 - \alpha) F}{RT} (E - E^0) \right\} \]

Small \( k^0 \), large overpotential needed to get reaction Going. Low efficiency
Tafel Equation

\[ R_{net} = \frac{i}{nF} = [k_f [O] - k_r [R]] \]

\[ i = nFk^0 [O] \exp \{-[\alpha nF / RT](E - E^0)\} - [R] \exp \{[(1 - \alpha)nF / RT](E - E^0)\} \]

If we have a large overpotential, \( \eta \), where \( \eta = E - E^0 \)

Whether \( \eta \) is < or > 0

\( \eta = a + b \log i \) (Tafel equation)
Current versus Overpotential

Testing catalyst

Thermodynamic Threshold for water oxidation; $E^0 = 0.2$ Versus Ag/AgCl at pH 14

Quoted at 10 mA/cm²

This Current is due to the water oxidation reaction

This voltage is set so the counter electrode can pass the same current as the working electrode.

Potentiostat is an instrument that controls the voltage difference between a Working Electrode and a Reference Electrode.
Electrocatalysis Measurement

Thermodynamic Threshold for water Oxidation; $E^\circ = 0.2$
Versus Ag/AgCl at pH 14

Quoted at 10 mA/cm$^2$

$i = i_o \left[ e^{\frac{[(1-\alpha)nF}{RT}\eta}} \right]$
Electrocatalytic activity: Figures of merit

Primary figures of merit for electro-catalyst activity:

- Overpotential needed to reach a given current density
- Tafel slope, $b$ (mV/dec) (relating the rate of an electrochemical reaction)
- Exchange current density $i_0$ (mA/cm$^2$)
Thermodynamics of Water Oxidation Reaction

\[ E^0 = +1.23 \text{ V} \]

\[ \Delta G > 0 \]

\[ \Delta G^\circ = 237.1 \text{ kJ mol}^{-1} \]

\[ E^0 = +1.23 \text{ V} \]

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \text{ (oxidation)} \]

\[ \text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \text{ (reduction)} \]

\[ 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 \text{ (Overall reaction)} \]

- A single catalyst cannot catalyze both oxidation and reduction reactions.
**Concept of Overpotential**

- **Overpotential** is the additional voltage needed (above that predicted by $E^\circ$ values) to drive the reaction.

- $E^\circ = +1.23$ V for water oxidation
- $E^\circ = 0$ V for hydrogen evolution

**Diagram:**
- Current density (mA cm$^{-2}$)
- MoS$_2$ catalyst electrode
- RuO$_2$
- $ \frac{1}{2} \text{H}_2 $ and $ \text{H}^+ + e^- $ reactions
- Overpotential at 200mV
- E(V) vs RHE
- $\text{H}_2$ evolution
- PtNi laccase
- Water oxidation reaction
- $E^\circ = +1.23$ V for water oxidation
- $E^\circ = 0$ V for hydrogen evolution

**Equations:**
- $2 \text{H}_2 \text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 e^-$
- $2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2$
- $\text{O}_2 + 4 \text{H}^+ + 4 e^- \rightarrow 2 \text{H}_2\text{O}$

1.53V RuO$_2$
Zero valent copper intercalated Birnessite

Theoretical Investigation of the Activity of Cobalt Oxides for the Electrochemical Oxidation of Water

Michal Bajdich, Mónica García-Mota, Aleksandra Vojvodic, Jens K. Nørskov, and Alexis T. Bell

The Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
SUNYAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States
Department of Chemical and Biomolecular Engineering, University of California at Berkeley, Berkeley, California 94720, United States

\[ \text{OH}^- + S \rightarrow S - OH + e^- \]
\[ S - OH + OH^- \rightarrow S - O + H_2O + e^- \]
\[ S - O + S - O \rightarrow O_2 \]

And / Or

\[ S - O + OH^- \rightarrow S - OOCH + e^- \]
\[ S - OOCH + OH^- \rightarrow O_2 + H_2O + e^- \]
Descriptor for Catalysis
Water Oxidation

d^7 ions: Mn^{3+}, Ni^{3+}, Co^{2+}

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch12/crystal.php
1) Intermediates *OH, *O, *OOH bond through O atom
   *OH or *O from H₂O become easier due to the surface-O interaction
2) Steps like *O + H₂O → OOH⁻ + H⁺ + e⁻ is more difficult since surface-O bond is being broken.

Direction of Forum B

- Lots of room for improvement, even for the best precious-metal based systems (e.g., IrO$_2$, RuO$_2$).
- Screening process using descriptors for water oxidation is needed to focus us on materials of interest.
- New materials that can be synthesized that from computation have favorable properties.