Lecture #28 of 26!
(Will this ever end?)

Yes... at slide 1080

Semiconductors in Electrochemistry

... so you taught us that Marcus Theory led to an inverted region...
... is there evidence for the inverted region via electrochemistry?

• Three regions of electron transfer:
  (I) Normal, (II) Barrierless, (III) Inverted


The nuclear reorganization energy, $\lambda$, is the free energy required to reorganize the solvent (outer) and bonds (inner) when the electron moves from the reactant to the product potential-energy surface, while at the nuclear arrangement of the reactant (and $\Delta G_0^f = 0$)

... and we knew this had a Gaussian shape...

... to analyze this, we have to more fully derive interfacial Marcus theory... to analyze this, we have to more fully derive interfacial Marcus theory...

\[ f(E) = \left[ 1 + \exp \left( \frac{E - E_{\text{app}}}{kT} \right) \right]^{-1} \]  
... \( \rho \) has units of cm\(^{-2} \) eV\(^{-1} \)

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\[ f(E) = \left[ 1 + \exp \left( \frac{E - E_{\text{app}}}{kT} \right) \right]^{-1} \]  
... \( \rho \) has units of cm\(^{-2} \) eV\(^{-1} \)
... the rate of electron transfer is dictated by the law of mass action...

\[ k_D = \int e^{-\beta(E)} \nu(E) (1 - \nu(E)) dE \]

... resulting in (D)istributions of occupied metal states & molecule states

... experimental electrochemical validation of Marcus theory...

... but no direct observation of inverted-region behavior

To predict maximum rate, we also need to consider quantum mechanical tunneling...

\[ \kappa_0(x) = \kappa_0 \exp(-\beta x) \]

... experimental electrochemical validation of Marcus theory...
... but no direct observation of inverted-region behavior

\[ \lambda = 0.85 \text{ eV} \]

Chidsey, Science, 1991, 251, 919

... and no inverted-region behavior was observed because at large driving force there was always a state in the metal that overlapped the most probable D_0.

Chidsey, Science, 1991, 251, 919

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Chidsey, Science, 1991, 251, 919
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... and no inverted-region behavior was observed because at large driving force there was always a state in the metal that overlapped the most probable $D_0$.

Chidsey, Science, 1991, 251, 919

Well that was disappointing... how can inverted-region behavior be seen?... at semiconductors!

... but how?

Hamann, Ostrin, Brunswig & Lewis, JACS, 2005, 127, 7815 and JACS, 2005, 127, 13949

Well that was disappointing... how can inverted-region behavior be seen?... at semiconductors!

... but how?

... Vary the molecule, not the bias!

... but $\lambda$ must be "the same" for each!

Hamann, Ostrin, Brunswig & Lewis, JACS, 2005, 127, 7815 and JACS, 2005, 127, 13949
Well that was disappointing… how can inverted-region behavior be seen? at semiconductors!

\[ \lambda = 0.67 \text{ eV} \]

... but more work is still needed in order to really validate this!


RECALL...

Q: What processes occur in electrochemistry?

A: Winter, 2017: Those involving the motion/transport of charge—carried by entities other than unsolvated electrons and holes—through phase(s), or the transfer of charge across interface(s).

\textbf{IS THIS ELECTROCHEMISTRY? WHY OR WHY NOT?}

\textbf{NOT} electrochemistry: pn-junction photovoltaic cell


\[ \text{normal} \]

bandgap

\[ \text{inverted} \]

bandgap


... \( k \) in units of cm\(^3\) s\(^{-1}\)... a second-order rate constant (\( \ldots \times \) concentration\(^2\))
**RECALL**

Q: What processes occur in electrochemistry?

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than unsolvated electrons and holes – through phase(s), or the transfer of charge across interface(s).

**IS THIS ELECTROCHEMISTRY? WHY OR WHY NOT?**

Example: dye-sensitized solar cell

---

Example: photoelectrochemical water electrolysis (splitting)

---

As a subset of PEC... who cares what you call it, right? ... Maybe

Photoelectrochemical cells consist essentially of two electrodes in contact with an electrolyte, one electrode usually being a light-sensitive semiconductor electrode and the other an inert metal or graphite electrode. In principle, both electrodes can consist of semiconducting material of opposite types.

PEC is synonymous with semiconductor/liquid junction!
As a subset of PEC... who cares what you call it, right? ... Maybe

<table>
<thead>
<tr>
<th>Light “cause a net chemical conversion in the cell”?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photovoltaic Cell</td>
</tr>
<tr>
<td>Photoelectrolytic Cell</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Is the ΔG &lt; 0 for the net chemistry?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocatalytic Cell</td>
</tr>
<tr>
<td>Photo(electro)synthetic Cell</td>
</tr>
</tbody>
</table>

Bard, Memming & Miller, Pure & Appl. Chem. 1991, 63, 560

RECALL... Q: What processes occur in electrochemistry?
A: Winter, 2017: Those involving the motion/transport of charge—carried by entities other than unsolvated electrons and holes—through phase(s), or the transfer of charge across interface(s).

**IS THIS PEC? AND IF SO, WHAT TYPE?**
Example: dye-sensitized solar cell

**RECALL...**
Q: What processes occur in electrochemistry?
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**IS THIS PEC? AND IF SO, WHAT TYPE?**
Example: photoelectrochemical water electrolysis (splitting)

As a subset of PEC... who cares what you call it, right? ... Maybe

... Well, it gets worse... What happens when you have transparent thin “metal” layers and/or cocatalysts?

"We have to be focused on what will be durably better than conventional ways to make renewable hydrogen,” explains chief technology officer Tom Jarvi. Hydrogen from a solar panel and electrolysis unit can currently be made for about US$7 per kilogram, the firm estimates; the artificial leaf would come in at $6.50. (It costs just $1–2 to make a kilogram of hydrogen from fossil fuels).

Reece, ... Nocera, Science 2011, 334, 645

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IS THIS PEC? AND IF SO, WHAT TYPE?

PV Electrosynthetic, maybe?

Probably? ... Eh?!?!?

---

... Well, it gets worse... What happens when you have transparent thin “metal” layers and/or cocatalysts?

Maeda & Domen, J. Phys. Chem. Lett. 2010, 1, 2655
Reece, ... Nocera, Science 2011, 334, 645

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http://conservationmagazine.org/2012/09/the-mighty-leaf/
... Oh my gosh, Shane! Tomato, tomatoe... WHO CARES?

Condensed matter physics + this class (CHEM 248) will wholly explain these...

Cool? ... Maybe... but rather predictable (CHEM 267)!... ... Let's talk about something new and specific to PEC!

As a subset of PEC... who cares what you call it, right? ... Maybe

Photocatalytic cells consist essentially of two electrodes in contact with an electrolyte, one electrode usually being a light semiconducting material of opposite types.

Thank you, Al, Rüdiger, and Barry!
As a subset of PEC... who cares what you call it, right? ... Maybe

Photoelectrochemical cells consist essentially of two electrodes in contact with an electrolyte, one electrode usually being a light sensitive semiconductor electrode and the other an inert metal or graphite electrode. In principle, both electrodes can consist of semiconducting material of opposite types.

PEC is synonymous with semiconductor/liquid junction!

How do you know that this is a SC/liq junction, and not a M/liq junction?

... you really don't!

Let's see what Déjà vu? ...

As a subset of PEC... who cares what you call it, right? ... Maybe

Photoelectrochemical cells consist essentially of two electrodes in contact with an electrolyte, one electrode usually being a light sensitive semiconductor electrode and the other an inert metal or graphite electrode. In principle, both electrodes can consist of semiconducting material of opposite types.

PEC is synonymous with semiconductor/liquid junction!

Déjà vu? ... Double layer?
Standard requirement for PEC: a junction and/or selective contact!

**Schottky (SC-M) junction**

**pn (SC-SC) junction**

Semiconductor–Liquid junction

How do these differ?

... They "don't"!

How can one adjust $\phi_m$ (or $\phi_n$, or $E(A/A^\prime)$)?

Shockley, Bell Syst. Tech. J. 1949, 435


Tan, ... Lewis, Prog. Inorg. Chem. 1994, 41, 21

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How do Schottky barriers differ from SC/liq junctions?

**They mostly don't!**

PEC does have, however,

• Non-fixed “work function” metal contacts, if designed appropriately and carefully

• A tunable solution “work function” = $E(A/A^\prime)$

• Tunable species concentrations (think Nernst equation)...

... Could that be useful? **Just wait!**

... And, making a conformal coating is a cinch!

---

How do Schottky barriers differ from SC/liq junctions?

... Schottky barriers have **fixed** metal contact potentials...

... but not usually based on the values shown here...

... due to interfacial trap states that form due to chemical reactions that occur between the semiconductor and the metal, e.g. silicon + hot metals = silicides

---

Fig. 2: Metal work function for a clean metal surface in a vacuum versus atomic number. Note the periodic nature of the increase and decrease of the work functions within each group. (After Ref. 12.)

How do Schottky barriers differ from SC/liqu junctions?

**Schottky (SC–M) junction**

\[ V_0 = \frac{2kT}{q} \left( \frac{N_0 - N_D}{N_D} - \frac{V}{kT} \right) \]

\[ C_M = \frac{q}{T(\text{perm.})} \]

Equation can be written in the form

\[ \frac{C_M}{q} \]

\[ kT \frac{N_0 - N_D}{N_D} \]

So maybe not that much!

See & Ng, Physics of Semiconductor Devices, 3rd edition, Wiley, 2007

---

Recall... Here is the Nyquist plot for the “full” typical Randles equivalent circuit:

... theoretically, a Warburg impedance, \( Z_W \), has a phase angle of 45°

... for data analysis, fit frequency-dependent \( Z \) data to the model

... but this had no semiconductor for our SC/liqu junction....

... so how do we add one?
Recall... Here is the Nyquist plot for the “full” typical Randles equivalent circuit:

... theoretically, a Warburg impedance, $Z_W$, has a phase angle of 45°.

... for data analysis, fit frequency-dependent Z data to the model


... so how do we add one?

How do Schottky barriers differ from SC/liq junctions?

... if it barks like a dog, and it smells like a dog...

... then maybe we should model it as being a dog!

... Over which (C) capacitor does the potential drop?

Usually the semiconductor (C_{sc})...

... but if C_{ss} is large and being filling, then C_{dl}...

... when that occurs, one observes...

... so-called “Fermi-level pinning”


How do Schottky barriers differ from SC/liq junctions?

How many electrons are in a metal (C_{M})?

$\sim 10^{21} - 10^{23} \text{ cm}^{-3}$

How many electrons are in a semiconductor (C_{sc})?

$\sim 10^{12} - 10^{19} \text{ cm}^{-3}$, but it depends greatly on dopant density

... FYI, electrolytes have an intermediate number of charge states (C_{ss})... potential drop!... they differ from redox states!

Kumar & Lewis, J. Phys. Chem. 1990. 94, 6802
... look what happens when you change $E(A^+/A)$?
... quite informative... and fairly "easy" to test
... but what about changes in $[A^+]$ or $[A]$?
Lewis, J. Electrochem. Soc. 1984, 131, 2496

Assume that...
... $[A^+] = [A]... and [B^+] = [B]...
... that is, $E = E^0$, but $E(A^+/A) \neq E(B^+/B)$
... yet recombination rate, $v_{\text{Rec}} = k_f[e^{-}\text{[A/B]}]$, $v_{\text{Gen}}$... and no terms differ!
... so, $v_{\text{Rec,L}} = v_{\text{Rec,R}}$... but clearly, $V_{\text{oc,L}} \neq V_{\text{oc,R}}$
Rosenbluth & Lewis, J. Phys. Chem. 1989, 93, 3735

Now, assume that...
... $[A^+]_{\text{L}} = [A]_{\text{L}} = [A]_{\text{R}}$ but that $[A^+]_{\text{R}}$ is smaller or larger?
... larger?
... again $v_{\text{Rec}} = k_f[e^{-}\text{[A]}]$... but now $v_{\text{Rec,R}} > v_{\text{Rec,L}}$... due to $[A^+]$
... but interestingly, $V_{\text{oc,L}} = V_{\text{oc,R}}$
Rosenbluth & Lewis, J. Phys. Chem. 1989, 93, 3735
... and the effect was quite general...
... and unique to SC/liq junctions!

<table>
<thead>
<tr>
<th>( V_{oc} )</th>
<th>( \Delta V_{oc} )</th>
<th>( \Delta E_{oc} )</th>
<th>( \Delta E_{f} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.014 V</td>
<td>0.009 V</td>
<td>0.003 V</td>
<td>0.002 V</td>
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</tbody>
</table>

Table 1: Effect of Concentration on \( V_{oc} \)

Figure 1: Dependence of \( V_{oc} \) on \( I_{sc} \) when the concentration is constant. The exponential behavior of the initial slope \( I_{sc} \) (a) is observed only under conditions where the initial slope \( I_{sc} \) is small. \( I_{sc} \) is the position of the threshold value in the exponential behavior of the initial slope. A change in \( I_{sc} \) is observed in (b) as the temperature changes. The temperature in (b) is higher than that in (a)

... and how does one fabricate electrodes using materials found in the laboratory?

http://iopscience.iop.org/0957-4484/23/19/194013/article

How do Schottky barriers differ from SC/liq junctions?

Adaptive semiconductor/electrocatalyst junctions in water-splitting photoanodes

Fuding Lin and Shannon W. Boettcher*

High-efficiency photovoltaic/electrochemical water-splitting devices require the integration of electrocatalysts (ECs) with light-harvesting semiconductors (SCs), but the energetics and charge-transfer processes at SC EC interfaces are poorly understood. In this work, we explore the electronic and redox properties of selenium-doped NiO-based ECs as redox-active non-permeable ECs in MOX-photocatalytic water-splitting devices. Unlike traditional NiO-based ECs, selenium-doped NiO-based ECs provide a unique platform for studying the electronic and redox properties of selenium-doped NiO-based ECs as redox-active non-permeable ECs such as NiO/H, NiO/H+1, NiO/H+2, NiO/H+3, and NiO/H+4. To this end, we develop a model to predict the electronic and redox properties of selenium-doped NiO-based ECs as redox-active non-permeable ECs. This model is validated by experiments performed in a photoelectrochemical water-splitting device. This work provides a new class of adaptive semiconductor/electrocatalyst junctions for water-splitting devices.

Lin & Boettcher., Nat. Mater. 2014, 13, 81
Standard requirement for PEC: a junction and/or selective contact!

Let’s start with a thought experiment that is relevant to water splitting (water electrolysis), but via an unknown light-driven process.

... we must start at equilibrium in the dark, where rates of (G)eneration and (R)ecombination of H₂ + O₂ are the same... which will also hold under steady-state operation

![Standard requirement for PEC: a junction and/or selective contact!](image1)

Figure 6.1: Hypothetical chemical solar cell in which water is decomposed into hydrogen and oxygen by the absorption of photons. Hydrogen and oxygen can be separately removed through membranes which selectively pass hydrogen on the left and oxygen on the right.

Warwel, Physics of Solar Cells, Wiley, 2005

Standard requirement for PEC: a junction and/or selective contact!

... now introduce light, but have a means by which to collect the products of the chemical reactions... via selective membrane contacts...

What if the tanks had 1 bar of H₂ and O₂ yet you only generated a small amount of H₂ and O₂ with sunlight absorption?...

... That is, what direction would this run? Backward!!!

This is the same as with a solar cell (PV) if you are trying to charge a nearly fully charged battery, for example... but clearly not a fully discharged battery or a fan or a wire

![Standard requirement for PEC: a junction and/or selective contact!](image2)

Figure 6.1: Hypothetical chemical solar cell in which water is decomposed into hydrogen and oxygen by the absorption of photons. Hydrogen and oxygen can be separately removed through membranes which selectively pass hydrogen on the left and oxygen on the right.

Warwel, Physics of Solar Cells, Wiley, 2005

Standard requirement for PEC: a junction and/or selective contact!

external power (e.g., sunlight) driving the desired formation of H₂ and O₂

As \( \Delta G_{\text{cell}} \) rates cancel Backward!!!

What if the tanks had 1 bar of H₂ and O₂ yet you only generated a small amount of H₂ and O₂ with sunlight absorption?...

... That is, what direction would this run? Backward!!!

This is the same as with a solar cell (PV) if you are trying to charge a nearly fully charged battery, for example... but clearly not a fully discharged battery or a fan or a wire

![Standard requirement for PEC: a junction and/or selective contact!](image3)

Figure 6.1: Current of hydrogen, positive if flowing from the hydrogen tank in Figure 6.1 into the cell as a function of the deviation \( \Delta \alpha (\text{H}_2) \) of the chemical potentials of hydrogen and oxygen from their equilibrium values, without illumination (broken line) and with additional generation \( \Delta G_{\text{cell}} \) by illumination (solid line). A smaller and more realistic equilibrium generation rate \( \Delta G_{\text{cell}} \) than Figure 6.3 is assumed. The shaded rectangle is the largest current of chemical energy delivered by the cell.

Warwel, Physics of Solar Cells, Wiley, 2005
How does Regenerative PEC (PV) and Photoelectrosynthetic PEC differ?

1076

Electrolysis of Water at 5/10, Photovoltaics: Distinguishing between the Statistical and Bioelectronic Formulations for Electron-Transfer Processes in Fuel-Forming Photoelectrochemical Systems

Kumar, Santangelo, and Lewis, J. Phys. Chem. 1992, 96, 834

Postscript to photoelectrochemistry: junctions and selective contacts!

6.8 The role of the electric field in solar cells

The reader may find it confusing that the electric field which exists in the dark and, although somewhat reduced, also in the light in a p-n junction, is of no significance for our understanding of the solar cell. The intention for a solar cell structure is that electrons and holes are forced by membranes into different directions and that on their path their energy is conserved. When this condition is fulfilled, in some structures, e.g., in a p-n junction of uniform material, an electric field will be present between the membranes. The direction of the short-circuit current in a p-n solar cell agrees with the direction of this field. This seems to be sufficient to believe that it is also causing this current. To exaggerate somewhat, this is mere coincidence. It would be a completely unnecessary restriction to exclude structures for solar cells, in which no electric field is present, but which have the membrane function incorporated and which fulfill the condition of conservation of energy. The dry solar cell in Section 6.3 is a good example.

Wurzel, Physics of Solar Cells, Wiley, 2005

RECALL – Q: What processes occur in electrochemistry?

1078

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than unsolvated electrons and holes – through phase(s), or the transfer of charge across interface(s).

IS THIS PEC? I’M NOT SURE! BUT IT SEEMS RELEVANT TO PEC!

MAYBE Electrochemistry: Archaea photosynthesis

http://en.wikipedia.org/wiki/Bacteriorhodopsin
... and so we'll end with a shameless plug (2 slides) for Team Ardo!

<table>
<thead>
<tr>
<th>Crystalline Si Inorganic Photovoltaic</th>
<th>Aqueous Protonic Semiconductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-type h++ h+ n-type e- e-</td>
<td>CEM H+ H+ AEM OH- OH-</td>
</tr>
<tr>
<td>position, x</td>
<td>position, x</td>
</tr>
</tbody>
</table>

- Continuity of mass processes over $x,t$ are the same for Si and water
- Fact: Water-based rectifying protonic diodes are possible
- Claim: With proper light-absorbers, aqueous solar cells are possible

$J = \frac{1}{2} \sigma \nu (F - E + kT)$

$E_{oc} = 0.8 \text{V}$

$\sigma = 6.3 \times 10^{-4} \text{A/cm}^2$