1018

Lecture #21 <u>of 20+</u>!
(Will this ever end?)

Yes… at slide 1073

1018

1019

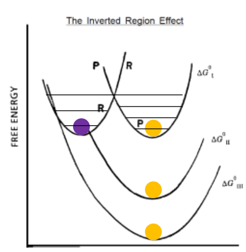
Semiconductors in Electrochemistry

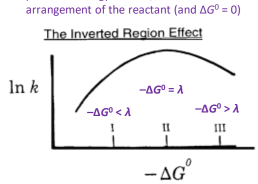
1019

… so you taught us that Marcus Theory led to an inverted region… 1020
… is there evidence for the inverted region via electrochemistry?

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

The nuclear reorganization energy, λ, 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 $\Delta G^0 = 0$)





$$k_{et} = \frac{2\pi}{\hbar}|H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G^{\circ})^2}{4\lambda k_b T}\right)$$

… and we knew this had a Gaussian shape…

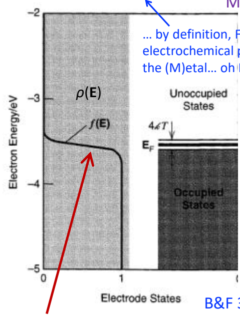
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1992/marcus-lecture.pdf

1020

… to analyze this, we have to more fully derive interfacial Marcus theory… 1021

$f(\mathbf{E}) = \{1 + \exp[(\mathbf{E} - \mathbf{E}_F)/kT]\}^{-1}$ … Thank you, Fermi, Marcus & Gerischer!

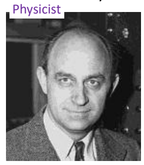
… by definition, Fermi level, $\mathbf{E}_F = \bar{\mu}_e^M$, the electrochemical potential of electrons in the (M)etal… oh Physicists!



B&F 3.6.3

from Wiki and http://www.fhi-berlin.mpg.de/pc/PChistory.html

Physicist



Enrico Fermi (1901–1954)

Electrochemist

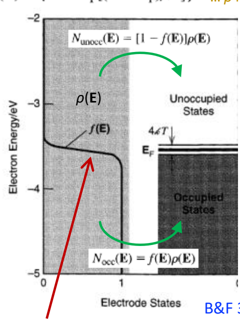
Heinz Gerischer (1919–1994)

E_{app} varies the probability function (0, 1)
… resulting in (D)istributions of occupied metal states

1021

… to analyze this, we have to more fully derive interfacial Marcus theory… 1022

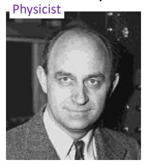
$f(\mathbf{E}) = \{1 + \exp[(\mathbf{E} - \mathbf{E}_F)/kT]\}^{-1}$ … ρ has units of cm^{-2} eV^{-1}



B&F 3.6.3

from Wiki and http://www.fhi-berlin.mpg.de/pc/PChistory.html

Physicist



Enrico Fermi (1901–1954)

Electrochemist

Heinz Gerischer (1919–1994)

E_{app} varies the probability function (0, 1)
… resulting in (D)istributions of occupied metal states

1022

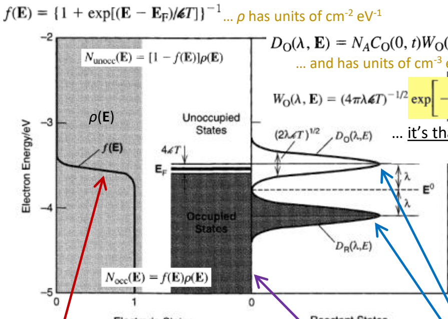
… to analyze this, we have to more fully derive interfacial Marcus theory… 1023

$f(\mathbf{E}) = \{1 + \exp[(\mathbf{E} - \mathbf{E}_F)/kT]\}^{-1}$ … ρ has units of cm^{-2} eV^{-1}

$D_O(\lambda, \mathbf{E}) = N_A C_O(0, t) W_O(\lambda, \mathbf{E})$
… and has units of cm^{-3} eV^{-1}

$W_O(\lambda, \mathbf{E}) = (4\pi\lambda kT)^{-1/2} \exp\left[-\frac{(\mathbf{E} - \mathbf{E}^0 - \lambda)^2}{4\lambda kT}\right]$

… it's that Gaussian term!



B&F 3.6.3

E_{app} varies the probability function (0, 1)
… resulting in (D)istributions of occupied metal states & molecule states

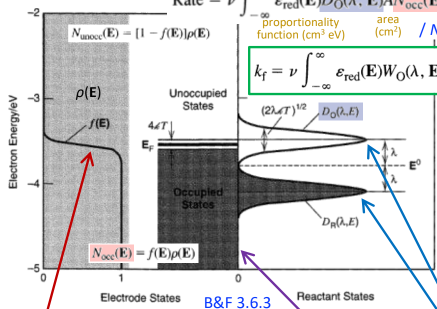
1023

… the rate of electron transfer is dictated by the law of mass action… 1024

$$\text{Rate} = \nu \int_{-\infty}^{\infty} \varepsilon_{\text{red}}(\mathbf{E}) D_{\text{O}}(\lambda, \mathbf{E}) A N_{\text{occ}}(\mathbf{E}) d\mathbf{E}$$

frequency factor (s^{-1}); proportionality function (cm^3 eV); area (cm^2); $/ N_A C_O(0, t)A = k_f$

$$\boxed{k_f = \nu \int_{-\infty}^{\infty} \varepsilon_{\text{red}}(\mathbf{E}) W_{\text{O}}(\lambda, \mathbf{E}) f(\mathbf{E}) \rho(\mathbf{E}) d\mathbf{E}}$$



B&F 3.6.3

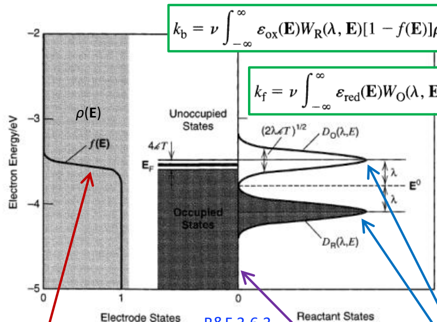
E_{app} varies the probability function (0, 1)
… resulting in (D)istributions of occupied metal states & molecule states

1024

… the rate of electron transfer is dictated by the law of mass action… 1025

$$\boxed{k_b = \nu \int_{-\infty}^{\infty} \varepsilon_{\text{ox}}(\mathbf{E}) W_{\text{R}}(\lambda, \mathbf{E}) [1 - f(\mathbf{E})] \rho(\mathbf{E}) d\mathbf{E}} \approx 0$$

$$\boxed{k_f = \nu \int_{-\infty}^{\infty} \varepsilon_{\text{red}}(\mathbf{E}) W_{\text{O}}(\lambda, \mathbf{E}) f(\mathbf{E}) \rho(\mathbf{E}) d\mathbf{E}}$$

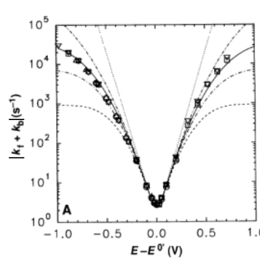


B&F 3.6.3

E_{app} varies the probability function (0, 1)
… resulting in (D)istributions of occupied metal states & molecule states

1025

… experimental electrochemical validation of Marcus theory… 1026
… but no direct observation of inverted-region behavior



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

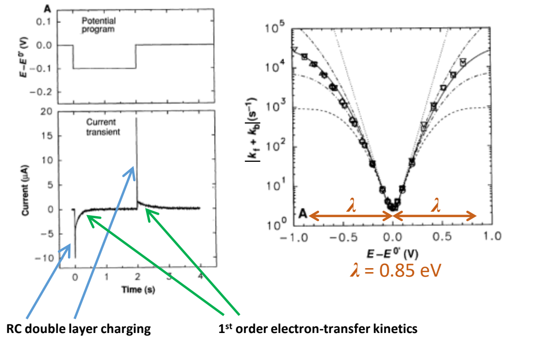
$$\kappa_{\text{el}}(x) = \kappa_{\text{el}}^{0} \exp(-\beta x) \qquad \text{B\&F 3.6.4} \qquad (3.6.39)$$

Sikes, Smalley, Dudek, Cook, Newton, Chidsey & Feldberg, *Science*, 2001, *291*, 1519
Chidsey, *Science*, 1991, *251*, 919

1026

… experimental electrochemical validation of Marcus theory… 1027

… but no direct observation of inverted-region behavior

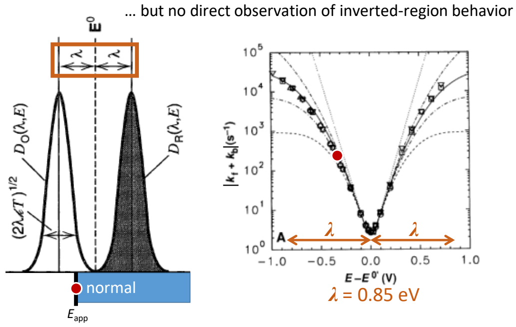


Chidsey, *Science*, 1991, *251*, 919

1027

… experimental electrochemical validation of Marcus theory… 1028

… but no direct observation of inverted-region behavior



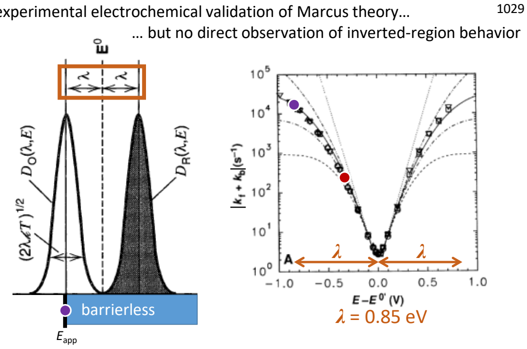
… and no inverted-region behavior was observed because at large driving force there was always a state in the metal that overlapped the most probable D_O

Chidsey, *Science*, 1991, *251*, 919

1028

… experimental electrochemical validation of Marcus theory… 1029

… but no direct observation of inverted-region behavior

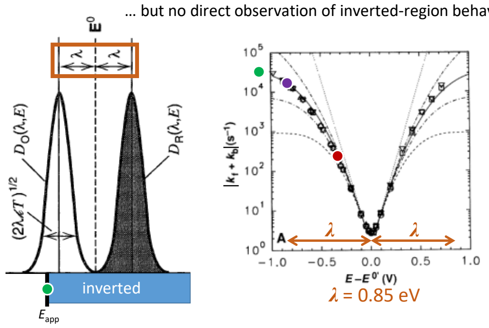


… and no inverted-region behavior was observed because at large driving force there was always a state in the metal that overlapped the most probable D_O

Chidsey, *Science*, 1991, *251*, 919

1029

… experimental electrochemical validation of Marcus theory… 1030
… but no direct observation of inverted-region behavior

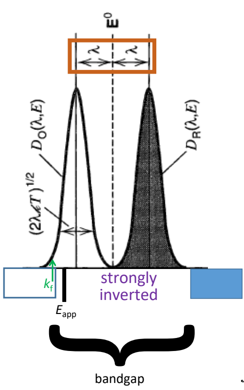


… and no inverted-region behavior was observed because at large driving force there was always a state in the metal that overlapped the most probable D_O

Chidsey, *Science*, 1991, *251*, 919

1030

Well that was disappointing… how can inverted-region behavior be seen? 1031
… at semiconductors!

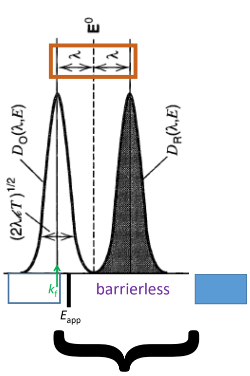


… but how?

Hamann, Gstrein, Brunschwig & Lewis, ***JACS*, 2005, *127*, 7815** and *JACS*, 2005, *127*, 13949

1031

Well that was disappointing… how can inverted-region behavior be seen? 1032
… at semiconductors!



… but how?

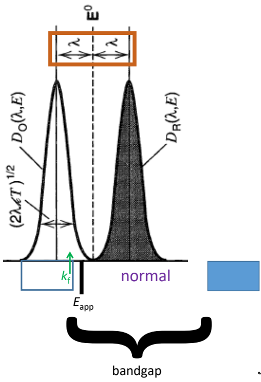
… Vary the molecule, not the bias!
… but λ must be "the same" for each!

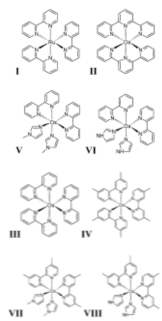
Hamann, Gstrein, Brunschwig & Lewis, ***JACS*, 2005, *127*, 7815** and *JACS*, 2005, *127*, 13949

1032

Well that was disappointing… how can inverted-region behavior be seen? 1033

… at semiconductors!



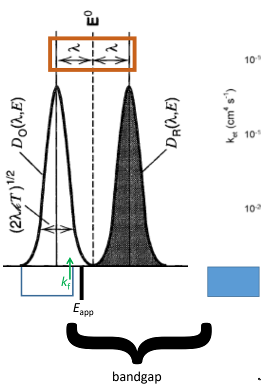


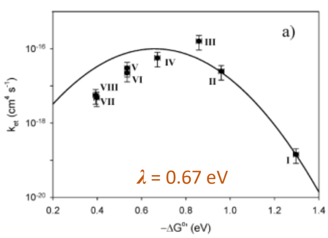
Hamann, Gstrein, Brunschwig & Lewis, ***JACS*, 2005, *127*, 7815** and *JACS*, 2005, *127*, 13949

1033

Well that was disappointing… how can inverted-region behavior be seen? 1034

… at semiconductors!





… k in units of cm^4 s^{-1}… a second-order rate constant (… x concentration^2)

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

Hamann, Gstrein, Brunschwig & Lewis, ***JACS*, 2005, *127*, 7815** and *JACS*, 2005, *127*, 13949

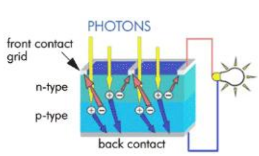
1034

RECALL… Q: What processes occur in electrochemistry? 1035

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?

NOT electrochemistry: pn-junction photovoltaic cell



http://www.azom.com/article.aspx?ArticleID=3744

http://newscenter.lbl.gov/2011/09/15/tracking-the-sun-iv/

1035

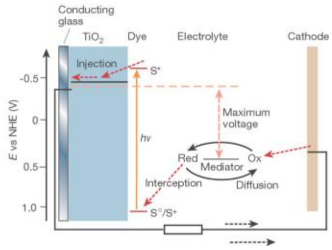
RECALL… Q: What processes occur in electrochemistry? 1036

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

Prof. Michael Grätzel (EPFL)



Grätzel, *Nature*, 2001, *414*, 338

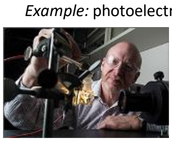
1036

RECALL… Q: What processes occur in electrochemistry? 1037

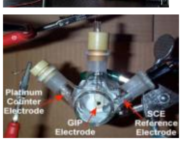
A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

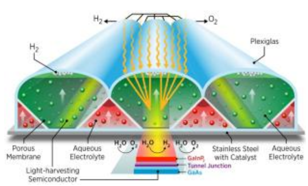
IS THIS ELECTROCHEMISTRY? WHY OR WHY NOT?

Example: photoelectrochemical water electrolysis (splitting)



Dr. John Turner (NREL)





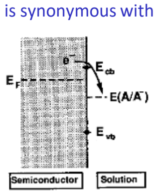
http://www.nrel.gov/hydrogen/proj_production_delivery.html

1037

As a subset of PEC… who cares what you call it, right? … Maybe 1038

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!



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

Bard, Memming & Miller, *Pure & Appl. Chem.* 1991, *63*, 569

1038

As a subset of PEC… who cares what you call it, right? … Maybe 1039

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.

Does light "cause a net chemical conversion in the cell"?
- No → Photovoltaic Cell
- Yes → Photoelectrolytic Cell
  - Is the $\Delta G < 0$ for the net chemistry?
    - No → Photocatalytic Cell
    - Yes → Photo(electro)synthetic Cell

Bard, Memming & Miller, *Pure & Appl. Chem.* 1991, *63*, 569

1039

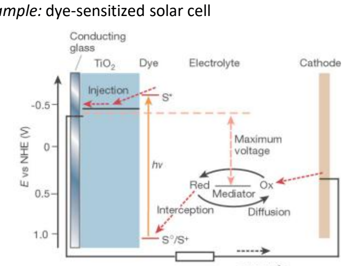
RECALL… Q: What processes occur in electrochemistry? 1040

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

Prof. Michael Grätzel (EPFL)



Grätzel, *Nature*, 2001, *414*, 338

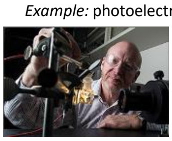
1040

RECALL… Q: What processes occur in electrochemistry? 1041

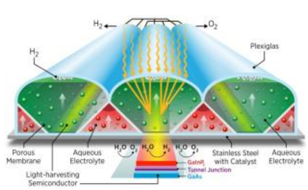
A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

IS THIS PEC? AND IF SO, WHAT TYPE?

Example: photoelectrochemical water electrolysis (splitting)



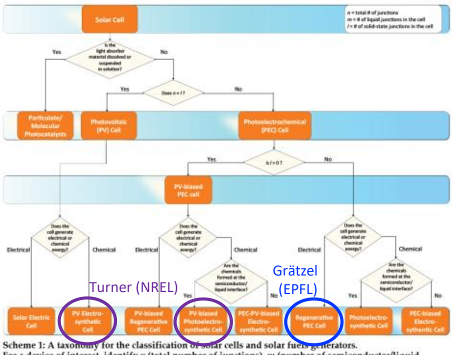
Dr. John Turner (NREL)



http://www.nrel.gov/hydrogen/proj_production_delivery.html

1041

As a subset of PEC… who cares what you call it, right? … Maybe 1042

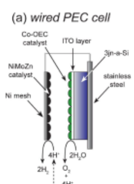


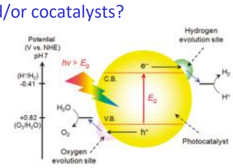
Scheme 1: A taxonomy for the classification of solar cells and solar fuels generators.
For a device of interest, identify n (total number of junctions), m (number of semiconductor/liquid junctions), and l (number of buried junctions), then proceed through the flow chart to determine the appropriate name for the device.

Nielander, …, Lewis, *Energy Environ. Sci.* 2015, *8*, 16

1042

… Well, it gets worse… What happens when you have transparent thin “metal” layers and/or cocatalysts? 1043





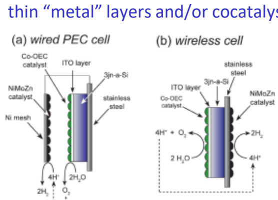
Maeda & Domen, *J. Phys. Chem. Lett.* 2010, *1*, 2655
Reece, … Nocera, *Science* 2011, *334*, 645

IS THIS PEC? AND IF SO, WHAT TYPE?

PV Electrosynthetic, maybe? Probably? … Eh?!?!?!

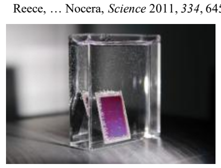
1043

… Well, it gets worse… What happens when you have transparent thin “metal” layers and/or cocatalysts? 1044



"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

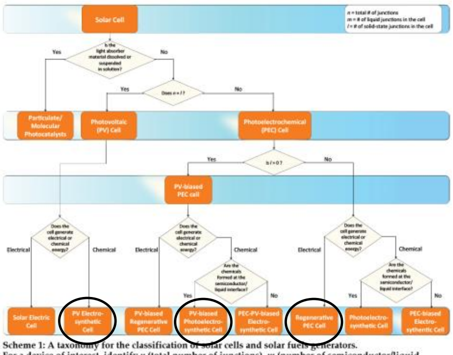


http://www.nature.com/news/artificial-leaf-faces-economic-hurdle-1.10703
http://conservationmagazine.org/2012/09/the-mighty-leaf/

1044

… Oh my gosh, Shane! Tomato, tomatoe… WHO CARES?

1045



Scheme 1: A taxonomy for the classification of solar cells and solar fuels generators.
For a device of interest, identify n (total number of junctions), m (number of semiconductor/liquid junctions), and l (number of buried junctions), then proceed through the flow chart to determine the appropriate name for the device.

Nielander, …, Lewis, *Energy Environ. Sci.* 2015, *8*, 16

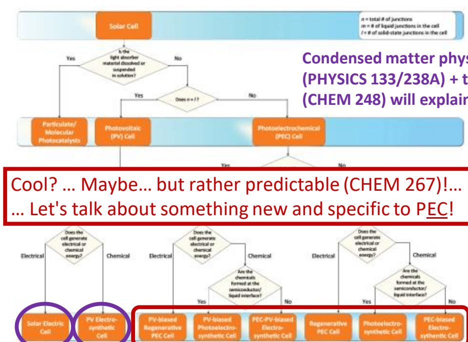
1045

… Oh my gosh, Shane! Tomato, tomatoe… WHO CARES?

1046

Condensed matter physics (PHYSICS 133/238A) + this class (CHEM 248) will explain these…

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



Scheme 1: A taxonomy for the classification of solar cells and solar fuels generators.
For a device of interest, identify n (total number of junctions), m (number of semiconductor/liquid junctions), and l (number of buried junctions), then proceed through the flow chart to determine the appropriate name for the device.

Nielander, …, Lewis, *Energy Environ. Sci.* 2015, *8*, 16

1046

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

1047

Photoelectrochemical cells consist essentially of two electrodes in contact with an electrolyte, one electrode usually being a light

Thank you, Al, Rüdiger, and Barry!

semiconducting material of opposite types.

Does light "cause a net chemical conversion in the cell"?

No — Photovoltaic Cell

Yes — Photoelectrolytic Cell

Is the ΔG < 0 for the net chemistry?

No — Photocatalytic Cell

Yes — Photo(electro)synthetic Cell

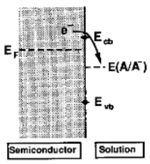
Bard, Memming & Miller, *Pure & Appl. Chem.* 1991, *63*, 569

1047

As a subset of PEC… who cares what you call it, right? … Maybe 1048

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!

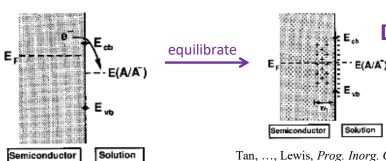
Tan, …, Lewis, *Prog. Inorg. Chem.* 1994, *41*, 21
Bard, Memming & Miller, *Pure & Appl. Chem.* 1991, *63*, 569

1048

As a subset of PEC… who cares what you call it, right? … Maybe 1049

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?

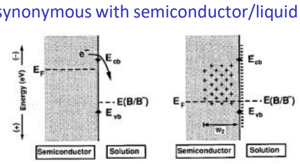
Tan, …, Lewis, *Prog. Inorg. Chem.* 1994, *41*, 21
Bard, Memming & Miller, *Pure & Appl. Chem.* 1991, *63*, 569

1049

As a subset of PEC… who cares what you call it, right? … Maybe 1050

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!



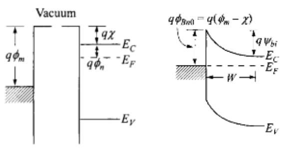
Déjà vu? … Double layer?

Tan, …, Lewis, *Prog. Inorg. Chem.* 1994, *41*, 21
Bard, Memming & Miller, *Pure & Appl. Chem.* 1991, *63*, 569

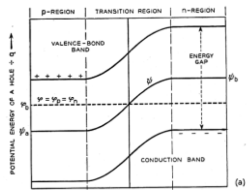
1050

Standard requirement for PEC: a **junction** and/or selective contact! 1051

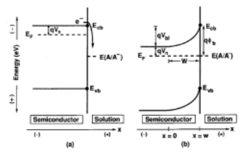
Schottky (SC–M) junction



pn (SC–SC) junction



Semiconductor–Liquid junction



How do these differ?

… They "don't"!

How can one adjust ϕ_m (or ϕ_b, or $E(A/A^-)$)?

Shockley, *Bell. Syst. Tech. J.* 1949, 435
Sze & Ng, *Physics of Semiconductor Devices*, 3rd edition, Wiley, 2007
Tan, …, Lewis, *Prog. Inorg. Chem.* 1994, *41*, 21

1051

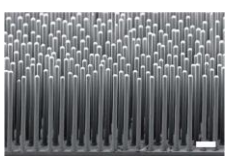
How do Schottky barriers differ from SC/liq junctions? 1052

They mostly don't!

PEC does have, however,
- Non-fixed "work function" metal contacts, if designed appropriately and carefully
- A tunable solution "work function" = $E(A/A^-)$
- Tunable species concentrations (think Nernst equation)…

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

… And, making a conformal coating is a cinch!



Shaner, …, Lewis, *Energy Environ. Sci.* 2014, *7*, 779

1052

How do Schottky barriers differ from SC/liq junctions? 1053

… 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

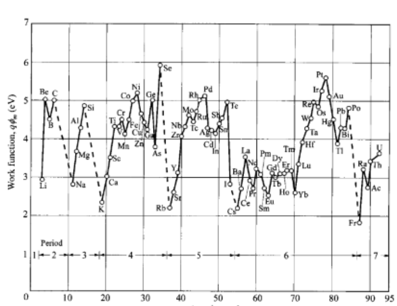


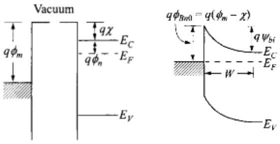
Fig. 2 Metal work function for a clean metal surface in a vacuum versus atomic number. Note the periodic nature of the increase and decrease of the work functions within each group. (After Ref. 12.)

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

1053

How do Schottky barriers differ from SC/liq junctions? 1054

Schottky (SC–M) junction



$$W_D = \sqrt{\frac{2\varepsilon_s}{qN_D}\left(\psi_{bi} - V - \frac{kT}{q}\right)}$$

$$Q_{sc} = qN_DW_D = \sqrt{2q\varepsilon_sN_D\left(\psi_{bi} - V - \frac{kT}{q}\right)} \quad (8)$$

$$C_D \equiv \frac{\varepsilon_s}{W_D} = \sqrt{\frac{q\varepsilon_sN_D}{2[\psi_{bi} - V - (kT/q)]}}. \quad (9)$$

Equation 9 can be written in the form

$$\frac{1}{C_D^2} = \frac{2[\psi_{bi} - V - (kT/q)]}{q\varepsilon_sN_D} \quad (10)$$

or

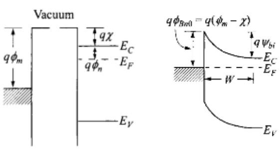
$$N_D = \frac{2}{q\varepsilon_s}\left[-\frac{1}{d(1/C_D^2)/dV}\right]. \quad (11)$$

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

1054

How do Schottky barriers differ from SC/liq junctions? 1055

Schottky (SC–M) junction… Mott–Schottky Plot



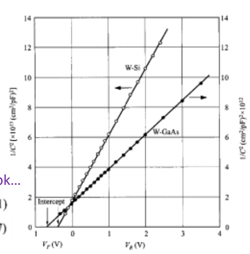


Fig. 30 $1/C^2$ versus applied voltage for W-Si and W-GaAs diodes. (After Ref. 44.)

… and look what I found in this physics textbook…

$$L_p \equiv \sqrt{D_p\tau_p}. \quad (61)$$

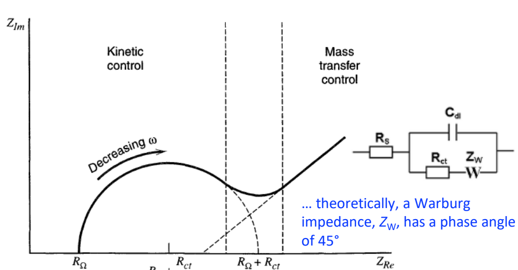
$$J_p = q\mu_p p_n \mathscr{E} - qD_p\frac{dp_n}{dx}. \quad (97)$$

… so maybe not that much!

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

1055

Recall… Here is the Nyquist plot for the "full" typical Randles equivalent circuit: 1056



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

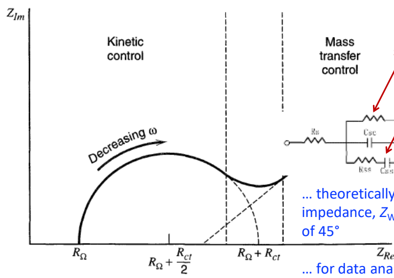
… for data analysis, fit frequency-dependent Z data to the model

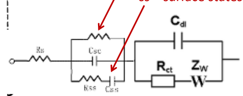
… but this had no semiconductor for our SC/liq junction…

… so how do we add one?

1056

Recall… Here is the Nyquist plot for the "full" typical Randles equivalent circuit: 1057





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

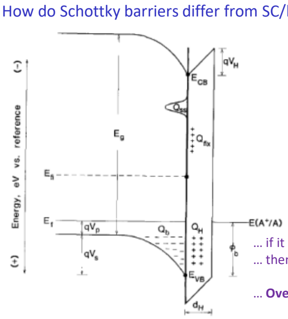
… for data analysis, fit frequency-dependent Z data to the model

… but this had no semiconductor for our SC/liq junction…

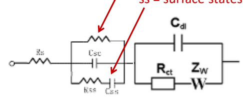
http://www.google.com/patents/WO2012097242A1?cl=en … so how do we add one?

1057

How do Schottky barriers differ from SC/liq junctions? 1058



Scheme I. Representation of the energetic parameters of a semiconductor/liquid interface at charge transfer equilibrium. The energy scale is depicted using the electrochemical potential convention, where increasing negative potentials indicate energies closer to the vacuum level. The diagram is appropriate for a moderately doped, p-type semiconductor, and neglects image force effects or Schottky barrier lowering. The potential drop in the electrolyte is assumed to occur entirely across the Helmholtz layer, which is characterized by a thickness d_H with dielectric constant ϵ_H.



… 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)apacitor 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"

Lewis, *J. Electrochem. Soc.* 1984, *131*, 2496

1058

How do Schottky barriers differ from SC/liq junctions? 1059

Short-Wavelength Spectral Response Properties of Semiconductor/Liquid Junctions

Amit Kumar and Nathan S. Lewis*

Division of Chemistry and Chemical Engineering,† California Institute of Technology, Pasadena, California 91125 (Received: December 11, 1989)

We report the first measurements of photocurrent quantum yields
region of the spectrum (200–600 nm). The key feature of this wavel
photon (less than 100 Å), which allows measurement of the major
for semiconductor/liquid, semiconductor/metal, and semiconductor
(n-Si, p-Si, n-GaAs, n-InP, a-Si:H), the spectral responses of the
metal junctions, indicating greater majority carrier losses at the
redox species, solvent, supporting electrolyte, and metal overlayer.
Schottky barrier behavior from electrocatalytic behavior of metal o
semiconductor/metal film junctions in contact with electrolytes.

How many electrons are in a metal (C_M)?
~$10^{21} – 10^{23}$ cm^{-3}

How many electrons are in a semiconductor (C_{sc})?
~$10^{12} – 10^{19}$ cm^{-3}, but it depends greatly on dopant density

… FYI, electrolytes have an intermediate number of charge states (C_{dl})… **potential drop?… they differ from redox states!**

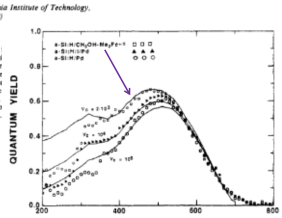


Figure 8. Spectral response of an $a\text{-}Si_{0.9}H_{0.1}/CH_3OH$–1.0 M $LiClO_4$–dimethylferrocene$^{+/0}$ liquid junction, along with the analogous a-Si:H MIS and Schottky contacts. The low drift velocity for electrons in this material allows measurement of the collection velocities for all these devices. No effect on the spectral response was observed over the Me_2Fe^+ concentration range of 0.1–0.001 mM. The poor agreement between the experimental and theoretical curves for wavelengths shorter than 300 nm is discussed in the text.

Kumar & Lewis, *J. Phys. Chem.* 1990, *94*, 6002

1059

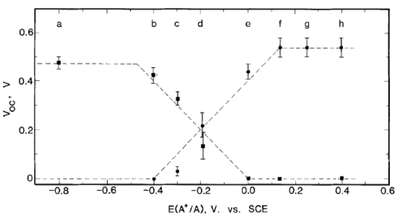
How do Schottky barriers differ from SC/liq junctions? 1060

A Quantitative Investigation of the Open-Circuit Photovoltage at the Semiconductor/Liquid Interface

Nathan S. Lewis*

Department of Chemistry, Stanford University, Stanford, California 94305

Fig. 1. Open-circuit photovoltage vs. solution redox potential for n-Si and p-Si photoelectrodes in 1.0M KCl/CH_3OH solution. The redox couples used were: (a) cobaltocene$^{+/0}$, (b) N,N′-dimethyl-4,4′-bipyridinium dichloride$^{2+/+}$, (c) N,N′-dibenzyl-4,4′-bipyridinium dibromide$^{2+/+}$, (d) decamethylferrocene$^{+/0}$, (e) N,N,N′,N′-tetramethylphenylenediamine$^{+/0}$, (f) dimethylferrocene$^{+/0}$, (g) ferrocene$^{+/0}$ and (h) acetylferrocene$^{+/0}$. A tungsten-halogen bulb was used to provide light intensities which yielded short-circuit photocurrent densities of 25-30 mA/cm².



… 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

1060

How do Schottky barriers differ from SC/liq junctions? 1061

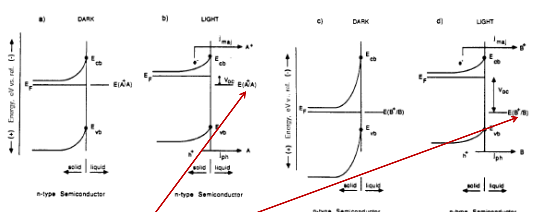


Figure 1. Dependence of V_{oc} on $E(A^+/A)$ when the redox pair is changed. (a) Equilibrium behavior of an n-type semiconductor in contact with the redox couple A^+/A. (b) Open circuit behavior under illumination of system in (a). Here, E_f represents the position of the electron quasi-Fermi level in the semiconductor, which determines the photostationary-state voltage measured relative to the solution phase. (c) Equilibrium behavior of the same semiconductor with a different redox couple, B^+/B. (d) Open circuit behavior under illumination of system in (c). Note that if $[B^+] = [A^+]$ and $[B] = [A]$, then V_{oc} in panel d is predicted to be much larger than V_{oc} in panel b.

Assume that…

… [A⁺] = [A]… and [B⁺] = [B]…

… that is, $E = E^{0\prime}$, but $E(A^+/A) \neq E(B^+/B)$

… yet recombination rate, $v_{Rec} = k_f[e^-][A/B^+]$, $= v_{Gen}$… and no terms differ!…

… so, $v_{Rec,A+/A} = v_{Rec,B+/B}$…

… but clearly, $V_{oc,L} \neq V_{oc,R}$ Rosenbluth & Lewis, *J. Phys. Chem.* 1989, *93*, 3735

1061

How do Schottky barriers differ from SC/liq junctions? 1062

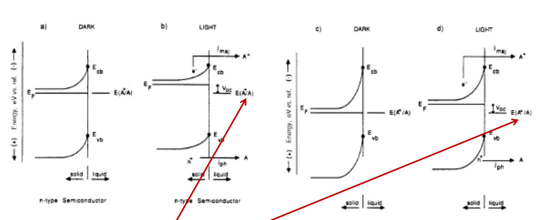


Figure 2. Dependence of V_{oc} on $E(A^+/A)$ when the concentration ratio $[A^+]/[A]$ is varied. (a) Equilibrium behavior of an n-type semiconductor in contact with the redox couple A^+/A. (b) Open circuit behavior under illumination of the system in panel a. Here, E_f represents the position of the electron quasi-Fermi level in the semiconductor, which determines the photostationary state voltage measured relative to the solution phase. (c) Equilibrium behavior of the semiconductor/liquid interface in panel a after $E(A^+/A)$ has been changed by increasing [A⁺] (while holding [A] constant). (d) Open circuit behavior under illumination of system in (c). Note that V_{oc} in panel b is identical with V_{oc} in panel d, in contrast to the case in Figure 1 where the identical change in magnitude of the solution redox potential did effect a change in V_{oc}.

Now, assume that…

… $[A^+]_{Left} = [A]_L = [A]_R$ but that $[A^+]_{Right}$…

… is smaller or larger?

… larger!

… again $v_{Rec} = k_f[e^-][A^+] = v_{Gen}$… but now $v_{Rec,Right} > v_{Rec,Left}$, due to [A⁺]…

… but interestingly, $V_{oc,L} = V_{oc,R}$! Rosenbluth & Lewis, *J. Phys. Chem.* 1989, *93*, 3735

1062

How do Schottky barriers differ from SC/liq junctions? 1063

… and the effect was quite general…

… and unique to SC/liq junctions!

Table II. Effect of Concentration on V_{oc}

entry	$[Me_2Fc]$, M	$[Me_2Fc]^+$, M	V_{oc}, mV[a]
1	0.20	0.0010	641
2	0.20	0.0050	642
3	0.20	0.0100	643
4	0.10	0.0050	643
5	0.010	0.0005	645[b]

[a] 0.2 ohm-cm (100) n-Si in 1.0 M $LiClO_4$–CH_3OH at 18 °C. J_{sc} = 20 mA/cm². [b] Measured at 70 mW/cm² incident light intensity; J_{sc} data unavailable due to mass transport limitations. For comparison, 70 mW/cm² in entry 1 yielded J_{sc} = 18.3 mA/cm², and there is slightly less optical loss in the solution of entry 5.

TABLE II: V_{oc} vs Concentration of Me_2Fc^+ [a]

$[Me_2Fc^+]$, M	V_{oc}(20.0 mA/cm²), V	V_{oc}(10.0 mA/cm²), V	V_{oc}(1.0 mA/cm²), V
0.0001	0.635	0.616	0.548
0.001	0.635	0.617	0.551
0.010	0.635	0.616	0.549
0.050	0.634	0.614	0.551
0.100	0.625	0.604	
0.200	0.625	0.604	

[a] The concentration of Me_2Fc was 0.200 M in all cases, with a cell temperature of 298 K. Measurements were made on three samples with a variation in V_{oc} of <3 mV from sample to sample.

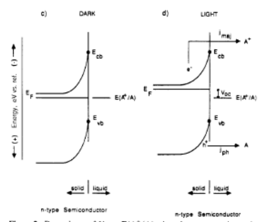
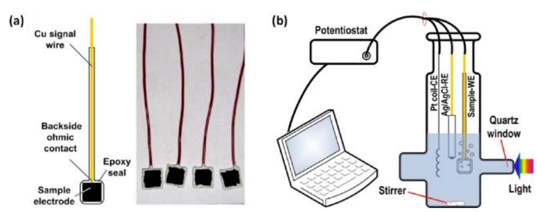


Figure 2. Dependence of V_{oc} on $E(A^+/A)$ when the concentration ratio $[A^+]/[A]$ is varied. (a) Equilibrium behavior of an n-type semiconductor in contact with the redox couple A^+/A. (b) Open circuit behavior under illumination of the system in panel a. Here, E_f represents the position of the electron quasi-Fermi level in the semiconductor, which determines the photostationary state voltage measured relative to the solution phase. (c) Equilibrium behavior of the semiconductor/liquid interface in panel a after $E(A^+/A)$ has been changed by increasing $[A^+]$ (while holding [A] constant). (d) Open circuit behavior under illumination of system in (c). Note that V_{oc} in panel b is identical with V_{oc} in panel d, in contrast to the case in Figure 1 where the identical change in magnitude of the solution redox potential did effect a change in V_{oc}.

Rosenbluth & Lewis, *J. Am. Chem. Soc.* 1986, *108*, 4689
Kumar & Lewis, *J. Phys. Chem.* 1991, *95*, 7021
Rosenbluth & Lewis, *J. Phys. Chem.* 1989, *93*, 3735

1063

… and how does one fabricate electrodes using materials found in the laboratory? 1064



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

1064

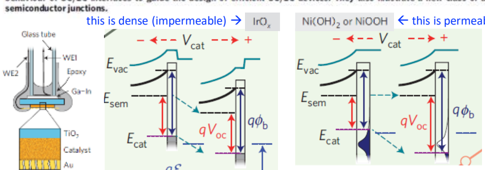
How do Schottky barriers differ from SC/liq junctions? 1065

Adaptive semiconductor/electrocatalyst junctions in water-splitting photoanodes

Fuding Lin and Shannon W. Boettcher*

High-efficiency photoelectrochemical water-splitting devices require the integration of electrocatalysts (ECs) with light-absorbing semiconductors (SCs), but the energetics and charge-transfer processes at SC/EC interfaces are poorly understood. We fabricate model EC-coated single-crystal TiO_2 electrodes and directly probe SC/EC interfaces *in situ* using two working electrodes to independently monitor and control the potential and current at both the SC and the EC. We discover that redox-active ion-permeable ECs such as $Ni(OH)_2$ or NiOOH yield 'adaptive' SC/EC junctions where the effective Schottky barrier height changes *in situ* with the oxidation level of the EC. In contrast, dense, ion-impermeable IrO_x ECs yield constant-barrier-height 'buried' junctions. Conversion of dense, thermally deposited NiO_x on TiO_2 into ion-permeable $Ni(OH)_2$ or NiOOH correlated with increased apparent photovoltage and fill factor. These results provide new insight into the dynamic behaviour of SC/EC interfaces to guide the design of efficient SC/EC devices. They also illustrate a new class of adaptive semiconductor junctions.

this is dense (impermeable) → IrO_x | $Ni(OH)_2$ or NiOOH ← this is permeable to ions



Lin & Boettcher, *Nat. Mater.* 2014, *13*, 81

1065

Standard requirement for PEC: a junction and/or **selective contact**! 1066

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 $H_2 + O_2$ are the same…
… which will also hold under steady-state operation

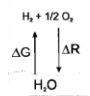


Figure 6.1: Hypothetical chemical solar cell in which water is decomposed into hydrogen and oxygen by the absorption of photons. Hydrogen and oxygen can be separately removed through membranes which selectively pass hydrogen on the left and oxygen on the right.

Würfel, *Physics of Solar Cells*, Wiley, 2005

1066

Standard requirement for PEC: a junction and/or **selective contact**! 1067

… 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 H_2 and O_2 yet you only generated a small amount of H_2 and O_2 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

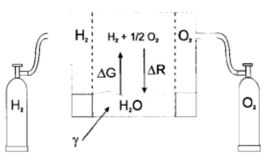


Figure 6.1: Hypothetical chemical solar cell in which water is decomposed into hydrogen and oxygen by the absorption of photons. Hydrogen and oxygen can be separately removed through membranes which selectively pass hydrogen on the left and oxygen on the right.

Würfel, *Physics of Solar Cells*, Wiley, 2005

1067

Standard requirement for PEC: a junction and/or **selective contact**! 1068

What if the tanks had 1 bar of H_2 and O_2 yet you only generated a small amount of H_2 and O_2 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

external power (e.g. sunlight) driving the desired formation of H_2 and O_2

At V_{oc}, rates cancel each other out

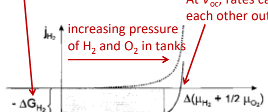


Figure 6.4: Current of hydrogen, positive if flowing from the hydrogen bottle in Figure 6.1 into the cell as a function of the deviation $\Delta(\mu_{H_2} + \frac{1}{2}\mu_{O_2})$ of the chemical potentials of hydrogen and oxygen from their equilibrium values, without illumination (broken line) and with additional generation ΔG_{H_2} by illumination (solid line). A smaller and more realistic equilibrium generation rate $G^0_{H_2}$ than in Figure 6.3 is assumed. The shaded rectangle is the largest current of chemical energy delivered by the cell.

Würfel, *Physics of Solar Cells*, Wiley, 2005

1068

How does Regenerative PEC (PV) and Photoelectrosynthetic PEC differ? 1069

Electrolysis of Water at $SrTiO_3$ Photoelectrodes: Distinguishing between the Statistical and Stochastic Formalisms for Electron-Transfer Processes in Fuel-Forming Photoelectrochemical Systems

Amit Kumar, Patrick G. Santangelo, and Nathan S. Lewis*

Division of Chemistry and Chemical Engineering,† California Institute of Technology, Pasadena, California 91125 *(Received: July 10, 1991; In Final Form: September 10, 1991)*

Conventional photoelectrochemical and photovoltaic theory predicts a light intensity threshold for sustaining the net electrolysis of water using semiconductor electrodes, but a stochastic charge-transfer formalism for photoelectrolysis reactions does not predict such threshold behavior. This work examines the theoretical and experimental aspects of light-assisted water electrolysis using n-type $SrTiO_3/H_2O$ interfaces. A theoretical framework, based upon simple chemical kinetic considerations, has been formulated to describe the behavior of such photoelectrosynthetic cells. Experiments conducted on the n-$SrTiO_3$/5.0 M NaOH(aq)/Pt photoelectrosynthetic cell have revealed a threshold in the short-circuit electrolysis current at 5×10^{-5} W/cm^2 of 325-nm illumination. Additional theory and experiments have provided insight into relationships between two-electrode regenerative photoelectrochemical cells, two-electrode photoelectrosynthetic cells, and three-electrode potentiostatic cells. These experiments and theory indicate that a conventional chemical kinetic treatment of interfacial electron-transfer rates appears to be sufficient to describe the photoelectrochemical behavior of $SrTiO_3$ and TiO_2/aqueous junctions.

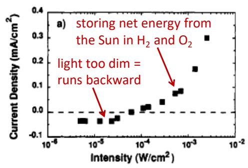


Figure 4. (a) Plot of short-circuit current density as a function of the illumination intensity for a two-electrode photoelectrolysis cell. The $SrTiO_3$ electrode and the Pt electrode were kept in different compartments that were separated by a ceramic frit. An O_2 pressure of 1 atm was maintained over the semiconductor electrode, and a H_2 pressure of 1 atm was maintained over the Pt electrode. The threshold in net photoelectrolysis current was observed at 5×10^{-5} W/cm^2. (b) Linear plot of the positive current values reported in Figure 6a. At high enough current densities, where the magnitude of the short-circuit majority carrier dark current was negligible, the total current density was proportional to the illumination intensity.

Kumar, Santangelo & Lewis, *J. Phys. Chem.* 1992, *96*, 834

1069

1070

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 pn-junction, is of no significance for our understanding of the solar cell. The criterion for a solar cell structure is that electrons and holes are forced by membranes into different directions and that on their path their entropy is conserved. When this condition is fulfilled, in some structures, e.g., in a pn-junction of uniform material, an electric field will be present between the membranes. The direction of the short-circuit charge current in a pn 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 fulfil the condition of conservation of entropy. The dye solar cell in Section 6.3 is a good example. The intimate mixture of electron membrane (TiO_2), dye and hole membrane (electrolyte) on a nanometer scale, does not allow the formation of an extended space charge and of a field. Another example will be given at the end of this section.

Würfel, *Physics of Solar Cells*, Wiley, 2005

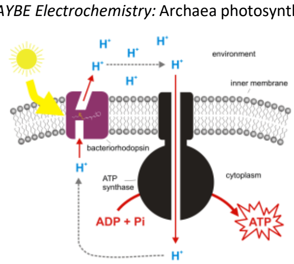
1070

RECALL… Q: What processes occur in electrochemistry? 1071

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!

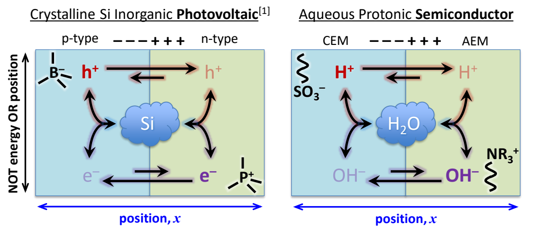
MAYBE Electrochemistry: Archaea photosynthesis



http://en.wikipedia.org/wiki/Bacteriorhodopsin

1071

… and so we'll end with a shameless plug (2 slides) for Team Ardo! 1072



Rate(x)$_{\text{dissociation}}$ = constant   Rate(x)$_{\text{association}}$ α $[-]^1[+]^1$ Flux(x)$_{\text{diffusion}}$ α $(d[-/+]/dx)^1$ Flux(x)$_{\text{drift}}$ α $[-/+]^1(d\phi/dx)^1$

- ❑ **Continuity of mass processes over x, t are the same for Si and water**[2]
- ❑ **Fact:** Water-based rectifying protonic diodes are possible[3]
- ❑ ***Claim: With proper light-absorbers,*** *aqueous solar cells are possible*

[1] Shockley, *Bell Sys. Tech. J.*, **1949**, *28*, 435; Pearson, Chapin & Fuller, *Bell Laboratories*, **1954**

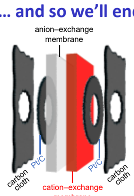
[2] Fuller, *Record Chem. Prog.*, **1956**, *17*, 75

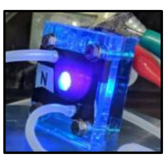
[3] Lovreček, Despić & Bockris, *J. Phys. Chem.*, **1959**, *63*, 750

White, Sanborn, Fabian & Ardo, *Joule*, 2018, *2*, 94

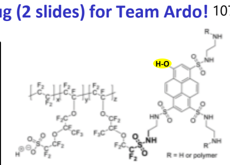
1072

… and so we'll end with a shameless plug (2 slides) for Team Ardo! 1073



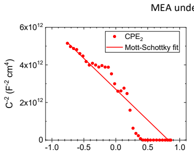


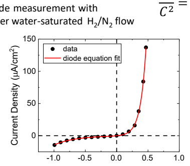
2-electrode measurement with MEA under water-saturated H_2/N_2 flow

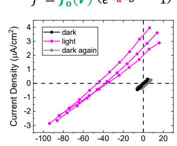


$$\frac{1}{C^2} = \frac{2}{q\varepsilon_r\varepsilon_o N}\left(E_{fb} + E - \frac{k_B T}{q}\right)$$

$$J = J_o(V)\left(e^{\frac{qV}{n_d k_B T}} - 1\right)$$







E_{fb} = 0.8 V
N = 0.9 mM (used ε_r = 80)

n_d = 2.7 (160 mV/decade)
J_o' = 6.3 x 10^{-8} A/cm^2
α_{WD}^{-1} = 13 (770 mV/decade)

Schulte, White, Renna & Ardo, *Joule, 2021*

1073