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Reaction Kinetics and Product Distributions in Photoelectrochemical Cells

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Reaction Kinetics and Product Distributions in Photoelectrochemical Cells

A. Summary

Semiconductor/liquid junction solar cells, also called photoelectrochemical cells (PEC), represent a versatile way to use solar energy. Photon energy can be used to make electricity and chemical fuels or can be used as an alternative to thermal activation energy in photocatalytic cells. Two fundamental processes associated with photoelectrochemical solar energy conversion were investigated experimentally. Reactions of "hot" electrons by solution redox species has the potential to increase the efficiencies or to alter the product distribution in liquid junction solar cells. In previous work, we observed the first distinct product of a hot carrier redox reaction at the p-InP/CH₃CN interface using a Cu(II,I) complex ion. This reaction is quite limited with respect to further exploration of hot carriers; therefore, we developed additional redox systems and experimental techniques that allow us to explore the phenomenon in greater detail. Electrode kinetics at 2-dimensional materials were investigated in order to understand the mechanism of majority carrier charge transfer to solution redox species. In particular, we were interested in the mechanism for couples with reduction potentials in the bandgap of the semiconductor, i.e. those of greatest importance for photoelectrolysis. These studies utilized the nearly ideal properties of 2-dimensional semiconducting materials such as WSe₂ in conjunction with an electrochemical minicell that we developed. Key aspects of these mechanistic studies were rates measured over extended concentration ranges of redox species. In addition to completing the objectives summarized above, we initiated a project to investigate the use of solar photochemistry to control the rates and selectivity of molecular transport through liquid and polymer membranes.

B. Reactions of "hot" electrons

Matching the solar spectrum to the adsorption spectrum of a photoconversion device presents severe constraints on the efficiency of solar energy conversion. The conversion device (plant, homogeneous molecular system, semiconductor electrode) must absorb light at long wavelengths in order to collect a large fraction of solar photons; however, the extra energy in the short wavelength photons, relative to the absorption onset, tends to be inefficiently converted into electricity or chemical free energy. One way to think about the excess energy in short wavelength photons is that, upon absorption, it creates "hot" charge carriers. By assuming that the excess energy results in carriers with increased kinetic energy of $3/2 kT$, a photon with 0.5 eV of excess energy would create a carrier with an effective temperature of about 4000 K above the temperature of the lattice. In condensed phases, this excess energy will be dissipated as heat to the system unless the "hot carrier" can be trapped and utilized. Since currently available conversion devices are unable to prevent thermalization losses of this type, theoretical energy conversion efficiencies are near 30%. Devices that could utilize hot carriers could have efficiencies in excess of 60%.

The chemistry and physics of hot carriers is currently under investigation in a variety of fields. A majority of these papers appear in the solid state physics or surface science literature (over 100 papers annually). Topics being addressed include experimental and theoretical investigations of hot electron transport in semiconductors, especially III-V heterostructures, and of emission of hot electrons into vacuum. Reactions of hot carriers by molecules adsorbed on semiconductors and metals is receiving attention in UHV studies. For example, it has been shown that hot electron photoreduction of CH_3Cl through buffer layers of Ar and H_2O occurs on GaAs and Ni surfaces. Interest in how hot carriers might effect photoelectrochemical phenomena was provoked by theoretical studies by Williams and Nozik and subsequent experimental work by Nozik and co-workers at NREL. There are a variety of fundamental questions regarding the generation and fate of hot electrons and holes in semiconducting materials. Clearly, a key issue with respect to solar photoelectrochemistry is whether the excess energy available in hot carriers can be used to generate products or catalyze reactions that would not be possible with thermalized minority carriers.

Our goal was to develop a variety of systems and techniques in which reactions of hot electrons can be unambiguously observed. Ideally, these systems also display stable and efficient overall photon to photocurrent conversion and

semiconductor-solution interfacial properties that can be characterized by standard electrochemical methods. By studying stable and efficient systems, it is easier to determine whether observed product distributions are real and reproducible (not due to artifacts or photocorrosion) and whether high yields of hot products can be achieved. The ability to characterize the interface facilitates interpretation of the results in the context of theoretical models.

Our previous research on hot electron reactions at the p-InP / CH₃CN interface revealed the following list of essential and/or desirable features for redox systems used to investigate hot carriers in photoelectrochemical cells:

- 1) The system must consist of a hot and thermalized electron acceptor. The reduced form of the thermalized electron acceptor must be stable so that this couple can be used to poise the solution potential. The hot electron acceptor must only be reduced at potentials negative of the conduction band edge. The reduced form of the hot electron acceptor must convert rapidly and irreversibly to a product that can be sensitively detected in the presence of the other components of the system.
- 2) All redox species must be stable with respect to each other, not suffer photodecomposition (preferably not absorb light) in the spectral regions of interest, and not adsorb on the semiconductor surface.
- 3) It should be possible to independently vary the concentrations of the thermalized and hot electron acceptors and, by using derivatives of the acceptors, to shift the E⁰ or E_{1/2} of the redox couples with respect to the conduction band edge (CBE) of the semiconductor.

After examining many potential systems, we investigated the reduction of dibromoethylbenzene (hot electron acceptor) in the presence of metallocene couples (thermalized electron acceptor) utilizing rotating ring disk electrodes (publications 1 and 2. Rotating ring disk electrodes (RRDE) consisting of n- and p-InP disks and Pt rings were constructed. In solutions containing dibromoethylbenzene (DBEB) and decamethylferrocene^{+,0} (DFER) the following reactions were shown to occur:

At the InP disk:

conduction band)

At the Pt ring:

When p-InP disks are illuminated, photogenerated electrons can reduce either DFER⁺ or DBEB. Since the rate of the DBEB reduction increases rapidly as the

potential of the electrode becomes more negative, hot electrons are more likely to cause the DBEB reduction than are thermalized electrons. The amount of DBEB reduction that occurs can be measured by sensing the oxidation of Br^- at the ring.

The results of these experiments demonstrated that at highly-doped p-InP electrodes, reduction of DBEB can be very efficient (>30%). As expected, the fraction of DBEB reduction observed at low doped electrodes was much lower due to the fact that the space charge region is much wider. The amount of DBEB reduction is also influenced by the interfacial energetics and the light intensity. These results are important because they demonstrated that hot electron reaction can be observed at steady state for a reaction in which products are not deposited on the electrode surface (as was the case with our earlier system). The magnitude of the hot reduction current is highly dependent on the preparation of the InP surface suggesting that tunneling through a thin surface oxide may be important.

C. Electrode kinetics at 2-dimensional materials

There are several ways in which fundamental research on semiconductor electrokinetic studies of dark currents is related to photoelectrochemical processes. Consider the dark, reduction process at an n-type material. Under illumination (net photooxidation), this process represents the back reaction for the photoinduced charge separation process and significant currents due to this reaction represent losses in efficiency for the photocell. In general, this reaction will be slowed due to the electric field in the space charge region that drive electrons away from the interface or due to poor overlap of the solution acceptor with band edge or to an unexpectedly low pre-exponential factor. Careful kinetic studies will help to resolve these factors. Understanding the kinetics of dark reduction reactions at n-type semiconductors is also important for photoreductions at p-type materials. By employing the concept of quasi-Fermi levels, one should be able to understand the reactivity of photogenerated minority carriers in a p-type material by studying the reactivity of majority carriers in the same material with n-type doping.

Since photoelectrochemical cells began to be investigated as possible solar conversion devices in the 1970's, a vast majority of the results have been interpreted within the framework of a model developed by Gerischer. Numerous experimental results have been interpreted qualitatively, and in some cases semi-quantitatively, within the framework of this model. It is our opinion that few or none of these simple predictions have actually been verified for couples that lie within the band gap. The experimental problem with making these critical measurements is that

currents are small and tend to be dominated by leakage through defects, surface states, stray illumination, etc. While no surface will be completely free of defects, we chose to use 2-dimensional semiconducting materials, specifically metal chalcogenides, for our kinetic studies. The smooth, unreactive Van der Waals surfaces of these materials exhibit very low dark currents in solutions that do not contain redox molecules due to a low density of defects and surface states.

Layered metal dichalcogenide semiconductors have excellent properties as semiconductor electrodes. However, edge sites and crystal defects must be masked so that only the defect-free basal plane of the two-dimensional material is exposed to solution. Conventional epoxy encapsulation of the crystal epoxy can introduce deleterious effects. Therefore, a electrochemical minicell was developed to perform experiments in a single drop (1-3 mm diameter) of electrolyte held against the working electrode (publication 4). The electrochemical behavior and operational considerations of the cell for aqueous and nonaqueous systems were investigated. Spatially-resolved electrochemistry was demonstrated for n-WSe₂ and highly ordered pyrolytic graphite.

The minicell was used to investigate electron transfer at nonilluminated n-WSe₂/dimethylferrocene^{+/0} interfaces (publications 3 and 5). This semiconductor is resistant to corrosion and has remarkably stable interfacial energetics. Interfaces with excellent diode behavior could be obtained by probing different regions of the surface. Electron transfer at these high quality surfaces was studied over an extensive solution concentration range. Contrary to standard predictions, the rate of electron transfer was independent of solution acceptor concentration from 5 μ M to 0.25 M. The electron transfer data can be explained by assuming a surface-state mediated mechanism.

An excellent WSe₂ crystal region was selected for investigation of high concentration behavior. This interface always provided high quality MS plots, no anomalous blank electrolyte behavior, and superior diode blocking. A series of redox solutions ranging in concentration from 25 mM to 250 mM DMFER^{+/0} was prepared. A conventionally sealed WSe₂ electrode was immersed in these solutions and analyzed via semi-integral cyclic voltammetry. This method can provide quantitative and qualitative information about surface adsorbing species. Even at 250mM, no adsorption of DMFER⁺ to the WSe₂ surface was detected.

The series of redox solutions was contacted via the minicell to the aforementioned crystal region. Tafel parameters for these experiments are

summarized in the table below. The exchange current density is independent of solution acceptor concentration and $j^0 = 0.03 \pm 0.01 \mu\text{A}/\text{cm}^2$.

crystal	[DMFER ^{+/0}], mM	j^0 , $\times 10^{-8} \text{ A}/\text{cm}^2$	mv / log j
#1	0.005	3.5	142
	0.05	3.0	118
	0.5	2.0	118
	5	4.2	106
#2	25	2.0 ± 0.6	79 ± 4
	100	2.7 ± 0.5	79 ± 2
	200	2.8	80
	250	3.6 ± 0.7	92 ± 1
overall avg. $j^0 = 3.0 \pm 0.8$			

The minicell was an excellent tool for selecting high quality WSe₂ interfaces. These SEI's showed near-ideal diode behavior and the good IE expected for WSe₂ electrodes. Only a very few crystal regions provided exceptional diode blocking behavior. The other advantage of the minicell was the ability to re-cleave damaged crystals to form fresh surfaces. The supply of electrons from the semiconductor bulk to the surface was consistent with the theoretical activation mechanism, since Tafel slopes were near 59 mV. Despite the good diode performance of the interfaces studied, the ET mechanism did not conform to the bimolecular rate law suggested by the standard Gerischer model. The exchange current density was found to be independent of solution acceptors even with a concentration range spanning six orders of magnitude. The results can be interpreted by introducing a surface state contribution to the Gerischer model.

D. Other research completed

Publication 6 is an extensive review of the literature on electron transfer at semiconductor electrodes published since 1985; it was written by invitation from the editors of Chemical Reviews and contains the following sections:

- I. Introduction / Organization
- II. Other Review Articles
- III. Types of Semiconductor-Electrolyte Interfaces
- IV. Techniques for Investigating the Semiconductor/Electrolyte Interface
- V. Aspects of Interfacial Energetics
- VI. Mechanisms of Interfacial Electron Transfer Reactions
- VII. Rates of Interfacial Electron Transfer Reactions
- VIII. Theory of Interfacial Electron Transfer Reactions
- IX. Concluding Remarks

The emphasis is on papers relating to fundamental issues as opposed to applications. Application advances will be mentioned in order to provide the reader with a context for the interest in a particular subfield. Rather than attempting to examine specific questions in detail, the goal of this review is to educate the reader with respect to the breadth of systems encountered in photoelectrochemistry and to indicate how these systems can be used to examine fundamental ET issues.

The development and characterization of a flow-through semiconductor-based titanium dioxide photoelectrochemical detector for flow injection analysis and liquid chromatography is described in publication 7. The detector is nonselective, responding to a variety of organic analytes including amines, aromatic alcohols, hydroquinones, aldehydes, and furans with redox potentials less positive than the valence band edge of the titanium dioxide semiconductor. An investigation of the illuminated photoelectrochemistry and dark semiconductor electrochemical properties of the detector was carried out as a function of solvent system, electrochemical potential and TiO_2 production variables. Illumination intensity, titanium oxidation temperature and electrode potential controlled the magnitude of the photoelectrochemical currents. Duration of thermal oxidation and the amount of hydrogen doping determined the ratio of the light to dark current for the analyte. Linearity over two orders of magnitude and detection limits in acetonitrile of 40 pmole and 140 pmole, for p-aminoacetanilide and diethyl amine, respectively, were demonstrated. Illumination of the semiconducting TiO_2 wire electrode along a cylindrical electrochemical cell indicated the possible application of this spatially-resolved detection technique to whole column detection chromatography.

After completing his Ph.D. thesis under the direction of Prof. Koval (publication 8), Dr. B.B. Smith was supported from DOE Grant No. DE-FG02-84ER13247 to further explore certain theoretical ideas pertaining to the project under the direction of Prof. J.T. Hynes. Publications 9-12 describe these endeavors and acknowledge partial support of this grant.

During the past year, a new project was initiated to investigate the possibility of using photochemistry to control the rates of mass transport through membranes. Under certain conditions it appears to be possible to use light to pump molecules against their concentration gradient, thereby storing chemical free energy. The results obtained on this project to date are included in our renewal proposal.

E. Bibliography of publications emanating from this project.

(* reprint or preprint attached to this report)

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- 4.* J.N. Howard and C.A. Koval, "Design and Performance of a Minielectrochemical Cell for Spatial Resolution of 2-D Structures," Anal. Chem., (1991) **63**, 2777-86.
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