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"Reaction Kinetics and Product Distributions in Photoelectrochemical Cells"

Principal Investigator: Carl A. Koval

Major recent accomplishments including experimental and theoretical approach, techniques used, resources applied, with supporting data and their significance.

Reactions of "hot" electrons.

Our research on hot electron reactions at the p-InP / CH_3CN 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 $E^{o'}$ 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 are presently studying the reduction of dibromoethylbenzene (hot electron acceptor) in the presence of metallocene couples (thermalized electron acceptor) utilizing rotating ring disk electrodes.

Rotating ring disk electrodes (RRDE) consisting of n- and p-InP disks and Pt rings were constructed. In solutions containing dibromoethylbenzene (DBEB) and decamethylferrocene$^{+,o}$ (DFER) the following reactions were shown to occur:

At the InP disk:

$DFER^+ + e^- \longrightarrow DFER \quad E^{o'} = -0.40$ (positive of InP conduction band)

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DBEB + 2 e^- $\longrightarrow$ styrene + 2 Br^- $E_{1/2} = -1.50$ (negative of InP conduction band)

At the Pt ring:

2 Br^- $\longrightarrow$ Br_3^- $\longrightarrow$ Br_2 + 2 e^- $E_{p,a1} = +0.50$, $E_{p,a2} = +0.70$

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 demonstrate 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 is much lower due to the fact that the space charge region is much wider. These results are important because it demonstrates 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.A. Koval and R. Torres, "Reduction of Dibromoethylbenzene by Hot Electrons at p-InP/Pt Rotating Ring Disk Electrodes", in preparation.

Electrode kinetics at 2-dimensional materials.

Charge transfer at semiconductor/electrolyte interfaces is the critical process in photoelectrochemical systems. Although the basic model for these interfaces was formulated three decades ago, many aspects of this theory have yet to be experimentally verified. Specifically, there are few, if any, reliable measurements of the fundamental electron transfer rate at nonilluminated semiconductors. Much of this situation stems from experimental limitations imposed by most semiconductor electrode surfaces.

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 minielectrochemical cell was developed to perform experiments in a single drop (1-3 mm diameter) of electrolyte held against the working electrode. The electrochemical behavior and operational considerations of the cell for aqueous and nonaqueous systems were investigated. Spatially-resolved electrochemistry was demonstrated for n-WSe_2 and highly ordered pyrolytic graphite.

The minicell was used to investigate electron transfer at nonilluminated n-WSe_2/dimethylferrocene$^{+/0}$ interfaces. 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 μM to 0.25 M. The electron transfer data can be explained by assuming a surface-state mediated mechanism.

An excellent WSe_2 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 WSe_2 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 WSe_2 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 $j_0 = 0.03 \pm 0.01$ $\mu A/cm^2$.

crystal	[DMFER$^{+/0}$], mM	j_0, x 10^{-8} A/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 ± 0.8	

The minicell was an excellent tool for selecting high quality WSe_2 interfaces. These SEI's showed near-ideal diode behavior and the good interfacial energetics expected for WSe_2 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 a surface state contribution to the Gerischer model.

J.N. Howard, "Electron Transfer at Semiconducting Metal Dichalcogenide / Liquid Electrolyte Interfaces", Ph.D. Thesis, University of Colorado, 1992.

C.A. Koval and J.N. Howard, "Kinetics of Electron Transfer at n-Type Tungsten Diselenide / Acetonitrile Interfaces", in preparation.

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