

Thermodynamic and Kinetic Studies of Dye-Sensitized Nanocrystalline TiO₂ Solar Cells

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Dye sensitized TiO₂ solar cells show great promise as a low cost method of converting light to electricity, with overall efficiencies exceeding 10%. This study is focused on developing an in-depth understanding of both the thermodynamics and kinetics of working sensitized TiO₂ solar cells, with an overall goal of designing more efficient cells. This type of cell is based on the solar excitation of a ruthenium or osmium based dye, followed by injection of an electron into the conduction band of TiO₂. After injection, the reduced form of a redox couple in solution, most commonly iodide/triiodide, regenerates the oxidized dye. The oxidized form of this redox couple is subsequently reduced at the counter electrode, completing the regenerative cycle.

Transient absorption data for a homologous series of Ru and Os polypyridyl sensitizer complexes, both in solution and adsorbed on TiO₂ photoelectrodes, were obtained to probe the underlying dynamics. For the sensitized TiO₂ photoelectrodes, kinetic processes ascribed to charge injection from the Franck-Condon ¹MLCT and low-energy ³MLCT excited states were observed on femtosecond and picosecond time scales, respectively. This assignment was supported by variable-wavelength excitation studies of a Ru complex adsorbed to TiO₂, where direct excitation into the ³MLCT state eliminates the ultrafast injection component that is observed following ¹MLCT excitation. Indirect support for this model comes from studies of Os sensitizers, where the greater relative amplitude of the picosecond injection component is attributed to enhanced competition from intersystem crossing to the ³MLCT. Across the entire series, the picosecond charge injection decay component becomes slower as the excited state formal potential of the metal complex becomes more positive. Thus, decreasing the electronic coupling between the sensitizer and the TiO₂ or reducing the driving force for charge transfer for the ³MLCT state into the TiO₂ will eventually reduce quantum yield for injection and limit the energy conversion properties of photoelectrochemical cells.

In order to improve the efficiency of the cell, it is also important to understand the deleterious back reactions so that they can be minimized. We synthesized a series of dyes whose ground state spanned a wide range of redox potentials to determine which back reaction is rate determining in these systems. If recombination of the injected electron with the oxidized dye were dominant, then we would expect to see a variance in the open circuit voltage at a constant current. If, however, the back reaction to the redox couple in solution dominated, there would be no significant variance in the open circuit voltage. This was investigated by preparing TiO₂ electrodes with low dye coverage to ensure a constant photocurrent for each sample. As speculated in the current literature, we have shown that recombination of the injected electron with the oxidized dye is not the principal back reaction, as we observe no change in open circuit voltage as a function of dye redox potential.

The loss of the injected electron from TiO₂ to the hole carrier in solution, in this case I₃⁻, may thus be a more important back reaction. Samples of varying TiO₂ thickness were prepared, and effect of the surface area of the nanocrystalline TiO₂ film on the rate of the back reaction was measured. For each TiO₂ electrode, profilometry was used to determine the film thickness and the dark current density was measured as a function of the electrode potential. The results reveal a linear dependence of the recombination rate as a function of TiO₂ surface area at a given potential. This strongly supports the hypothesis that recombination with the electrolyte solution is the dominant back reaction in working TiO₂ solar cells.

Another possible limitation to the efficiency of the cell is escape of the injected electron in TiO₂ to the solution via the surface bound sensitizer, which can act as a molecular wire. By varying the distance between the metal center on the sensitizer and the TiO₂ surface, the back reaction can be minimized while keeping the rate of injection sufficiently fast. A series of dyes, with phenylene spacers between the TiO₂-binding carboxyl group and the metal center, has been synthesized to measure the back reaction rates as a function of this separation.