

The Use of Alternative Redox Couples in Dye Sensitized  
Nanocrystalline Semiconductor Solar Cells

Elizabeth I. Mayo, Kristine Kilså, Michael S. Freund,  
Nathan S. Lewis and Harry B. Gray  
California Institute of Technology  
M/C 127-72, Pasadena, CA 91125

Dye sensitized nanocrystalline TiO<sub>2</sub> solar cells show great promise as a cost-efficient means of converting light to electricity with overall efficiencies exceeding 10%. This type of solar cell is based on excitation of a ruthenium or osmium based dye followed by electron injection into the conduction band of TiO<sub>2</sub>. After injection, the oxidized dye is regenerated by the reduced form of a redox couple in solution, most commonly iodide/triiodide. The oxidized form of this redox couple is subsequently reduced at the counter electrode.

The redox couple is crucial in that it shuttles electrons between the counter electrode and the oxidized dye. Furthermore, it also determines the maximum amount of open circuit potential ( $V_{oc}$ ) that can be achieved in these cells. One way to improve the  $V_{oc}$  of these cells would be to work with redox couples that have a very positive formal potential. However, the only redox couple found to produce reasonably high efficiencies in Grätzel solar cells is the iodide/triiodide redox couple ( $I^-/I_3^-$ ).

The  $I^-/I_3^-$  redox couple is a two electron redox couple. It is known to have slow electron transfer kinetics with titanium dioxide, minimizing the deleterious back reaction that decreases cell efficiency. The mechanism by which this redox couple works within the context of these systems is not clear and is the subject of much controversy. Attempts to use fast one-electron redox couples such as ferrocene/ferrocenium ( $Fc/Fc^+$ ) fail. The lack of efficiency in these systems is presumably due to the increased rate of back electron transfer between the injected electrons (either at the conducting SnO<sub>2</sub> back contact or in the TiO<sub>2</sub>) and the acceptor in solution.

We have undertaken a study of the interaction of a series of two electron redox couples with titanium dioxide. This series includes thiols, thiocyanagens and bromide/tribromide systems. The electron transfer kinetics between these redox couples and TiO<sub>2</sub> will be discussed and preliminary results showing that bromide/tribromide, in particular, can show enhanced efficiencies in dye sensitized solar cells.