Experimental Methods for Characterization of Dye Sensitized Nanocrystalline Photovoltaic Cells

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Characterization of the physical and chemical processes involved in the functioning of dye-sensitized cells presents an interesting experimental challenge, and there is a need to test theoretical models using relevant experimental data. Key steps in the conversion of solar radiation into electrical power include light harvesting by the adsorbed dye, injection of electrons into the conduction band of the nanocrystalline matrix, transport, trapping and back reaction of electrons, mass transport of electrolyte species and regeneration of the supersensitizer at the cathode. Several aspects of these processes remain controversial. For example, slow electron transport to the anode has been attributed on the one hand to electron cation interaction (ambipolar diffusion) and on the other to trapping/detrapping. The extent to which interparticle 'necks' limit electron transport is unknown at present. The mechanism and kinetics of the back reaction of electrons with tri-iodide species is also unresolved, and the importance of back reaction at the anode is unclear. Clarification of these issues is important in the context of attempts to optimize cell performance. This contribution reviews a number of useful experimental methods and relevant progress in theoretical modeling of dyesensitized cells.

Electron transport can be studied using small amplitude pulse or sinusoidal perturbation superimposed on steady state illumination (intensity modulated photocurrent spectroscopy: IMPS). This approach allows linearization of the system response. By contrast, interpretation of the transient photocurrents induced by large amplitude laser pulses is more difficult, particularly if illumination is strongly inhomogeneous, as is the case when UV excitation is used with dye-free systems. It is particularly important to work in an intensity (or electron occupation) regime that corresponds to the conditions under which practical cells operate (i.e.0.1 - 1 sun).

The back reaction of photoinjected electrons with tri-iodide ions (or equivalent species in the case of analogues of the liquid cell) can in principle occur either at the surface of the nanocrystalline oxide (generally  $TiO_2$ ) or at the conducting glass substrate. The role of blocking layers is important in this context. These back reactions can be studied by several methods, including transient photovoltage, intensity modulated photovoltage spectroscopy (IMVS) and a charge extraction method that determines the time dependent electron concentration during open circuit decay. Time or frequency resolved spectroscopic methods that detect either electrons or the oxidized dye are also useful way to study the kinetics of dye regeneration. back reaction and Photoelectrochemical- -al impedance spectroscopy also gives information that can be related to the time and frequency resolved measurements.

Theoretical models of the cell are being developed using a number of different approaches, including numerical simulation based on finite difference, finite element, boundary element and Monte Carlo methods. There is a need to relate the predictions of these models to the results of carefully designed experiments designed to address the key issues that determine cell function and performance.

This contribution will present recent results fro a range of dye-sanitized cells with the objective of illustrating the information obtained by different methods. The experimental data will be related to some of the recent modeling work that is being carried out in our laboratories.