Interfacial layers and charge transport in porous thin-film photovoltaics

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Since the advent of dye-sensitized, nanoporous metal oxide ("Grätzel") solar cells (*DSSC*s), incorporating a liquid redox electrolyte for charge transfer, several concepts expanding this idea to inorganic, all solid-state photovoltaic devices have been proposed. One of these is the "extremely thin absorber" (*ETA*) solar cell, comprising an ultra-thin coating of a light absorbing semiconductor, on a mesoporous oxide (eg TiO_2, separated from the bottom contact by a dense oxide layer) and completed with a pore-filling hole conductor (eg CuSCN). So far, these have failed to achieve efficiencies approaching those of *DSSC*s. The reasons for this are not fully clear, although solid-state dye-sensitized cells also lag behind their liquid electrolyte counterparts.

The very slow rate of the reduction reaction of the liquid electrolyte at the metal oxide interface, relative to the rate of electron recombination with holes in the analogous *p*-type semiconductor is one likely reason for the better performance of liquid- over solid-state cells. Furthermore, in an *ETA* cell, much faster recombination between electrons in the oxide and holes in the absorbing semiconductor, relative to electron recombination with an excited dye molecule, may also be important. Adding a 'buffer layer', generally a wide band-gap semiconductor, between the (*n*-type) metal oxide and (*p*-type) electrolyte / semiconductor at this mesoporous interface, was found to improve *DSSC*s, and is often essential in the case of solid state cells.

Recently, we have begun to investigate the function of organic monolayers at photovoltaic interfaces. We found that a dense, self-assembled organic monolayer, directly bound to an oxide-free surface of *n*-type silicon, forms a near-ideal insulator, outperforming inorganic films (eg Si-O) of comparable thickness (1.5-2.5 nm). Furthermore, thickness of the organic monolayer can be tuned using different chain lengths, and also serves to passivate the interfacial Si layer. We show that such a layer with a semi-transparent top electrode yields a hybrid organic-inorganic *MIS* – or "Metal - Organic Insulator - Semiconductor" (*MOIS*) – solar cell.

Such a layer provides a potentially useful tool in the study and construction of oxide *ETA* cells. We examine cells of the type TiO_2*-absorber-CuSCN*, with CdS or $Cu_{2-x}S$ absorber layers. Additionally for $Cu_{2-x}S$, a buffer layer of $In_xOH_yS_z$ is employed at the metal oxide interface. However, problems of incomplete buffer layer surface coverage, and uncertainty in layer morphology and function, hinder both performance of, and efforts to characterize, $Cu_{2-x}S$ cells. An insulating organic monolayer with high surface coverage opens the possibility to carefully control which species – out of absorber, hole conductor and / or inorganic buffer layer, is present at the TiO_2 interface. Using time-dependent voltage decay measurements, we aim to determine which of the charge mechanisms are most important at the mesoporous oxide interface. Additionally, we hope that a high-coverage insulating layer, applied to the exposed oxide surface after deposition of the buffer and / or absorber layer, will restrict recombination while selectively allowing charge transport between the *n*- and *p*-type phases through the buffer-absorber. This has potential to address the problem of the high relative rate of recombination in *ETA* cells between (abundant) oxide surface states and the solid absorber and/or hole conductor, relative to, respectively, the DSSC dye and liquid electrolyte.