

Iodide electron transfer kinetics in dye-sensitised solar cells

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Electron transfer kinetics play a key role in determining the energy conversion efficiency of dye-sensitised solar cells, as illustrated in figure 1. This talk will address the kinetic competition following the photoinduced electron injection¹ between charge recombination of the injected electrons with dye cations (k_{CR1}) and the alternative dye cation re-reduction by iodide in the hole transporting medium (HTM) (k_{RR}).

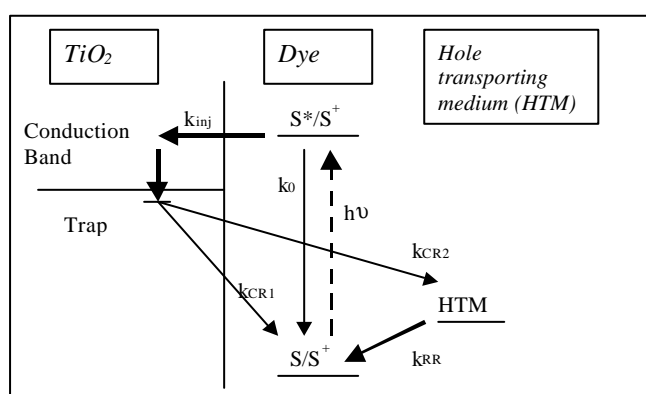


Fig.1 Electron transfer kinetics at the TiO_2 / dye / HTM interface, including excited state decay to ground (k_0), electron injection and trapping (k_{inj}), dye cation rereduction by liquid or solid state hole transporting media (k_{RR}) and charge recombination between electrons in the TiO_2 and dye cations (k_{CR1}) or oxidised HTM (k_{CR2}).

Transient absorption spectroscopy has been employed to study the events following electron injection in $\text{Ru}(\text{dcbpy})_2(\text{SCN})_2$ sensitised nanocrystalline TiO_2 electrodes in the presence of different iodide concentrations in propylene carbonate. This competition was monitored spectroscopically both by determination of the dye cation decay kinetics and the formation of I_2^- species generated by the re-reduction reaction. As we have shown previously², the recombination process k_{CR1} is strongly dependent upon the electrical bias applied to the TiO_2 electrode, and the concentration of potential determining cations in the electrolyte. In contrast, the re-reduction rate k_{RR} was found to be independent of applied voltage but strongly dependent on the concentration of iodide. No evidence was observed for specific complexation of iodide species with sensitizer dyes. The decay kinetics of the I_2^- states generated by the dye cation re-reduction are observed to be independent of applied bias, and are assigned to dismutation yielding I_3^- and I^- . Comparison of data obtained with three different sensitizer dyes indicates the dye cation re-reduction kinetics and I_2^- yields were dependent upon the oxidation potential of the sensitizer dye. Kinetic competition is observed between k_{RR} and k_{CR1} as a function of applied bias and iodide concentration. The rate of the re-reduction reaction is found to be independent of applied bias in the presence of concentrations of iodide comparable to the ones used in complete solar cells. At high iodide concentrations, the re-reduction reaction is sufficiently fast to compete successfully with the recombination reaction for bias up to -0.4V vs. AgCl. At more moderate iodide concentrations, kinetic competition between k_{RR} and k_{CR1} results in the yield of I_2^- being dependent upon the applied voltage. This kinetic competition is modelled by employing a continuous time random walk of the electron in the semiconductor to model the recombination dynamics, and assuming k_{RR} is first order in iodide concentration. The model is found to be in good agreement with experimental data obtained both as a

function of Γ^- concentration and applied bias. Both the Γ^- re-reduction reaction kinetics and I_2^- yield were found to be largely independent of I_2 concentration.

These observations are extended to solid state dye sensitised solar cells employing a polymer electrolyte: poly(epichlorohydrin-co-ethylene oxide) containing NaI and I_2 ³. The dye cation re-reduction kinetics are found to be comparable to those observed for the propylene carbonate liquid electrolyte, consistent with the high ionic mobility of this polymer. The recombination reaction k_{CR1} is found to be essentially independent of cell voltage over the operating range of the device, attributed to the basic nature of the polymer employed. This has the consequence of minimising the voltage dependence of kinetic competition between k_{CR1} and k_{RR} , consistent with the high open circuit voltage obtainable with such devices.

References

- 1) Tachibana, Y.; Moser J.E.; Grätzel M.; Klug, D.R.; Durrant, J.R. *J. Phys. Chem.* **1996**, *100*, 20056
- 2) Haque, S. A.; Tachibana, Y.; Willis, R.L.; Moser, J.E.; Grätzel, M.; Klug, D.R.; Durrant, J.R.; *J. Phys. Chem. B* **2000**, *104*, 538.
- 3) Nogueira, A.F.; Durrant, J.R.; De Paoli, M.-A. *Adv. Mater.* **2001**, submitted.