

Kinetically Determined Solar Cells

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Abstract:

Solar cells are ideally defined as photoactive membranes with selective permeability for electrons and holes. Classical solar cells have approached and solved this problem, first empirically and later on the basis of elaborated solid state theories, by providing optimised charge mobility and electrical fields for charge separation. They are typically generated with well crystallized and therefore comparatively expensive materials. However in new solar cells, with easy to fabricate low cost nano-composite materials, electrical fields loose their significance and solar cell efficiency is controlled by selective kinetic electronic factors. In dye sensitisation solar cells the kinetic selectivity or electronic irreversibility is essentially given by the asymmetric electron exchange properties of the I^-/I_3^- redox couple. In composite polymer fullerene solar cells it is given by the property of fullerene molecules to capture an electron much more efficiently than to re-donate it. If these components are replaced by reversibly functioning molecular systems, the solar cell efficiency collapses, which can experimentally be demonstrated. In dye sensitisation solar cells, for example, replacing I^-/I_3^- for $Fe(CN)_6^{3-/4-}$ or quinone/ hydroquinone, or depositing Pt islands on the front contact to catalyse the iodine reduction, leads to a drastic drop in solar cell efficiency. Both presently investigated kinetically controlled solar cells have essentially been developed empirically and are still faced with photo-degradation problems, which also specifically involve these kinetically controlling molecular systems /1/2/.

Since also photosynthetic charge separation works via kinetic irreversibility, and since the dye solar cell and the polymer composite solar cell have to be developed beyond the present limitations imposed by the irreversibly functioning I^-/I_3^- and fullerene components, it is relevant to better elucidate the principle of kinetically determined solar cells and to learn more about electronic selectivity and irreversibility.

Possibilities to obtain and describe electron transfer irreversibility via the classical Marcus theory are discussed. More promising and innovative mechanisms can however be expected from far from equilibrium electron transfer. They do not any more rely on reversible Boltzmann statistics and enable stimulated and self organized electron transfer by allowing molecular electronic feedback processes /3/. Such mechanisms are inherently irreversible. They are shown to occur in the biological electron transfer chains. Evidence is specifically given that also the photosynthetic reaction centre itself with its quasi-symmetrical structure is taking advantage of irreversible thermodynamics for charge separation /4/. The question is raised how similar inherently irreversible mechanisms could be implemented in most simple composite solar cells. What are the most fundamental electronic-molecular factors determining irreversibility? May it be possible to generate irreversibility simply by properly surface modifying nano-particles with feed-back active molecular species? How could they be designed?

Our lack of knowledge on molecular electronic irreversibility is a key factor determining the present learning curve of dye and polymer composite cells. Besides of giving an outlook on the development challenges for kinetically determined nano-composite solar cells with photo-stable components, the contribution presents experimental results on molecular electronic irreversibility. It also gives an example of a composite dye solar cell applying a new type of selective interface, modelled on materials and mechanisms expected to function within the photosynthetic membrane /5/.

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