COMMENTS

Comment on "Diffusion Impedance and Space Charge Capacitance in the Nanoporous Dye-Sensitized Electrochemical Solar Cell" and "Electronic Transport in Dye-Sensitized Nanoporous TiO₂ Solar Cells—Comparison of Electrolyte and Solid-State Devices"

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The title papers assume that a dye-sensitized solar cell (DSSC) can be adequately[1] or at least approximately[2] described by the conventional model of a pn-junction. Both papers contain useful experimental data and discussions and are important contributions to the literature. However, both papers overlook an important point. There are two driving forces that must be taken into account in DSSCs: the electrical potential energy gradient, ∇U and the *photoinduced* chemical potential energy gradient, $\nabla \mu_{h\nu}$. Both papers neglect the latter force.

The standard equation for a one-dimensional electron flux

$$J_n(x) = n(x)\mu_n\{\nabla U(x) + \nabla\mu(x)\} = n(x)\mu_n\nabla E_{Fn}(x)$$

shows that ∇U and $\nabla \mu$ are *equivalent* forces (both of which can have photoinduced components). Here $n(x)$ is the electron density, μ_n is the electron mobility, and $\nabla E_{Fn}(x)$ is the gradient of the quasi Fermi level (electrochemical potential energy) of electrons. In the treatment of conventional pn-junction solar cells, $\nabla \mu_{h\nu}$ is neglected. This approximation is valid *only* for materials in which both electrons and holes are photogenerated together in the same phase and in which both carriers are highly mobile. These conditions do not apply to DSSCs or to most other organic-based photovoltaic (PV) cells. In organic PV cells, electrons are photogenerated in one phase and holes are photogenerated, *already separated* from electrons, in a different chemical phase. Therefore, a large carrier concentration gradient (large $\nabla\mu_{h\nu}$) is photogenerated on each side of the heterointerface. This constitutes a powerful driving force for carrier transport and it is known to play a significant, sometimes dominant, role in organic PV cells (see, for example, ref 3). A number of papers in the past decade considered various aspects of this mechanism. A detailed comparison of organic to inorganic PV cells has been published.[4]

The fact that $\nabla U(x) \approx 0$ throughout most of a DSSC, because of the presence of mobile electrolyte ions, ensures the predominant importance of $\nabla\mu_{h\nu}$ in DSSCs. Furthermore, numerous papers have shown that built-in electrical potentials have little effect on DSSCs (e.g., see refs 8, 16, 20–22 in ref 2). Nevertheless, both papers focus entirely on ∇U and neglect $\nabla\mu_{h\nu}$. A great deal of thought and effort has gone into both of these papers. Unfortunately, however, because the authors use a model that neglects a powerful, even dominant, driving force in DSSCs, their conclusions must be met with some skepticism.

References and Notes

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(3) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1990**, *94*, 1586–1598.

(4) Gregg, B. A.; Hanna. *J. Appl. Phys.* **2003**, *93*, 3605–3614.