

Physica E 14 (2002) 61-64



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Photovoltaics and photoelectrochemistry: similarities and differences

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Accepted 12 January 2002

Abstract

Similarities and differences between semiconductor-based photovoltaic and photoelectrochemical devices for solar energy conversion are briefly reviewed. © 2002 Published by Elsevier Science B.V.

Keywords: Photovoltaics; Photoelectrochemistry; Solar energy conversion

1. Introduction

Photovoltaic (PV) and photoelectrochemical (PEC) devices for solar energy conversion have similarities and differences that can be instructive to explore. The defining difference is that a PEC device contains an electrolyte phase, in which ions carry the moving charge, and electrode/electrolyte interfaces at which electrochemical reactions occur. A PV cell, on the other hand, is a purely solid-state device in which holes or electrons carry the moving charge and there is no accompanying chemical change. The defining similarity between PEC and PV devices is that both are designed to harness the energy of hole-electron pairs created by light absorption (usually in a semiconductor or a molecule), by separating them and causing them to recombine through a work-producing route. Electronic charge carriers in semiconductors are usually very mobile and can diffuse appreciable distances (Table 1), and this is key to the success of semiconductor-based devices.

Crucial to both types of device is a junction between two materials across which there is an electrochemical potential difference at equilibrium. It is the combination (in different proportions, according to the device) of the electric and chemical potential differences across this junction that causes holes and electrons to flow in opposite directions, producing the photocurrent. The junction in a PV device is typically a p-n homojunction or heterojunction or a p-i-n junction, formed from doped or intrinsic semiconductors that are also the light-absorbing phases. The junction in a PEC device is typically formed between a semiconductor electrode and an electrolyte solution, sometimes with an interposed sensitizing dye layer. The light is absorbed either in the semiconductor or in the sensitizer. There are also PEC devices, such as photogalvanic cells, in which the light is absorbed by the solution and drives a photoredox reaction, the products of which are harnessed by the electrodes. Because of the slowness of molecular diffusion and the short distance that excited states or photoredox products can

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^{1386-9477/02/\$ -} see front matter @ 2002 Published by Elsevier Science B.V. PII: \$1386-9477(02)00450-2\$

Table 1

Typical diffusion coefficients D, lifetimes τ and diffusion lengths $L = \sqrt{D\tau}$ for molecules in solution and charge carriers in semiconductors

	$D (cm^2 s^{-1})$	τ (s)	<i>L</i> (µm)
Molecules in solution			
Singlets	$10^{-6} - 10^{-5}$	$10^{-12} - 10^{-9}$	$10^{-5} - 10^{-3}$
Triplets	$10^{-6} - 10^{-5}$	$10^{-8} - 10^{-5}$	$10^{-3} - 10^{-1}$
Photoredox			
products	$10^{-6} - 10^{-5}$	$10^{-6} - 10^{-3}$	1-100
Minority carriers in semiconductors			
Organic polymers			
(h ⁺ in PPV)	10^{-6}	10^{-5}	~ 1
Direct gap			
(e ⁻ in GaAs)	200	10^{-9}	~ 5
Indirect gap			
(e ⁻ in c-Si)	40	10^{-6}	~ 50

diffuse in solution (see Table 1), these are inefficient devices, and we shall not consider them further here. Rather we summarize the similarities and differences between semiconductor-based PV and PEC devices, under four headings.

2. Basics

To begin with a restatement, there is no (deliberate) electrochemistry in a PV device (although there may be more incidental chemistry than meets the casual eye), but fundamental to the operation of a PEC device is a light-driven electrochemical reaction that can produce useful chemicals, such as hydrogen, or destroy unwanted ones, such as organic pollutants. PEC cells can also be configured as 'wet PV devices' such as the Grätzel cell, in which the electrochemical process at the dark electrode reverses that at the illuminated electrode (but at a different potential) so the cell produces electrical power without net chemical change in the electrolyte. The possibility of net electrochemistry is, however, the 'unique selling proposition' of a PEC device. Unfortunately, the electrochemistry and the liquid solution are also a major source of instability in PEC devices-electrodes can corrode and solvents can evaporate. It is difficulties with semiconductor stability that have led to the popularity of wide-band-gap oxide semiconductors such as TiO₂ in PEC devices, rather than the more covalent semiconductors used in PV such as Si and CdTe, which have band gaps that are better tailored to the solar spectrum. It is difficulties with solvent containment that have driven the developers of the Grätzel cell away from the original aqueous iodine/tri-iodide solution towards a solid-state hole conductor such as OMeTAD [1], incidentally turning a PEC device into a PV device en route.

Against these disadvantages should be offset the ease of junction formation in a PEC device—the electrode surface must simply be appropriately prepared and then immersed in the solution to form the junction. Forming most PV junctions, on the other hand, is a time-consuming and expensive operation requiring controlled deposition of several layers in vacuum conditions.

3. Junction structure

The Galvani (inner) potential varies across PV and PEC junctions in characteristically different ways, as illustrated in Fig. 1. In a PV p–n junction, the contacting phases have quite similar charge densities (with doping levels typically 10^{16} – 10^{18} cm⁻³) and the region of changing potential is extended on both sides of the metallurgical interface over a space-charge region of width ~ 0.1–1 µm. The region of changing potential across a PEC semiconductor electrode/electrolyte interface, by contrast, extends over the space-charge region in the semiconductor as before but does not extend into the solution phase because of the much higher ionic charge density in the electrolyte (~ 10^{21} cm⁻³ in a 1 M electrolyte solution).

In sufficiently defect-free interfaces, the band-edge energies are 'pinned', that is, determined by the work functions of the two contacting phases, leaving the Fermi levels free to float (Fig. 2a). This allows the maximum photovoltage to be achieved on illumination. However, surface states are common, in PV junctions because of lattice mismatch between the two phases or other crystallographic defects, in PEC junctions because of lattice truncation, surface defects and adsorbed redox-active ions. These states are deleterious if they act as recombination centres, limiting the photocurrent. A sufficient density of surface states will pin the Fermi level (Fig. 2b), which tends to limit the band bending and the photovoltage. Band-edge positions can, however, be advantageously adjusted (Fig. 2c), in favourable cases by up to several tenths of an eV, by adsorption of polar molecules at the



Fig. 1. Variation of inner electric potential ϕ across (a) a typical p-n junction; (b) a typical n-type semiconductor electrolyte junction.



Fig. 2. The valence and conduction band edges $U_{v.s}$ and $U_{c.s}$ are pinned in a defect-free device while the Fermi level floats in a Schottky-type barrier; (b) the Fermi level $U_{F.s}$ (and hence the band bending) is pinned by a sufficient concentration of active surface states in a Bardeen-type barrier; (c) band-edge positions in both PV and PEC devices can be altered by the adsorption of polar molecules.

junction, and this can be used to overcome sub-optimal band-edge alignments in both PV and PEC devices.

4. Optical properties

Optimizing the optical properties of a photoconverter for solar energy absorption is essential to producing a high-efficiency device. The optical properties of elemental and binary semiconductors used are rather inflexible, but ternary and higher alloys with good miscibility ranges, such as the $Ga_xAl_{1-x}As$ and $CuIn_xGa_{1-x}Se_2$ series, allow optoelectronic properties to be varied over a wide range. The creation of impurity bands in a bulk semiconductor can improve solar light absorption, as well as providing one route to 'third generation' devices [2], in which the Shockley–Queisser constraints on the efficiency of a single-junction device are overcome. Space quantization in Q layers, wires and dots produces pronounced lengthening of excited-state lifetimes, and is becoming an important stratagem in device design [3]. The creation of 'photofunctional interfaces' by dye sensitization of nanoporous semiconductors, especially TiO₂, or by interpolation of a thin highly absorbing narrow semiconductor [4] is also a favoured stratagem, following the success of the Grätzel cell.

As for organic semiconductors and molecular chromophores, their optical (and redox) properties can be flexibly tailored by molecular substitution, usually in the aromatic ring, but optical excitation creates excitons rather than 'free' holes and electrons. Excitons are short-lived and typically diffuse only a few nm before decaying. However, this difficulty can be overcome by co-blending two phases to create a 'soft' or 'extended junction', for example in the polymer co-blend cell of Saricifti and co-workers [5], which allows efficient exciton collection by ensuring that most excitons are formed within a few diffusion lengths of a phase boundary.

5. Device physics

The different junction and charge carrier types in PV and PEC devices lead to some differences in their typical device parameters. In both, the open-circuit photovoltage $V_{\rm oc}$ can be expressed as

 $V_{\rm oc} = (\beta kT/q) \ln[1 + i_{\rm ph}/i_{\rm o}],$

where β is the diode quality factor, q the charge on an electron, i_{ph} the photocurrent and i_o the reverse-bias saturation current density (in a PV device) or the exchange current density (in a PEC device). Electrochemical exchange current densities in PEC devices are very small when the kinetic barrier to interfacial electron transfer is substantial (i.e., when the Marcus reorganization energy of the redox couple is substantial) and this typically leads to smaller i_o values and higher open-circuit photovoltages in PEC as compared with PV devices. The photocurrents in PEC devices are, however, usually smaller on account of the higher band gap of most PEC electrodes as compared with PV electrodes.

The diode equation

$$i_{\rm j} = i_{\rm o} \exp[(qV/\beta kT) - 1],$$

where i_j is the junction (dark) current, is widely used to describe the shape of the dark current–voltage curves

of PV and PEC devices. There is scant justification for this, however, where β departs from a physically reasonable value of 1–2 and the junction is not a diode.

PV p–n homo- and hetero-junctions are minoritycarrier devices (that is, the charge carriers that carry the dark current become minority carriers once they have crossed the junction), whereas semiconductor/electrolyte junctions behave like metal/semiconductor junctions and are majority carrier devices. As such, the dark currents in the latter are less adversely affected (increased) by poor materials quality.

6. Conclusion

There are similarities between PV and PEC devices that is instructive to consider. In nanoscale devices, the distinction between molecules and semiconductors is partly blurred by space quantization. The mode of action of solid-state and 'wet' dye-sensitised solar cells is fundamentally similar. Apparent differences are sometimes exaggerated by differences in discipline: physicists and chemists working on photoconversion devices should strive for a common language or at least good mutual understanding.

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