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Electrochemical photovoltaic cells – review of recent developments

Di Wei,* Piers Andrew and Tapani Ryhänen

Abstract

Photoelectrochemistry is attracting extensive attention from scientists worldwide for its use in converting light energy into electricity in electrochemical photovoltaic cells, the most common form of which, dye sensitized solar cells (DSSCs), can offer both flexibility and transparency. Their efficiencies are now comparable with amorphous silicon solar cells but at a much lower cost. This review covers not only the fundamentals of electrochemical photovoltaic cell operation but also recent advances in research and development for industrial applications. The most recent research topics relating to DSSCs, for example, applications of nanostructured n-type semiconducting electrodes, ionic liquid electrolytes and graphene and carbon nanotube electrodes are all included. In addition, the storage of electrochemical energy by electrochemical photovoltaic cells has also been reviewed.

Keywords: electrochemical photovoltaic cells; dye sensitized solar cells (DSSC)

INTRODUCTION

One of the most important aspects to using solar energy is its conversion from solar radiation into electric energy. The most striking difference between electrochemical photovoltaic cells and conventional silicon (Si) based photovoltaics is that the former contains two interfaces at which charge transport has to switch from electronic to ionic and vice versa, as in batteries. Electrochemical photovoltaic cells have the following advantages when compared with Si based photovoltaics. First, they are insensitive to defects in the semiconductor materials. Second, the solid/liquid junction is easy to form and thus is economical to manufacture. Third, it is possible to realize direct energy transfer from photons to chemical energy in electrochemical photovoltaic cells. An electrochemical photovoltaic cell is generally composed of a photoactive semiconductor working electrode and a metallic counter electrode (e.g. Pt). Both electrodes are immersed in electrolyte containing suitable redox couples. If the semiconductor–electrolyte interface (SEI) is illuminated with light having energy greater than the bandgap of the semiconductor, photogenerated electrons/holes are separated. The photogenerated minority carriers arrive at the interface of the semiconductor–electrolyte, while the majority carriers accumulate on the back face of the semiconductor. With the help of a charge-collecting substrate, photogenerated majority carriers are transported via a load to the counter electrode where these carriers electrochemically react with the redox electrolyte. A pioneering photoelectrochemical experiment was realized by obtaining a photocurrent between two platinum electrodes immersed in an electrolyte containing metal halide salts.[1] It was later found that the photosensitivity can be extended to longer wavelengths by adding a dye to silver halide emulsions.[2] Interest in photoelectrochemistry of semiconductors led to the discovery of wet-type photoelectrochemical solar cells.[3–5] Grätzel then extended the concept to dye sensitized solar cells (DSSC) by adsorption of dye molecules onto nanocrystalline TiO_2 electrodes.

Electrochemical photovoltaic cells without dyes

In electrochemical photovoltaic cells without dyes, both the semiconductor electrode and the counter electrode are immersed in the redox electrolyte. Incident light creates excitons in the semiconductor electrode and the photogenerated electrons and holes are separated in the space charge region. Specific reactions occur only at the semiconductor and the metal counter electrode as shown in Fig. 1(a) (n-type semiconductor) and Fig. 1(b) (p-type semiconductor).

In these types of cells, charge balance due to oxidation and reduction processes is maintained. However, such wet-type photoelectrochemical cells suffer from instability of the semiconductor in aqueous media. Unsensitized photoelectrochemical photovoltaic cells cannot replace silicon based photovoltaics unless some photoelectrochemically stable semiconductor materials possessing a band gap of approximately 1.4 eV can be found.[6–9]

Dye sensitized solar cells (DSSC)

A novel solar cell based on a dye sensitized porous nanocrystalline TiO_2 photoanode with attractive performance has been reported by Grätzel *et al.*[10–12] Interest in porous semiconductor matrices permeated by an electrolyte solution containing dye and redox couples has been stimulated by their reports. The earlier photoelectrochemical studies of dye sensitization of semiconductors focused on flat electrodes, but these systems

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* *Correspondence to: Di Wei, Broers Building, 21 JJ Thomson Avenue, Cambridge, CB3 0FA, UK. E-mail: di.wei@nokia.com*

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Nokia Research Centre, Broers Building, 21 JJ Thomson Avenue, Cambridge, CB3 0FA, UK

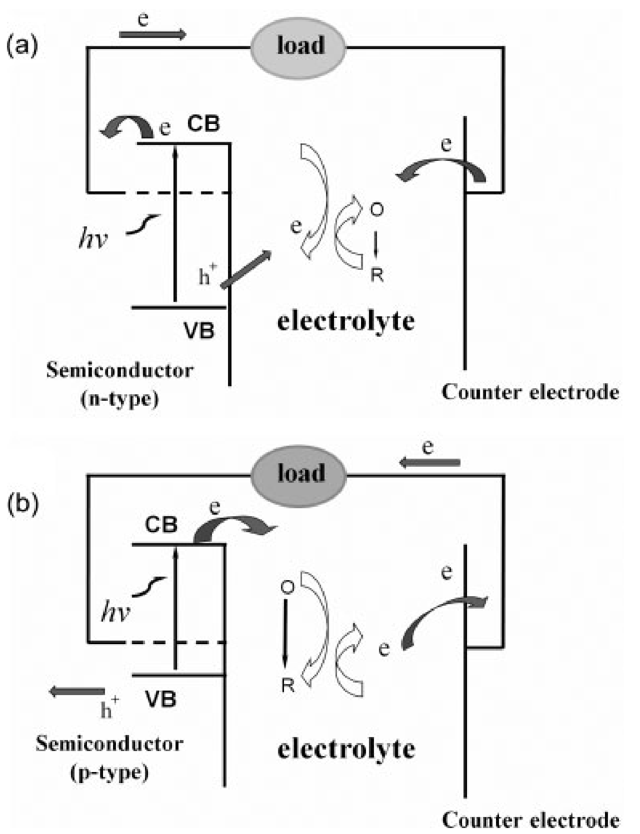

Figure 1. Operating mechanism of electrochemical photovoltaic cells with (a) n-type semiconductor working electrode, and (b) p-type semiconductor working electrode. O/R: redox couple, e: electrons, h+: holes.

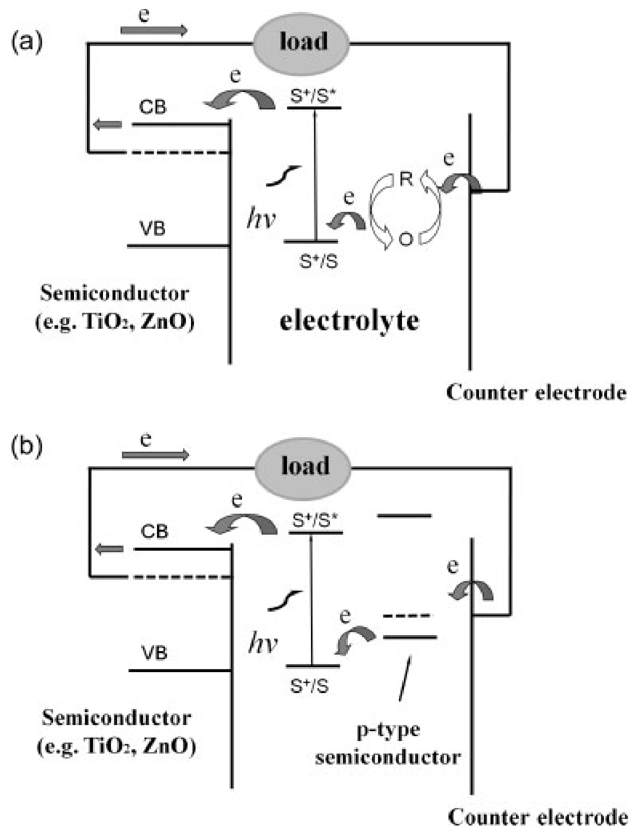

Figure 2. Operating mechanism of an electrochemical dye sensitized solar cell (DSSC). S: dye sensitizer, S*: excited dye sensitizer, S^+: oxidized dye sensitizer O/R: redox couple (e.g. I_3^-/I^-). (a) Wet-type DSSC with redox couple in the liquid electrolyte; (b) solid state DSSC with a p-type semiconductor replacing the electrolyte containing the redox couple.

faced an intrinsic problem.[13] Only the first monolayer of adsorbed dye results in effective electron injection into the semiconductor, but such light-harvesting from a single dye monolayer is extremely small. By application of nanoporous TiO_2, the effective surface area can be enhanced 1000-fold. An intriguing feature in the nanocrystalline TiO_2 film is that the charge transport of the photo-generated electrons passing through all the particles and grain boundaries is highly efficient.[14] Electrochemical photovoltaics based on a dye sensitized porous nanocrystalline TiO_2 photoanode with attractive performance was first reported by Grätzel *et al.*[12,15] These reports raised interest in nanoporous semiconductor matrices permeated by an electrolyte solution containing dye and redox couples. The power conversion efficiency of the DSSC has improved to 11.5%[16] since the first DSSC was reported with an efficiency of 7.1%,[9] and efficiencies are now comparable with those of amorphous Si cells.[17] Large-size DSSCs have been prepared on a silver grid embedded in a fluorine-doped tin oxide (FTO) glass substrate by the screen printing method.[18] Under standard test conditions, an energy conversion efficiency of the active area of 5.52% was achieved with a 5 × 5 cm device, which is comparable with 6.16% of a small-size Si cell prepared under similar conditions. G24 Innovation Ltd., based on the technology invented by Grätzel, use a low-cost, roll-to-roll process to make its flexible DSSC modules, which produce 0.5 W under direct sunlight. Miyasaka *et al*. developed a 2.1 m × 0.8 m DSSC module with thickness of 0.5 mm by connecting eight panels with six embedded cells. The module conversion efficiency was approximately 3% and the module was displayed at the first International Photovoltaic Power Generation Expo in 2008.

In a DSSC, the initial photoexcitation occurs in the light absorbing dye as shown in Fig. 2. Nanoporous semiconductors such as TiO_2 not only act as support for the dye sensitizer but also function as electron acceptor and electronic conductor. Subsequent injection of electrons from the photo-excited dye into the conduction band of semiconductors results in the flow of current travelling across the nanocrystalline TiO_2 film to the charge collecting electrode and then to the external circuit. Sustained conversion of light energy is facilitated by regeneration of the reduced dye sensitizer either via a reversible redox couple (O/R), which is usually I_3^-/I^- (Fig. 2(a)) or via electron donation from a p-type semiconductor (Fig. 2(b)).

Figure 2(a) shows the mechanism of a traditional wet-type DSSC containing redox couples in the electrolyte. The photoanode, made of a nanoporous dye-sensitized n-type semiconductor, receives electrons from the photo-excited dye sensitizer (S*) which is thereby oxidized to S^+. The neutral dye sensitizer (S) can be regenerated by the oxidation reaction (R→O) of the redox species dissolved in the electrolyte. The mediator R will then be regenerated by reduction at the cathode (O→R) by the electrons circulated through the external circuit.

The need for DSSC to absorb far more incident light was the driving force for the development of mesoscopic semiconductor materials with an enormous internal surface area. The major breakthrough in DSSC was the use of a high surface area nanoporous TiO_2 layer. A single monolayer of the dye on the semiconductor surface was sufficient to absorb essentially all the incident light in a reasonable thickness (several µm) of the semiconductor film. TiO_2 became the semiconductor of choice with the advantages of being cheap, abundant, and non-toxic.[19] The choice of dye is also an important parameter. The first organic-dye photosensitization was reported in 1887.[20] In traditional DSSC, the standard dye was tris(2,2′-bipyridyl-4,4′-carboxylate)ruthenium (II) (N_3 dye). The function of the carboxylate group in the dye is to attach to the semiconductor oxide substrate by chemisorption.[19] The dye must carry attachment groups such as carboxylate or phosphonate to firmly graft itself to the TiO_2 surface. The attachment group of the dye ensures that it spontaneously assembles as a molecular layer upon exposing the oxide film to a dye solution. Thus ensuring a high probability that, once a photon is absorbed, the excited state of the dye molecule will relax by electron injection to the semiconductor conduction band. The photovoltaic performance of the N_3 dye has not been exceeded by other dye complexes since 1993.[21] A credible challenger was identified with tri(cyanato-2,2′,2″-terpyridyl-4,4′,4″-tricarboxylate)Ru(II) (black dye),[8] whose response extends 100 nm further into the IR than the N_3 dye.[22] It was not until recently that a high molar extinction coefficient heteroleptic ruthenium complex was synthesized and demonstrated as a more efficient sensitizer for DSSCs.[10]

Owing to the corrosion of the pink-coloured I_3^-/I^- redox couple in liquid electrolytes, a lot of effort has been put into looking for a mild and 'transparent' substitute. Recently a new disulfide/thiolate redox couple that has negligible absorption in the visible spectral range has been reported.[23] Because of a further encapsulation problem posed by the use of liquid in the conventional wet-type DSSC, much work is being done to make an all solid state DSSC.[24,25] The use of solvent-free electrolytes in the DSSC is supposed to offer very stable performance for the device. To construct a full solid-state DSSC, a solid p-type conductor should be chosen to replace the liquid electrolyte. The redox levels of the dye and p-type materials have to be adapted carefully as Fig. 2(b) shows. It results in an electron in the conduction band of n-type semiconductors (e.g. TiO_2) and a hole localized on the p-type conductor. Hole transporting amorphous materials have been used in nanocrystalline TiO_2-based DSSCs to transport hole carriers from the dye cation radical to the counter electrode instead of using the I_3^-/I^- redox species.[24,26] Early work focused on the replacement of I_3^-/I^- liquid electrolyte with CuI. CuI is a p-type conductor that can be prepared by precipitation from an acetonitrile solution at room temperature and it is also a solid state ionic conductor. Cells made this way gave solar efficiencies of several per cent, but their stability is relatively poor due to the lability of CuI to air and light.[25] In addition to CuI, CuSCN has also been tried.[27,28] Organic hole transporting materials will offer flexibility and easier processing. Bach *et al*. used a hole conducting amorphous organic solid deposited by spin coating.[24] However, deposition in nanoporous materials cannot easily be achieved by traditional methods such as evaporation or spin coating. Electrochemical deposition of organic semiconductors on high surface area electrodes for solar cells has also been described.[29] A thin layer of organic semiconductors can be electrochemically deposited on a nanoporous TiO_2 electrode. One of the first solid state dye sensitized heterojunctions between TiO_2 and a conducting polymer was reported by Murakoshi and coworkers.[30] The prototype of this kind of solid state DSSC is shown in Fig. 3.

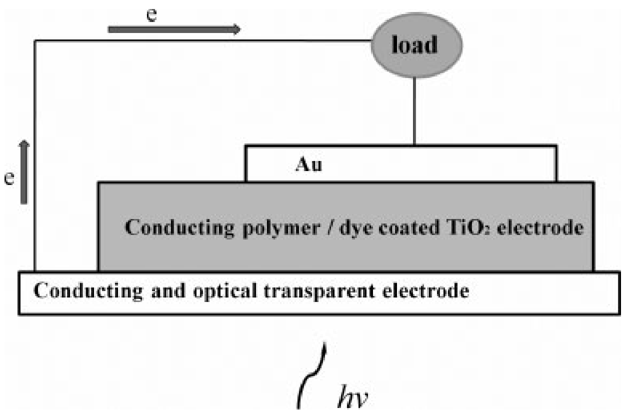

Figure 3. The prototype solid state DSSC.

A conducting polymer such as pyrrole was electrochemically polymerized on a porous nanocrystalline TiO_2 electrode, sensitized by N_3 dye. Polypyrrole successfully worked as a hole transport layer connecting dye molecules anchored on TiO_2 to the counter electrode. Conducting polyaniline has also been used in solid state solar cells sensitized with methylene blue.[31] This solid state DSSC was fabricated using conducting polyaniline coated electrodes sandwiched with a solid polymer electrolyte, poly(vinyl alcohol) with phosphoric acid. The phosphoric acid is to protonate the polyaniline to retain its conducting form. It exhibits good photoresponse to visible light. The presence of illumination enhances the electrochemical reaction (doping of polyaniline by migration of anions). The observed I–V characteristics are the superposition of the ohmic charge transport and the electrochemical reaction. Recently, a low bandgap polymer consisting of alternating thiophene and benzothiadiazole derivatives was used in a bulk heterojunction DSSC. This solid state DSSC using conducting polymer exhibited a power conversion efficiency of 3.1%.[32] To date, the highest power conversion efficiency obtained with organic hole-transport materials in DSSC is over 5%, reported by Snaith *et al*.[33]

Construction of quasi-solid-state DSSC has also been explored. Quasi-solid-state DSSCs can be made based on polymer grafted nanoparticle composite electrolyte,[34] cyanoacrylate electrolyte matrix,[35] and a novel efficient absorbent for liquid electrolyte consisting of a poly(acrylic acid)-poly(ethylene glycol) hybrid.[36] The polymer gels in the above cases function as ionic conductors. Room temperature ionic liquids are also known as good ionic conductors.[37,38] DSSCs using imidazolium type ionic liquid crystal systems as effective electrolytes have been reported.[39] Solid state DSSCs based on ionic liquids were reported to enhance the conversion efficiency of DSSCs.[40] Ionic liquid oligomers, prepared by incorporating an imidazole ionic liquid with polyethylene oxide oligomers have also been tried as an electrolyte for DSSC.[41] It has been shown that increase of the polyethylene oxide molecular weight in ionic liquid oligomers results in faster dye regeneration and lower charge transfer resistance of I_3^- reduction leading to improved DSSC performance. However, the main limiting factors in DSSCs based on ionic liquids compared with conventional wet-type DSSCs are higher recombination and lower injection of charge. At low temperatures, higher diffusion resistance in the ionic liquid may also be a main limiting factor through its effect on the fill factor.[42] The non-volatile character of ionic liquids also offers easy packaging for printable DSSCs. Plastic and solid state DSSCs incorporating single walled carbon nanotubes (SWNTs) and imidazorium iodide derivative have also been fabricated.[43] The introduction of carbon nanotubes will improve the solar cell performance through reduction of the series resistance. TiO_2

coated carbon nanotubes (CNTs) were recently used in DSSCs. Compared with a conventional TiO$_2$ cell, the TiO$_2$-CNT (0.1 wt%) cell gives an increase to short circuit current density (J_{SC}), which results in ∼50% increase in conversion efficiency from 3.32 to 4.97%.[44] It is supposed that the enhancement of J_{SC} is due to improvement in interconnectivity between the TiO$_2$ particles and the TiO$_2$-CNTs in the porous TiO$_2$ film. Anchoring dye-SWCNs to the TiO$_2$/electrolyte interface resulted in an increase of Voc by as much as 0.1 V.[45] This increase can be attributed to the negative shift of the conduction band edge resulting from the basicity of the TiO$_2$ surface caused by the NH groups of ethylenediamine moieties of dye-SWCNs. When employing SWNTs as conducting scaffolds in a TiO$_2$ based DSSC, the photoconversion efficiency can be boosted by a factor of 2.[46] In the absence of an SWNT network, a maximum internal photon-current efficiency (IPCE) of 7.36% (350 nm) at 0 V (vs. SCE) was observed. The IPCE was enhanced significantly to 16% when the SWNT scaffolds support the TiO$_2$ particles. TiO$_2$ nanoparticles were dispersed on SWNT films to improve photoinduced charge separation and transport of carriers to the collecting electrode surface.

Another type of carbon nanomaterial, graphene, was also recently introduced to the study of DSSCs. Transparent, conductive, and ultrathin graphene films, as an alternative to the ubiquitously employed metal oxides window electrodes are used for solid-state DSSCs.[47] These graphene films are fabricated from exfoliated graphite oxide, followed by thermal reduction. The films obtained exhibit a high conductivity of 550 S cm^{-1} and a transparency of more than 70% over 1000–3000 nm. Furthermore, they show high chemical and thermal stabilities as well as an ultrasmooth surface with tunable wetability. A strong increase in energy conversion efficiency could also be observed when t-butylpyridine was introduced into the matrix of the organic hole conductor[48] with similar effects for classic DSSC with electrolyte/TiO$_2$ junctions.[21] The increase in V_{oc} may be due to either a charging of surface states or a shift of the conduction band edge.[49] Lithium ion interactions into TiO$_2$-B nanowires,[50] nanocrystalline rutile TiO$_2$ particles[51] and a class of perovskite based lithium ion conductors[52] have been reported. Photovoltages of nanoporous TiO$_2$ based DSSCs were improved by up 200 mV with negligible decrease in photocurrent by treating TiO$_2$ electrodes with an intercalation of Li$^+$.[53] The enhancement of photovoltage is explained in terms of the formation of a dipole layer due to adsorption of Li$^+$ on the TiO$_2$ surface generated by the reaction of intercalated Li atoms with moisture in the air. Addition of lithium salt $Li[(CF_3SO_2)_2N]$ to the spin coating solution of the hole conductor also resulted in a strong performance increase in the final device. The underlying mechanism remained unidentified although charge screening due to partial ionic mobility inside the hole conductor matrix and/or the effect of the present lithium ions on the flat band potential of TiO$_2$ were postulated as possible mechanisms.[54]

Other n-type semiconducting electrodes besides TiO$_2$ have been probed for DSSCs. The best studied of the alternative materials is ZnO.[55–57] ZnO has similar band gap (3.2 eV) and band edge position to TiO$_2$[13] with similar or smaller crystallite sizes than typical TiO$_2$. The fabrication of DSSC with a branched structure of ZnO nanowires was recently reported.[58] ZnO nanoparticles and nanowires have been used, enabling lower temperature fabricated DSSC electrodes.[59,60] Unlike TiO$_2$, ZnO does not need a high-temperature annealing process and extends the electrodes to flexible polymer substrates. The striking optical properties of nanoporous silicon obtained by photoanodic etching[61] extended the scope of materials research in photoelectrochemistry to other porous crystalline semiconductors.[62] At present, there is considerable effort being devoted to DSSC with nanoporous photoanodes.[15,63] Nanoporous semiconductor electrodes have been further investigated within the scope of quantum dots. Photoelectrochemical activity has been shown when quantum dots such as CdS and PbS are attached to a metal electrode in a sub-monolayer array.[64–68] An ordered or disordered monolayer/sub-monolayer of nanometer sized semiconductor particles (e.g. PbS quantum dots) can be attached to a conducting substrate either directly or via a self-assembled organic monolayer.[69,70] Photoelectrochemical study of organic–inorganic hybrid thin films via electrostatic layer by layer assembly has been reported.[71] This provides a new way to produce nanoporous semiconductor electrodes for DSSCs.

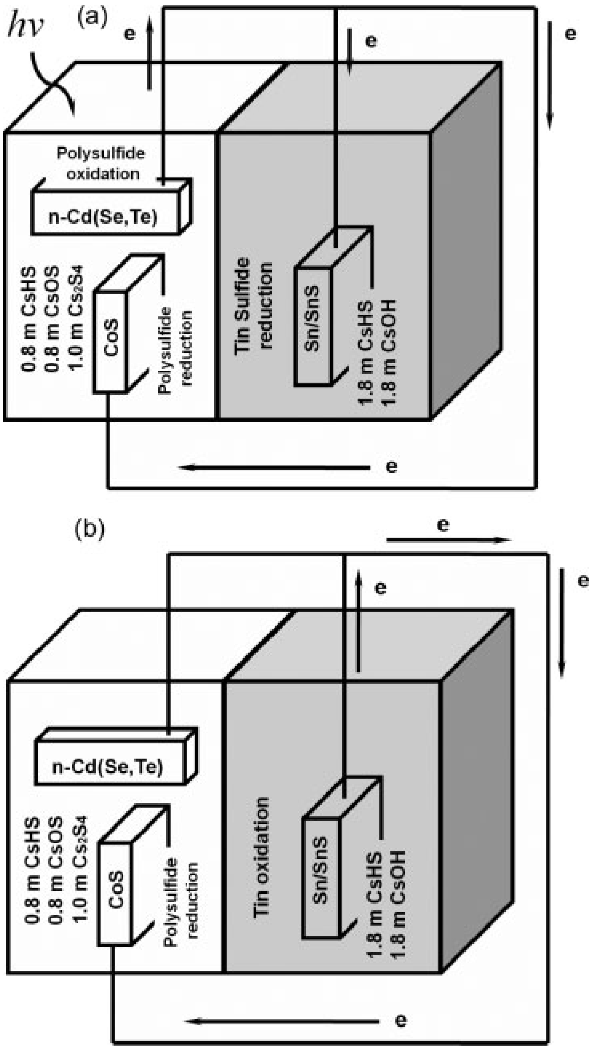

Figure 4. Schematic of a photoelectrochemical solar cell combining both solar conversion and storage capabilities: (a) under illumination; (b) in the dark.

Storage of electrochemical energy by electrochemical photovoltaic cells

It is also possible to make a rechargeable battery with *in situ* storage capability by using electrochemical photovoltaic cells.[72–74]

Figure 4 presents the configuration of a photoelectrochemical cell combining *in situ* electrochemical storage and solar conversion capabilities that provides continuous output insensitive to daily variations in illumination.[72] A high solar to electric conversion efficiency cell configuration of this type was demonstrated in 1987 and used a Cd (Se, Te)/S_x conversion half cell and a Sn/SnS storage system, resulting in a solar cell with a continuous output.[72] Under illumination, as shown in Fig. 4(a), the photocurrent drives an external load. Simultaneously, a portion of the photocurrent is used in the direct electrochemical reduction of metal cations ($Sn^{2+} \rightarrow Sn$) in the device storage half-cell. In the dark or below a certain level of light, the storage compartment spontaneously delivers power by metal oxidation ($Sn \rightarrow Sn^{2+}$) as seen in Fig. 4(b). This idea was further developed and the DSSC performance was improved significantly by using multi-band gap cells with storage.[73]

Because of the low fraction of short wavelength solar spectrum, wide band gap solar cells generate a high photovoltage but have low photocurrent. Smaller bandgap cells can use a large fraction of the incident photons, but generate lower photovoltage. Multiple band gap devices can overcome these limitations. In stacked multijunction systems, the topmost cell absorbs (and converts) energetic photons, but it is transparent to lower energy photons. Subsequent layers absorb lower energy photons. Thus conversion efficiency can be enhanced. High solar conversion and storage efficiencies have been attained with a system that combines efficient multiple bandgap semiconductors, with a simultaneous high capacity electrochemical storage.[73,75] It provides a nearly constant energy output in illuminated or dark conditions. The cell generates a light variation insensitive potential of 1.2–1.3 V with total solar-electric energy conversion efficiency over 18%.[73]

CONCLUSIONS

Effective electrochemical photovoltaic cells can be realized by different electrochemical methods. Solid state and printable DSSCs have a promising future for the development of efficient and flexible optoelectronics. Even though DSSCs have lower light-to-electricity conversion efficiency than the best thin film Si solar cells, they are considerably cheaper to make and can be printed on flexible substrates. Amorphous Si thin-film cells degrade in sunlight over time, and their efficiencies also go down if the sunlight hits them at some special incident angle. DSSCs are longer lasting and work at wide angles of incidence. In addition, DSSCs work more efficiently in indoor light, because the dye absorbs diffuse sunlight as well as fluorescent lighting. With improvements in non-volatile electrolytes, organic dyes and nanoporous semiconducting electrodes, cheaper but more robust DSSCs will definitely take their share in the solar cell market competing with the traditional thin film solar technologies. In addition, energy storage is a crucial topic nowadays with different energy harvesting technology developments and application of electric vehicles as well as smart grids. Storage of electrochemical energy by electrochemical photovoltaic cells provides a unique and practical solution to make energy harvesting and storage from solar feasible.

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