Application aspects of polymer electrolytes in solar cells

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Dye-sensitized solar cells (DSSCs) have aroused intense interest owing to their easy fabrication, low cost, simple preparation procedures and high energy conversion efficiency. Considering the fact that leakage and volatilization of liquid electrolytes hinder their practical applications in the case of DSSCs, polymer electrolytes with high ionic conductivity, excellent thermal and long-term stability are being used as alternatives to liquid electrolytes. This review focuses mainly on recent progress witnessed in the field of quasi-solid-state electrolytes suitable for DSSCs. The dependence of photovoltaic performance on the polymer content within the electrolyte employed in DSSCs, their working principles as well as latest developments are also discussed.

Keywords: Energy conversion, Solar cells, Polymer electrolytes, Dyes

1 Introduction

The direct conversion of sunlight into electric power by solar cells is of particular interest because it has many advantages over most presently used electrical power generation methods. Since the prototype of a dye-sensitized solar cell (DSSC) was reported in 1991 by Gratzel, it has aroused intense interest owing to its low cost, simple preparation procedure, and benign effect on the environment compared with traditional photovoltaic devices. In “Gratzel cells”, the functions of light absorption and charge-carrier transportation are separated, which is different from photo-regenerative and synthetic cells. The dye-sensitized solar cell (DSSC) appears to have significant potential as a low-cost alternative to conventional p-n junction solar cells. Such systems can reach solar to electric conversion efficiencies of about 10% but are still not produced on a large scale mainly because of technical problems such as sealing. However, the use of liquid electrolytes poses several practical problems including leakage of the electrolyte, desorption of the sensitizing dye by the organic solvent used in the electrolyte, and toxicity of some of the organic solvents. Thus, many efforts have been made to overcome this drawback, replacing the liquid electrolytes with room temperature ionic liquids organic and inorganic hole-transport materials, or gel electrolytes. Another alternative approach to retain the good device properties of the liquid electrolytes while maintaining solid-like mechanical properties is the use of quasi-solid polymer gel electrolytes. The analysis of general principles is scientifically interesting and useful for understanding new kinds of solar cells, even though empirical optimization played a major role in the development of most of today’s best cells.

2 Generation of Solar Cells

Solar cells developed so far may be classified into four generations as follows:

2.1 First Generation Solar Cells

First generation photovoltaic cells are the dominant technology in the commercial production of solar cells, accounting for more than 86% of the solar cell market. These cells are typically made using a crystalline silicon wafer and it consists of a large-area, single layer p-n junction diode. It includes ingots which may be either monocrystalline or multi-crystalline. Most common approach is to process discrete cells on wafers sawed from silicon ingots. More recent approach which saves energy is to process discrete cells on silicon wafers cut from multi-crystalline ribbons. It has a band gap of ~1.11 eV.

2.2 Second Generation Solar Cells

Second generation is based on the use of thin-film deposits of semiconductors and use of thin-films reduces mass of material required for cell design whereas it contributes greatly to reduced costs for thin film solar cells. Devices initially designed are found to be highly-efficient, multiple junction photovoltaic cells. Second generation solar cells include four different types such as amorphous silicon cells,
polycrystalline silicon cells, cadmium telluride cells and copper indium gallium diselenide alloy cells.

2.3 Third Generation Solar Cells
These cells are quite different from those earlier versions of semiconductor devices and do not rely on a traditional p-n junction to separate photo-generated charge carriers. Common devices include: Nanocrystal solar cells, Photoelectrochemical cells, Polymer solar cells and Dye-sensitized solar cells.

Dye-sensitized solar cells (DSSCs) differ from conventional semiconductor devices in that they separate the function of light absorption from charge carrier transport. Dye sensitizer absorbs the incident sunlight and exploits the light energy to induce vectorial electron transfer reaction. Thus DSSCs have the following advantages as compared to those silicon-based photovoltaics: (i) It is not sensitive to the defects in semiconductors such as defects in Si. (ii) It is easy to form and cost effective for production. (iii) It is possible to realize the direct energy transfer from photons to chemical energy. Solar cell based on a dye sensitized porous nanocrystalline TiO$_2$ photoanode with attractive performance was first reported by Grätzel et al. Interest in nanoporous semiconductor matrices permeated by an electrolyte solution containing dye and redox couples has been stimulated by their reports. The power conversion efficiency of the DSSC has been currently improved to 11.5% (Ref. 12) since the first DSSC was reported with efficiency of 7.1% (Ref. 1), comparable with the amorphous Si cells$^{13}$. Large-size DSSC has been prepared on silver grid embedded fluorine-doped tin oxide (FTO) glass substrate by screen printing method$^{14}$. Under the standard test condition, energy conversion efficiency of active area was achieved to 5.52% in 5 cm x 5 cm device, which is comparable to 6.16% of small-size cell prepared at similar condition. G24 Innovation Ltd., based on the technology invented by Grätzel, uses a low-cost, roll-to-roll process to make its flexible DSSC modules, which produce 0.5 W of power under direct sunlight. Miyasaka et al$^{15}$ developed a 2.1 m x 0.8 m DSSC module by connecting eight pieces of 10 cm$^2$ panels with six embedded cells.

2.4 Fourth Generation Solar Cells
Fourth generation contains hybrid-nanocrystal/polymer cell. It is a composite photovoltaic technology combining elements of the solid state and organic PV cells and the use of polymers with nanoparticles mixed together to make a single multi-spectrum layer. Significant advances in hybrid solar cells have followed the development of elongated nanocrystal rods and branched nanocrystals involving more effective charge transport. The incorporation of larger nanostructures into polymers required optimization of blend morphology using solvent mixtures$^{16}$. This review deals with the importance of polymer electrolytes in dye-sensitized solar cells (DSSCs).

3 Polymer-based Solar Cells
A polymer solar cell is designed by applying semiconducting conjugated polymers as active components in the photocurrent generation and power conversion processes within thin film photovoltaic devices that convert solar light into electrical energy. In the year 2000, Heeger, MacDiarmid, and Shirakawa received the Nobel Prize for Chemistry for the “discovery and development of conducting polymers”, representing a new class of materials. Polymer solar cells are a type of flexible solar cell. They can come in many forms including: organic solar cell (also called plastic solar cell), or organic chemistry photovoltaic-cell that produce electricity from sunlight using polymers. There are also other types of more stable thin-film semiconductors that could be deposited on different types of polymers in order to create solar cells. This technology is relatively new, being actively researched by universities, national laboratories and several companies around the world. Currently, commercial solar cells are made from a refined, highly purified silicon crystal, similar to the material used in the manufacture of integrated circuits and computer chips (wafer silicon). The high cost of these silicon solar cells and their complex production process have generated interest in developing alternative photovoltaic technologies. Compared to silicon-based devices, polymer solar cells are lightweight (which is important for small autonomous sensors), potentially disposable and inexpensive to fabricate (sometimes using printed electronics), flexible, and customizable on the molecular level, and they have lower potential for negative environmental impact. There are four different types of polymer solar cells. They are: (i) polymer-fullerene, (ii) polymer–polymer, (iii) polymer–nanoparticle hybrids and (iv) polymer-carbon nanotube.

3.1 Polymer–fullerene solar cells
Since the discovery of photo-induced charge transfer from a conjugated polymer (MEH-PPV) to a
Polymer–polymer solar cells employ two different materials in bilayer geometry resulted in short circuit photocurrents following linearly the incident light intensity, even at higher illumination densities. This linear dependence has been confirmed by Halls et al. using the same bilayer structure but employing PPV as the electron donor. Later Roman et al. demonstrated optical modeling to be a useful tool for the optimization of such bilayer solar cells, which in their case was based on a polythiophene derivative and C60. In a next step of development a side group was attached to the C60 to allow for solution processing due to increased solubility in common organic solvents. PCBM provides the best performances in polymer-fullerene solar cells, even to date. The first bulk hetero-junction polymer solar cells were based on MEH-PPV and PCBM, and presented by Yu et al. In these bulk hetero-junctions, an intimate blending of the donor and acceptor components results in very efficient exciton dissociation and thus charge carrier generation throughout the whole volume of the blend. MEHPPV: PCBM blends with a mixing ratio of 1:4 spin-coated from ortho-1,2-dichlorobenzene (ODCB) exhibited the best power conversion efficiencies.

3.2 Polymer–polymer solar cells

Polymer–polymer solar cells employ two different polymers as donor and acceptor components in the photoactive layer. These two polymers require a molecular energy level offset between their HOMO and LUMO levels to enable a photoinduced charge transfer. Due to the close vicinity of the respective molecular energy levels, polymer–polymer solar cells allow high open circuit voltages to be reached. The first realizations of polymer–polymer bulk heterojunction solar cells were independently reported in the mid-1990s by Yu and Heeger as well as by Halls et al. These solar cells were prepared from blends of two poly(para-phenylenevinylene) (PPV) derivatives: the well-known MEH-PPV (poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene]) was used as donor component, while cyano-PPV (CN-PPV) served as acceptor component (identical to MEH-PPV with an additional cyano (−CN) substitution at the vinylene group). These blends showed increased photocurrent and power conversion efficiency (20-100 times) when compared to the respective single component solar cells.

3.3 Organic–inorganic hybrid polymers solar cells

Greenham et al. studied the first hybrid systems containing CdS or CdSe nanoparticles embedded in MEH-PPV. As an aggregation-preventing ligand for the nanoparticles, the surfactant triptycophosphine oxide (TOPO) was used. This surfactant, however, rather hinders charge transport between the nanoparticles and charge transfer from the conjugated polymer onto them. Further, an extension to the polymer absorption band could be achieved due to the added absorption of the nanocrystals. To reach relatively high photovoltaic performances, the system required a high load (> 80%) of nanocrystals to be incorporated, similar to the MEH-PPV: PCBM system. A major step in the development of hybrid polymer solar cells was achieved by blending CdSe nanoparticles with regioregular P3HT. In 2002, Huynh et al. reported AM 1.5 power conversion efficiencies of 1.7% and EQEs reaching 54% with that system. Many other systems based on different nanoparticles have been introduced, such as copper indium disulphide (CuInS2), copper indium diselenide (CuInSe2), cadmium telluride (CdTe), lead sulphide (PbS), lead selenide (PdSe) and mercury telluride (HgTe). Some of these systems show enhanced spectral response well into the infrared part of the solar spectrum. In most of the cases the absorption of the nanocrystals was, however, quantitatively small as compared to the conjugated polymers. One extensively studied material system among the nanocrystal–polymer blends is zinc oxide (ZnO) in combination with MDMO-PPV or P3HT. Beek et al. presented the first polymer solar cells containing ZnO nanoparticles, reaching power conversion efficiencies of 1.6%. In this case, the nanoparticles were prepared separately and then intermixed with MDMO-PPV in solution. Shortly after this study the Janssen group presented another route to ZnO-polymer hybrid solar cells by forming the nanocrystals in-situ inside the.In by applying a precursor. Closely related to liquid electrolyte dye-sensitized solar cells (DSSCs, also known as “Gratzel cells”), the class of solid-state DSSCs have been developed to improve device stability and reduce complications in the production process. Thus, although polymers could be utilized as replacements for sensitizing dyes (as in liquid electrolyte DSSCs), the main effort in applying conjugated polymers focuses on solid-state DSSCs. With environmentally-friendly production of this polymer based solid-state DSSC in mind, a device based on water-soluble polythiophene derivative has been presented as well.
3.4 Carbon nanotubes in polymer solar cells
Since their discovery in 1991, carbon nanotubes (CNTs) have been a constant source of scientific inspiration. Among the most intriguing properties of CNTs is the electric field enhanced electron emission from the nanotubes. Initial studies combining CNTs and conjugated polymers concentrated on the diode properties in a CNT–polymer heterojunction. Romero et al. demonstrated light-sensitive photodetectors in combination with a PPV derivative. It has been showed that hole injection from the CNT electrode proved to be much more efficient than using an ITO electrode, and related this phenomenon to the enhancement of the local electric field at the tip of the nanotubes. Curran et al. demonstrated the use of multi-walled carbon nanotubes (MWNTs) to increase the conductivity within PPV films. Blending about 15% (by mass) CNTs into the PPV films yielded improvements of five orders of magnitude and was accompanied by a reduction in photoluminescence efficiency. The application of MWNTs in the field of polymer solar cells was presented by Ago et al.

4 Fabrication of Polymer-based Solar Cells
4.1 Properties of TiO$_2$ Nanoparticles
The crystal structure of the most common form of TiO$_2$ is tetragonal. Initially, mesoporous films as shown in Fig. 1, of fractal dye derivatized TiO$_2$, with a surface roughness factor of 150 were used as the appropriate semiconducting material in contact with the polymer dye. As seen in the micrograph, there is more surface area as compared to a flat surface. Adsorption of the mono layer dye sensitizer on a flat surface will result in a limited amount of coverage. By increasing the contact area between the semiconductor and the dye, the amount of light harvesting is increased. The increased injection of electrons from the dye into the semiconductor film improved the efficiency but more was needed. In order to further improve the efficiency of light harvesting, nanoparticles of TiO$_2$ were utilized. Nanoscale properties could be exploited to increase the amount of electrons captured. One very important property of nanomaterials is the morphology. The size and shape of the nanocrystallites, as well as the surface topography remain as the key to increasing the efficiency of capturing electrons.

4.2 Device Fabrication
DSSCs are typically fabricated on transparent conducting oxide (TCO) glass substrates, enabling light irradiance through this substrate under photovoltaic operation. The conductive coating typically used is fluorine-doped SnO$_2$ (FTO), preferred over its indium-doped analogue (ITO) for reasons of lower cost and enhanced stability. Prior to deposition of the mesoporous TiO$_2$ film, a dense TiO$_2$ film may be deposited to act as a hole blocking layer, preventing recombination (shunt resistance) losses between electrons in the FTO and oxidised redox couple. The TiO$_2$ nanoparticles are typically fabricated by the aqueous hydrolysis of titanium alkoxide precursors, followed by autoclaving at temperatures up to 240°C to achieve the desired nanoparticle dimensions and crystallinity (anatase). The nanoparticles are deposited as a colloidal suspension by screen printing or by spreading with a doctor blade, followed by sintering at ~450°C to ensure good interparticle connectivity. After sintering, the above TiO$_2$ electrodes were immersed in a solution of an amphiphilic dye [Cis-di(thiocyanato)-N,N-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium (II)] dihydrate (N3 dye) in absolute ethanol for 24 h at 298 K and washed again with absolute ethanol and dried in a moisture-free atmosphere. All such polymer electrolyte solutions were directly cast onto such dye-adsorbed TiO$_2$ electrodes. Finally, those FTO photoelectrodes and Pt counter electrodes thus obtained were assembled in the form of a solid state cell having the subsequent configuration TiO$_2$/N3 dye/polymer electrolyte/Pt.

Fig. 1 — SEM picture of dye coated TiO$_2$ on FTO conducting plate
4.3 Device Characterization
The experimentally observed photocurrent-photovoltage (I-V) plots for the above DSSCs were monitored and recorded using a BAS 100A Electrochemical analyzer where these solar cells were irradiated by a tungsten halogen lamp (OSRAM Germany) which provided AM 1.5 illumination at an effective light intensity of 40 mW/cm². Fill factor (FF) and solar cell efficiency (η) may be calculated from Eqs (1 and 2) as follows:

\[ FF = \frac{(J\eta V)_{MAX}}{J_{SC} \times V_{OC}} \]  
\[ \eta = \frac{(J_{SC} \times V_{OC} \times FF) \div P_s}{P_s} \]

where \( J_{SC} \) is the short circuit current density, \( V_{OC} \) the open circuit voltage, \( FF \) the fill factor and \( P_s \) is the incident light intensity.

5 Conclusions
In conclusion, the field of polymer solar cells requires a high degree of inter-disciplinary approach involving macromolecular chemistry, supramolecular chemistry, physical chemistry, colloid chemistry, photophysics, photochemistry, device physics, nanostructural analysis and thin film technology. For the liquid cells employing the \( I^+ / I^- \) redox couple, a catalyst is required to reduce the concentration of \( I^- \) ion at the electrode and the best candidate is found to be platinum (expensive) but only a few nm are required even though high surface area graphite also works quite satisfactorily. For polymer cells or solid state cells, only an ohmic contact is required, be it either gold, graphite or any other conducting medium with the correct work function. Thus, polymer-based cells are expected to be much cheaper than other types of solar cells.

References