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### Keywords

Photoelectrochemical, Cells, Based, Inherently, Conducting, Polymers

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# Photoelectrochemical Cells Based on Inherently Conducting Polymers

G.G. Wallace, C.O. Too, D.L. Officer, and P.C. Dastoor

## Abstract

This review of photoelectrochemical cells (PECs) based on inherently conducting polymers (ICPs) deals with the mechanisms of operation and the various factors that influence the overall efficiency of PECs. The factors addressed include ICP composition and oxidation state, the use of nanostructured surfaces and interfaces, and the PEC electrolyte and redox mediator.

**Keywords:** *inherently conducting polymers, ionic liquids, photoelectrochemical cell, photovoltaics, polyanilines, polypyrroles, polythiophenes.*

## Introduction

Studies into the use of light-driven redox reactions can be traced back to the work of Becquerel in 1839,<sup>1</sup> wherein the illumination of solutions containing a metal halide salt produced a current between two platinum electrodes. Later work by Vogel on the dye sensitization of the halide semiconductor<sup>2</sup> not only led to the development of photographic film sensitization, but also to the sensitization of photoelectrodes. The development and utilization of this latter phenomenon with high-surface-area *n*-type semiconductor substrates has led to highly efficient photoelectrochemical cells. This has recently been reviewed by Grätzel.<sup>3</sup>

The specific photoelectrochemical cell (PEC) now bearing Grätzel's name utilizes dye-sensitized nanostructured TiO<sub>2</sub> on an electrode such as glass coated with SnO<sub>2</sub>:F as the anode, a redox couple in the form of a liquid electrolyte, and a platinized cathode (Figure 1; also see the article by Grätzel in this issue). Upon irradiation, the excited state dye (D\*), which passes an electron to the TiO<sub>2</sub>, is quenched by the reduced form of the redox mediator (El<sub>red</sub>) at the electrode-electrolyte interface. The amazing efficiencies attainable with the Grätzel cell (up to

10.6%) can be attributed to a number of factors. First, the dye attached to the TiO<sub>2</sub>, typically a ruthenium polypyridyl complex, provides photon collection spanning a wide range of the solar spectrum. Second, the nanoparticulate mesoporous TiO<sub>2</sub> film (5–20 μm thickness) provides a surface area for dye chemisorption over a thousand times that of an equivalent flat electrode, affording an incident photon-to-current conversion efficiency (IPCE) of more than 80%, a 600-fold improvement in photoelectrochemical efficiency compared with a single-crystal electrode. The mesoporous nature of the nanostructured anode also provides efficient transfer of holes to the redox mediator in the electrolyte, since the electrolyte can penetrate all the way to the back of the film. Third, the platinized cathode is a selective catalyst for the reduction of redox mediators such as iodine/triiodide in organic electrolytes.

The key to the high photoelectrochemical efficiency of mesoporous oxide films lies in the interconnectedness of the nanoparticles created through high-temperature (500°C) sintering of the nanoparticulate oxide, allowing electronic conduction to take place.

This, however, requires the films to be prepared on glass substrates or metal foils that can withstand the sintering temperature. The use of organic semiconductors would allow the development of PECs on plastic substrates and thus their use in a much wider variety of applications.

Inherently conducting polymers (ICPs) combine the electronic and optical properties of semiconductors with the mechanical and physical properties of polymers. A wide variety of ICP morphologies can be created, from nanoparticles and nanofibers to nanostructured films. As such, their potential use in solar cells is tantalizing. As with all photoelectrochemical cells, the overall efficiency of an ICP-based PEC depends on:

- the ability to absorb light and generate excitons,
- transport of these excitons to an interface (within 10 nm) before decay to the ground state occurs,
- charge transfer to the redox mediator,
- transport of the redox mediator to the counter electrode, and
- charge transfer to the counter electrode.

Next, we discuss the structure and properties of ICPs and the progress that has been made to date to improve PEC efficiency.

## Inherently Conducting Polymers

Inherently conducting polymers (ICPs) are polymers with a framework of alternating single and double carbon-carbon (sometimes carbon-nitrogen) bonds. Delocalization of the double bonds over the entire polymer molecule produces a valence and conduction bandgap for most semiconducting polymers that lies in the range of 1.5–3 eV. In addition, this leads to broadband visible light absorption, making ICPs particularly well suited for photo-

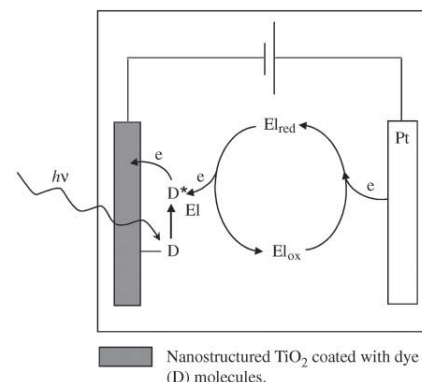
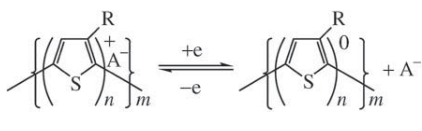


Figure 1. Schematic representation of a Grätzel photoelectrochemical cell. *D* is a dye molecule, *D\** is an excited-state dye molecule, and *El* is liquid electrolyte.

electrodes in PECs. In contrast to the semiconductor oxides, however, ICP semiconductors are generally *p*-type materials, favoring hole transport in their neutral or reduced state. Thus, an ICP-based PEC works in the reverse direction to that shown in Figure 1, with the light-excited semiconductor passing electrons to the redox electrolyte.

Although any of the wide variety of ICPs could be used in PECs, polythiophenes have proved to be the systems of choice for a number of reasons: They are easily synthesized either chemically or electrochemically, amenable to the formation of regioregular polymers, amenable to attachment of a range of functional groups using facile synthesis routes, stable in their reduced form, and environmentally robust.

Polythiophenes undergo a reversible oxidation/reduction process at moderate potentials, as illustrated by the cyclic voltammogram (current–voltage curve) shown in Figure 2. The redox processes can be described as shown in Reaction 1.



Reaction 1.

If the dopant anion ( $\text{A}^-$ ) is mobile, then it leaves the polymer upon reduction of the polymer. However, if the dopant anion is of moderate molecular weight with some hydrophobic component present, it tends to be trapped in the polymer, with charge compensation achieved via incorporation of cations when the polymer is reduced. Reduction of the polymer leads to a dramatic change in the UV–visible absorption spectra (Figure 3).

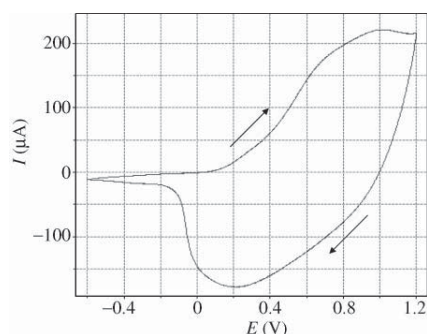


Figure 2. Post-polymerization cyclic voltammogram of polyterthiophene-modified platinum electrode in 0.1 M tetrabutylammonium perchlorate/ $\text{CH}_2\text{Cl}_2$ . Scan rate:  $100 \text{ mV s}^{-1}$ .

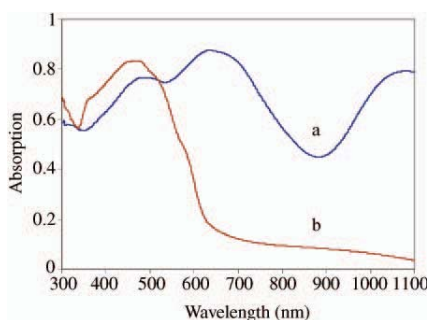


Figure 3. UV–vis absorption spectra of polyterthiophene on ITO-coated glass. (Curve a) Polymer in oxidized form; (Curve b) polymer after electrochemical reduction at  $-0.8 \text{ V}$  (versus  $\text{Ag}/\text{Ag}^+$ ).

However, the redox reaction (Reaction 1) belies the complexity of the electrochemistry and photoelectrochemistry of these heterogeneous systems. While in the oxidized state, the electronic conductivity of the polymer is highest, but the ability to generate and transport excitons is greatly hindered. Optimized photoelectrochemical efficiency is obtained when excitons can be generated (high resistance) and transported—but efficient electron transfer to an electrolyte depends on maintaining a low electrical resistance. It has been shown<sup>4</sup> that optimal PEC performance is obtained when the polymer is (predominantly) reduced.

**Light, Excitons, and Current Flow**

The charge generation and conduction mechanisms in conducting polymers are different from conventional inorganic semiconductors. Although the action of an incident photon upon a conducting polymer excites an electron from the valence band into the conduction band, the electron and hole produced are bound, and their motion through the material is coupled. These coupled moieties are known as excitons and are responsible for many of the electronic properties found in the most common and efficient polymer-based electronic devices. Excitons can diffuse through the material across short distances (usually a few tens of nanometers). The exciton can then dissociate or recombine through three main competing processes:

1. The electron and hole can recombine to produce a photon. This radiative recombination process is known as photoluminescence (PL) and has a distinctive lifetime for a specific material.
2. The electron and hole can recombine non-radiatively, with the excess energy being dissipated in the material in the form of lattice vibrations (phonons). This process

is typically governed by the impurities that are present in the device.

3. The electron and hole can dissociate to produce a free electron and hole. Charge dissociation typically occurs at interfaces.

The most obvious interfaces are those created at the junction between the electrode and the conducting polymer or, alternatively, the conducting polymer and the electrolyte. If excitons dissociate at the polymer–electrode interface, holes are collected at the high-work-function electrode (indium tin oxide, ITO), while electrons are transported to the polymer–electrolyte interface to reduce the redox couple in solution. Dissociation at the polymer–electrolyte interface requires the transport of holes back through the polymer to the ITO. As shown in Figure 4, for polymer electrochemical cells, the open-circuit voltage generated by these devices depends upon the standard potential (or work function) difference between the polymer–ITO interface and the polymer–electrolyte interface. The work function of the polymer–electrolyte interface will be governed by the chemical state of the interface layer. Chemical reactions between the electrolyte and polymer, and the presence of different dye molecules or even impurities can change the chemical potential of the interface and thus the open-circuit voltage produced by these polymer electrolytic devices.

Unfortunately, the lifetime of excitons is short, such that only excitons that are formed within about 10 nm of an interface will ever reach it. This short exciton range clearly limits the efficiency of these photovoltaic devices. Independent of where the dissociation occurs, holes are transported into the external circuit via the ITO electrode, and electrons are transferred to the redox mediator (note that this is the opposite of what happens in the Grätzel cell) in order to complete charge transport to the counter electrode.

All of these PEC devices contain a metal–semiconductor interface. In the case of the Grätzel cell, this interface occurs at the ITO– $\text{TiO}_2$  boundary, whereas in the case of the ICP devices of concern here,\* it occurs at the ITO–polymer interface. It is this interface that provides these polymer cells with their rectifying properties, and we have found that with devices constructed in our laboratory<sup>5</sup> (using liquid electrolytes), it is at this interface that the majority of the exciton dissociation occurs. However, in a number of other studies using photocurrent action spectra (and solid polymer elec-

\* Inherently conducting polymers have also been widely used in photoelectrochemical cells containing  $\text{TiO}_2$ . These examples are not covered in this review.

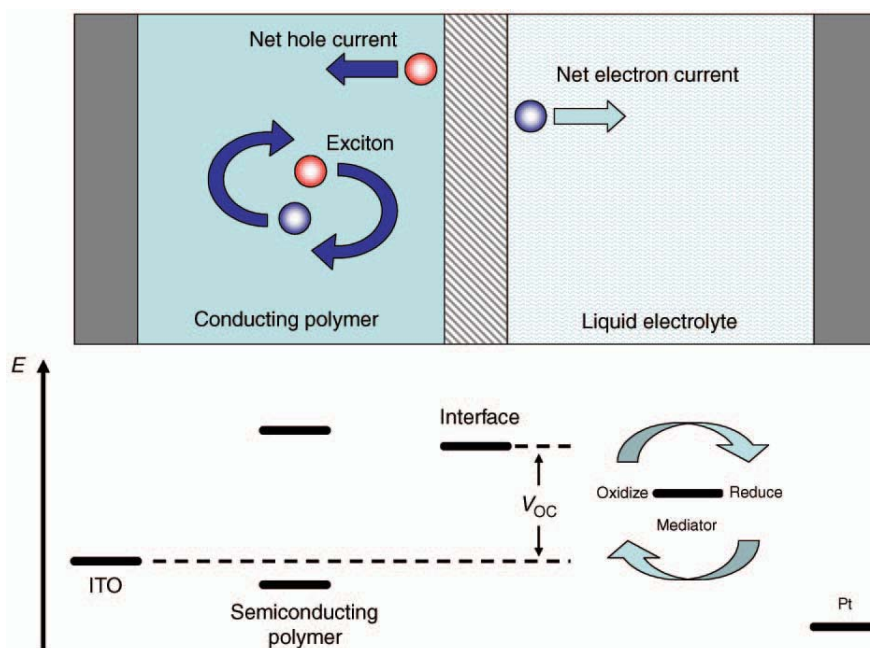


Figure 4. Schematic diagram of a typical polymer photoelectrochemical cell structure consisting of an ITO/polymer/electrolyte/Pt sandwich structure. The presence of an electrochemically different interface (between the conducting polymer and liquid electrolyte) has been explicitly included to illustrate the fact that the photovoltage is generated by the difference in standard electrode potential (work function) between the ITO–polymer interface and the polymer–electrolyte interface. However, the electrochemical potential of this interface may be equal to the redox potential of the mediator.

trolytes), Inganäs et al. have shown that exciton dissociation occurs at the ICP–electrolyte interface.<sup>6,7</sup> The critical nature of the PEC structure and polymer morphology is highlighted by these observed differences. Clearly, considerable further work is required to understand such effects.

### Substituents on Polythiophenes

The ability to induce high PL efficiency by attachment of bulky (anti-agglomeration) substituents to the polythiophene backbone has been clearly demonstrated.<sup>8</sup> Derivatization of polythiophene has also been used to redshift the polymer absorption maximum to improve photoinduced charge generation efficiency.<sup>9</sup> In other studies, poly(thiophene acetic acid)<sup>10</sup> and poly(3-hexylthiophene)<sup>11</sup> have been used as photoelectron donor materials. In our laboratories, we have shown that poly(terthiophene) performs better in PECs than poly(3-methylthiophene),<sup>12</sup> so we have produced a range of substituted terthiophenes (Chart 1)<sup>13</sup> in order to further improve the photovoltaic efficiency.

Monomer 1 was polymerized or copolymerized with terthiophene to form a homopolymer or copolymer. The nitrostyryl group increased the electron-withdrawing

ability of the polymer and so reduced its chemical potential, which resulted in a higher open-circuit voltage.<sup>14</sup> Polymerization of 2 or copolymerization of 2 with terthiophene was facile. The copolymer produced better photovoltaic performance than the homopolymer or polyterthiophene.<sup>15</sup> In order to enhance the light-harvesting capabilities of the polymer, we also investigated the photovoltaic performance of poly(terthiophene) with a porphyrin pendant group.<sup>12</sup> Copolymers of 3 with terthiophene were successfully grown and were photoactive but performed below expectations. Subsequently, another porphyrin

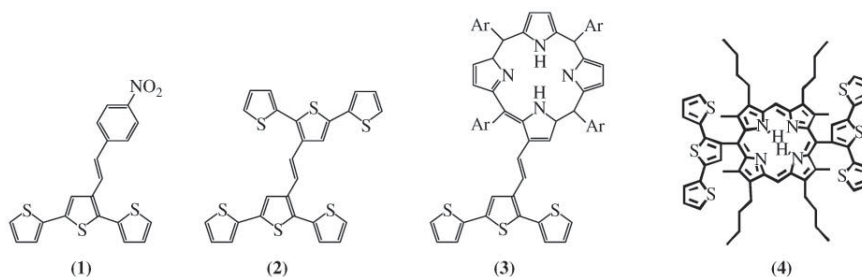


Chart 1. Substituted terthiophenes.

containing monomer 4 was considered.<sup>16</sup> A copolymer of 4 with terthiophene produced an energy conversion efficiency of 0.12% under white-light illumination after zinc incorporation. The addition of substituents undoubtedly has an effect at the molecular/macromolecular level. Substituents also influence electronic properties (e.g., work function, capacitance) and hence hole transfer (to ITO) characteristics, morphology and density of the polymer, and electron transfer characteristics (to/from redox mediator).

It is well known that the dopant anion ( $A^-$ ) incorporated into the ICP during synthesis has a dramatic effect on the electronic, chemical, and physical properties of the polymer.<sup>17</sup> However, only limited studies on the effect of the dopant on photovoltaic responses have been carried out.<sup>18</sup> De Paoli and co-workers<sup>19</sup> incorporated a dye molecule (indigo carmine) as the dopant, with a corresponding change in the photocurrent action spectra (photocurrent–wavelength curve), indicating that although the dye is present as a dopant, it still has an impact on exciton generation. These same researchers showed that the attachment of substituents to the polythiophene backbone alters the photocurrent action spectra by shifting the absorption characteristics.

### The Electrolyte + Redox Mediator

The overall efficiency of the Grätzel PEC is still limited by the rate of charge transfer from the photoactivated dye to the redox mediator in the electrolyte. Furthermore, the lack of environmental stability of the solvents traditionally used as the electrolyte host limits the lifetime of devices.

Similar challenges exist in ICP-based PECs.  $I^-/I_3^-$  is still the only extensively studied redox mediator couple. The  $Eu^{2+}/Eu^{3+}$  couple has been explored in combination with a polymer electrolyte, poly[oxymethylene-oligo(oxethylene)].<sup>6</sup> This couple did improve the open-circuit voltage ( $V_{oc}$ ) by 350 mV compared with the  $I^-/I_3^-$  couple; however, the low mobility of

the multivalent ions limits the short-circuit current ( $I_{sc}$ ) attainable. In another study, Yohannes and co-workers<sup>7</sup> showed that the ratio of concentration of the redox couple was also important. If the  $[I_3^-] / [I^-]$  ratio was increased from  $10^{-2}$  to 1, the poly(3-methylthiophene) layer eventually became doped (and conductive), with a concomitant loss in photoelectrochemical efficiency.

The fact that the open-circuit voltage appears to systematically depend upon the nature of the redox couple suggests that the work function of the polymer–electrode interface changes in the presence of different redox couples. However, further work is required to understand how the chemistry of the interface changes in various electrochemical environments.

In a novel study using two photoactive electrodes (one polythiophene-based, the other tetraphenyl porphyrin), hydroxymethyl ferrocene was used as the redox mediator.<sup>20</sup> Another important aspect of the redox mediator is that the reduced form should efficiently transfer electrons at the counter electrode. In the case of  $I_3^-$ , it has been found that electron transfer is efficient at platinumized ITO.<sup>21</sup> More recently Yohannes and Inganäs<sup>22</sup> have shown that PEDOT coated onto the counter electrode can also act as an efficient electron transfer mediator for  $I_3^-$ , eliminating the need for platinumization.

It has been shown that<sup>23</sup> ionic liquid electrolytes (sample structures shown in Chart 2) are highly effective electrolyte systems for inherently conducting polymers. The wide, stable electrochemical potential window available and their extremely low vapor pressure mean that stable electrochemical devices containing conducting polymers can be produced. In fact, the compatibility of selected ionic liquids (e.g., imidazolium-based ones) with some ICPs (e.g., polypyrrole) can even improve electro-mechanical properties. It has been previously shown that such ionic liquids also function well in Grätzel cells,<sup>24</sup> making use of the same inherently useful properties of ionic liquids.

## Conclusions and Future Developments

Chemical doping, for example, by covalent attachment of functional groups, can enhance the electron–hole conduction of ICP-based PECs, in which electrical current is produced by separating the excitons

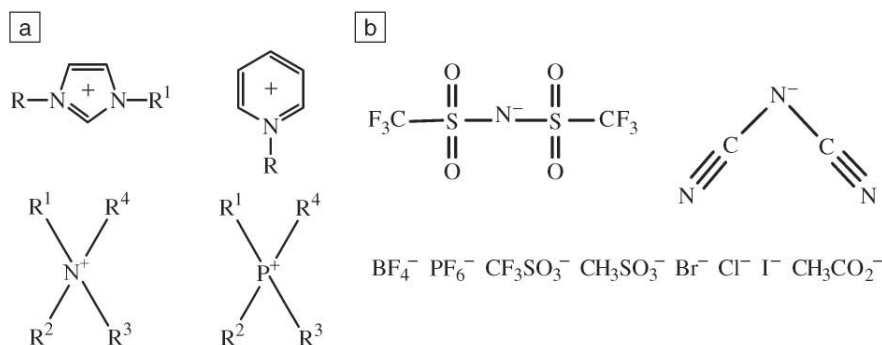


Chart 2. Examples of (a) cations and (b) anions in room-temperature ionic liquids.

(electron–hole pairs). Exciton splitting occurs at interfaces between materials having different ionization potentials and electron affinities. These interfaces can be created by coating layers of metals, inorganic oxides, and polymers. The nature of the redox couple can affect the open-circuit voltage, and the use of ionic liquids can enhance the stability of the PEC.

The efficiency of photoelectrochemical cells based on inherently conducting polymers has made progress in recent years. However, there is still room for vast improvements. To achieve this, each of the components of the cell—electrodes, polymer, electrolyte and interconnects—needs to be optimized.

## Acknowledgments

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