

# A photoassisted rechargeable cell with a polymer modified *p*-InP semiconductor anode and a polypyrrole cathode

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A novel system has been examined in which the charging cycle of a rechargeable cell was photoassisted. Rechargeable cells comprised of a *p*-type InP semiconductor anode coated with a polyanthraquinone redox polymer film and a polypyrrole-coated Pt cathode immersed in 0.1 M TEAP/CH<sub>3</sub>CN were photoelectrochemically charged and then discharged in the dark. These systems showed no degradation of electroactivity after 25 cycles. The charge storage capacity and the effectiveness of the photoassistance is limited by incomplete electroactivity of the redox polymer film and the small photovoltages generated by the *p*-InP/polyanthraquinone electrode. The role of Fermi level pinning in limiting the performance is assessed.

## 1. Introduction

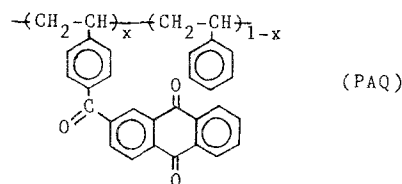
The electrochemistry and application of electroactive polymer films has received considerable attention over the past decade [1-6]. Electroactive polymer films have been employed with varying degrees of success in stabilizing narrow band gap semiconductors against photocorrosion in photoelectrochemical solar energy conversion system [7-13]. The polymer films function by facilitating the transfer of photogenerated charge from the semiconductor electrode to species in solution.

Films of electroactive polymers are of particular interest for use in rechargeable batteries [14]. Following the discovery that films of polyacetylene, (CH)<sub>x</sub>, on electrode substrates can be electrochemically cycled between the charged, conductive state and the neutral, insulating state, and that these materials have potential use as electricity storage media [15-20], a number of other organic conducting polymers have been synthesized and examined as rechargeable storage media [21-29].

Polyacetylene has a storage capacity (on a mass basis) superior to other organic conducting polymers due to the low molecular weight of the repeating CH unit. However, (CH)<sub>x</sub> can only be oxidized or reduced to the (CH<sup>0.10+</sup>)<sub>x</sub> and (CH<sup>0.18-</sup>)<sub>x</sub> states, respectively. Low molecular weight polymeric materials, which can be charged to a greater degree, should exhibit superior capacitative properties over (CH)<sub>x</sub> films. Such qualities may possibly be found in polymer films containing redox centres [30].

In this paper we describe the concept of the photoassisted rechargeable cell. The system utilizes a *p*-type InP semiconductor anode coated with a polymer film containing pendant reducible anthraquinone groups

(PAQ) and a Pt cathode coated with a film of polypyrrole.



## 2. Experimental details

### 2.1. Chemicals

Acetonitrile (CH<sub>3</sub>CN) (BDH, analytical grade) was fractionally distilled, dried over activated alumina (type WN-6, Sigma) and stored over N<sub>2</sub> in the presence of molecular sieve 4 Å. Pyridine and nitrobenzene (BDH, analytical grade) were used without further purification. Tetraethylammonium perchlorate (TEAP) (Aldrich) was recrystallized twice from distilled water and dried under vacuum for several days.

### 2.2. Film preparation

Poly[*p*-(9,10-anthraquinone-2-carbonyl)styrene]-co-styrene (PAQ) was synthesized by Dr P. P. M. Hoang according to the following method [31-33]. Polystyrene and 2-anthraquinone carbonyl chloride were allowed to react in dry nitrobenzene, in the presence of aluminum chloride at room temperature for 3 days. The product was purified by repeated precipitation from methanol and finally freeze dried under vacuum.

Copolymer compositions were characterized by IR spectroscopy, elemental analysis and gel permeation chromatography. The sample utilized had an anthra-

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quinone content of 47.0 mol% and was based on a polymer with a narrow molecular weight distribution in a chain containing approximately 2170 repeat units.

PAQ films on Pt and *p*-InP, were prepared by placing an aliquot of 0.5 wt % PAQ solution in pyridine on the electrode substrate and allowing the solvent to evaporate. The electrode was subsequently dried under vacuum for 5 min. The quantity of polymer deposited was  $1.09 \times 10^{-6} \text{ mol cm}^{-2}$  ( $\approx 5 \mu\text{m}$ ).

Polypyrrole films were electropolymerized on Pt electrodes ( $0.18 \text{ cm}^2$ ) from 0.1 M pyrrole in 0.1 M TEAP/ $\text{CH}_3\text{CN}$ . Films were grown using a constant current density of  $0.712 \text{ mA cm}^{-2}$ . Electrolysis was continued until  $662 \text{ mC cm}^{-2}$  of anodic charge had passed.

The thickness of the film was estimated from

$$d = \frac{M.Wt \times Q_{\text{form}}}{n \times 96485 \times \rho \times A}$$

where M.Wt is the molecular weight of a repeating pyrrole unit (plus dopant);  $n$  is the number of electrons associated with polymer formation (in the absence of doping) and is equal to 2;  $\rho$  is the estimated density of the film ( $1.5 \text{ g cm}^{-3}$ ) [34, 35];  $A$  is the electrode area; and  $Q_{\text{form}}$  is determined from  $Q_{\text{form}} = Q_{\text{tot}} - Q_{\text{ox}}$ .  $Q_{\text{tot}}$  is the total charge passed during electrolysis and  $Q_{\text{ox}}$  is the charge associated with electrochemical doping of the polymer, obtained by measuring the number of coulombs required to completely reduce a freshly formed film.

### 2.3. Electrochemistry

Pt electrodes ( $0.18 \text{ cm}^2$ ) (Beckman) were polished successively with SiC 600,  $3 \mu\text{m}$  diamond paste, and subsequently sonicated in distilled water for 10 min. Between experimental runs, the electrode was polished with  $1 \mu\text{m}$  diamond paste, sonicated in distilled water and dried under vacuum.

Samples of *p*-type InP (100 face) were purchased from Varian, Palo Alto, California, and mounted on glass with silicone adhesive. Ohmic contacts were prepared by placing Ga-In eutectic on the back of the sample and heating to  $450^\circ \text{C}$  for 2 h under vacuum. The heat treatment reduced the resistance of the contact from  $\approx 10 \text{ k}\Omega$  to  $8 \Omega$ . InP electrodes were etched with 5%  $\text{Br}_2$ /methanol for 30–60 s prior to use.

A single compartment cell (40 ml) incorporating a quartz window was employed in conjunction with a Pt counter electrode and a Ag/AgCl reference electrode. All potentials are reported with respect to the SCE. The electrolyte used for these studies was 0.1 M TEAP/ $\text{CH}_3\text{CN}$ . Solutions were flushed with  $\text{N}_2$  or Ar prior to use and an inert atmosphere maintained throughout the experiments. Leaching of water into the electrolyte was prevented by separating the reference electrode from the main compartment by an agar salt bridge saturated with NaCl. The reference electrode was further isolated by placing the salt bridge in an ancillary compartment containing 0.1 M TEAP/ $\text{CH}_3\text{CN}$ . The ancillary compartment was immersed in

the electrolyte and electrical contact achieved through a glass frit. The effect of trace water already present in solution was diminished by the addition of activated alumina (type WN-6, Sigma) ( $\approx 5 \text{ g}$ ). Standard commercial potentiostats and ancillary electrochemical equipment (Princeton Applied Research) were employed.

### 2.4. Chronocoulometry

Chronocoulometry of polypyrrole- (PP) coated electrodes was performed by measuring the charge passed following a potential step from an initial value of  $-0.55 \text{ V}$  to more positive values. The charge was recorded when the current had dropped to  $< 10 \mu\text{A cm}^{-2}$  (1–10 min). The charge associated with background processes was subtracted from the recorded value. The open circuit voltage of the oxidized PP-coated electrode was recorded immediately following the anodic potential step using a high impedance electrometer (Keithley).

### 2.5. Cyclic voltammetry

Cyclic voltammetry was performed with either two- or three-electrode systems. The two-electrode system was employed for rechargeable cell studies. Here, the working electrode terminal of the potentiostat was connected to one electrode (PAQ-coated) and the counter and reference electrode terminals attached to the second electrode (PP-coated). Prior to voltammetry, the PP film was electrochemically oxidized, such that the free standing potential of the film was  $+0.05 \text{ V}$  (SCE). Voltammetry at semiconductor electrodes was assisted by illumination from a 150 W tungsten lamp (Spectro). The illumination intensity was  $40 \text{ mW cm}^{-2}$  at the electrode surface.

### 2.6. Charge and discharge characteristics

Cells were charged at constant potential and discharged by short circuiting PAQ-coated anodes and PP-coated cathodes through a variable resistance.

## 3. Results and discussion

### 3.1. Electrochemistry of PAQ- and PP-coated electrodes

The electrochemically derived surface coverage of AQ units in the PAQ film was  $2.0 \times 10^{-7} \text{ mol cm}^{-2}$ , while that calculated from the quantity of material applied was  $1.09 \times 10^{-6} \text{ mol cm}^{-2}$ . The low  $\Gamma_{\text{obs}}/\Gamma_{\text{cal}}$  ratio, 0.18, is due to the poor mobility of polymer chains in this solvent preventing the required orientation for complete electron propagation through the film [36].

Potential step chronocoulometry was performed on PP films in order to determine the relationship between the dopant ( $\text{ClO}_4^-$ ) concentration and the free standing potential of PP films. The charge storage capacity of PP, as a function of applied potential, is shown in Fig. 1. At less positive potentials  $< -0.25 \text{ V}$ , the film

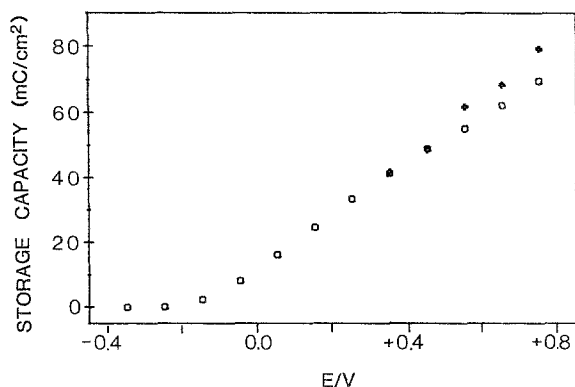


Fig. 1. Chronocoulometric determination of the storage capacity of polypyrrole as a function of applied potential: ( $\square$ ) single electrode used for all data points, (+) fresh film used for each data point. Electrolyte, 0.1 M TEAP/ $\text{CH}_3\text{CN}$ ; initial potential,  $-0.55$  V.

is neutral and the charge storage capacity is negligible. As the applied potential is made more positive, PP is oxidized to greater extents. The charge storage capacity is linearly dependent on applied potential above  $-0.2$  V. This result agrees with  $Q$ - $E$  curves obtained by other research groups [27, 37, 38]. The cumulative charge is actually a summation of faradaic and non-faradaic (capacitive charges) [39, 40], both of which increase linearly with applied potential. The  $Q$ - $E$  relationship is linear because doping with ionic charges produces an increase in electrostatic interaction potentials, and further oxidation of polypyrrole becomes progressively more difficult. Oxidation of PP is slightly irreversible above  $+0.5$  V as observed by the data obtained from a single PP film. Here, the same film was used for all chronocoulometric measurements, beginning with the smallest potential step and continuing with increasingly larger potential steps. When freshly prepared PP films were used to obtain each data point a linear relationship was observed.

PP films possess excellent charge memory characteristics. When the external voltage is removed. The film exhibits a free standing potential equivalent to that initially applied. The memory effect lasts for extremely long periods and is attributed to the stability of oxidized PP films.

The chronocoulometric data were used to calculate the mass of PP deposited and the concentration of dopant at any given potential. PP films prepared

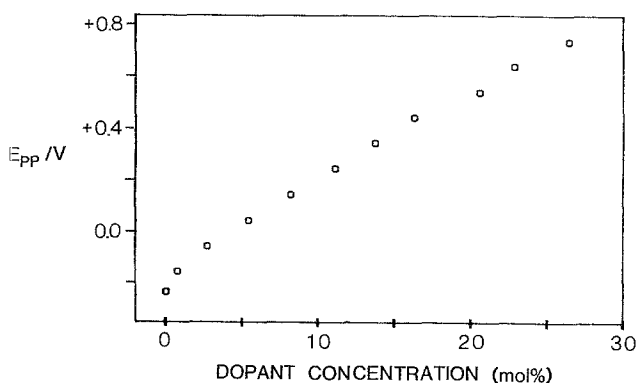


Fig. 2. Free standing potential of polypyrrole as a function of  $\text{ClO}_4^-$  dopant concentration.

under the conditions described developed a free standing potential of  $+0.59 \pm 0.015$  V (SCE). The cathodic charge required to completely reduce a freshly formed film,  $Q_{\text{ox}}$ , was  $62.2$   $\text{mC cm}^{-2}$ . The surface coverage of PP, estimated from  $\Gamma = Q_{\text{form}}/2F$ , was  $3.11 \times 10^{-6}$   $\text{mol cm}^{-2}$ , based on the pyrrole unit. Tentatively assigning a PP density of  $1.5$   $\text{g cm}^{-3}$  gives an approximate film thickness of  $1.8$   $\mu\text{m}$ .  $Q_{\text{ox}}$ , which is  $62.2$   $\text{mC cm}^{-2}$ , is equivalent to  $6.4 \times 10^{-7}$   $\text{mol cm}^{-2}$  of  $\text{ClO}_4^-$ . Combining  $\Gamma_{\text{PP}}$  and  $\Gamma_{\text{perchlorate}}$  yields a doping level of 21 mol%. In a similar manner, the dopant concentrations were calculated at various potentials and correlated to the free standing potential of PP films (Fig. 2).

### 3.2. Pt/PAQ//PP/Pt rechargeable cells

In conventional three-electrode voltammetry, AQ groups in PAQ films can be reversibly reduced to form radical anions,  $\text{AQ}^-$ , and dianions,  $\text{AQ}^{2-}$ , with concurrent oxidation of a substance at the counter electrode. When a two-electrode system is employed, in which the second electrode is a PP film, reduction of PAQ is accompanied by simultaneous oxidation of PP.

The cell notation is given by Pt/PAQ//PP/Pt. The cyclic voltammetry of this cell is shown in Fig. 3. The shift in peak potentials and smoothing of peaks associated with the reduction of PAQ is a result of the simultaneous change in oxidation state of PP. The free standing potential of the PP film increases from the initial value of  $+0.05$  V ( $\equiv$  5% doping) to  $+0.31$  V ( $\equiv$  13% doping) when PAQ is reduced to the  $\text{P}(\text{AQ}^-)$  state, and to  $+0.68$  V ( $\equiv$  24% doping) when reduced to the  $\text{P}(\text{AQ}^{2-})$  state.

The simultaneous reduction of PAQ and oxidation of PP can be considered as the charging cycle in a rechargeable cell. These electrodes release the stored energy and revert back to their original forms when short circuited. The stoichiometry of the electrochemical discharge reactions when PAQ is charged to the radical anion are given below, where  $(\text{AQ})_x \equiv \text{PAQ}$  and  $(\text{C}_4\text{H}_3\text{N})_x \equiv \text{PP}$ .

When PAQ is charged to the  $\text{P}(\text{AQ}^-)$  state, the anodic discharge reaction is

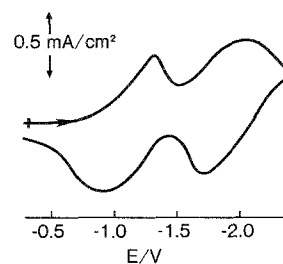
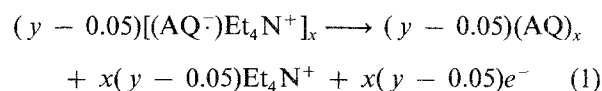
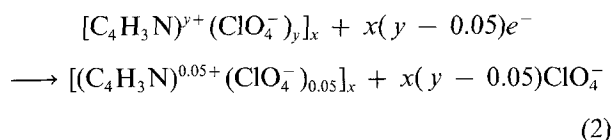


Fig. 3. Cyclic voltammetry of the Pt/PAQ//PP/Pt cell. Electrolyte, 0.1 M TEAP/ $\text{CH}_3\text{CN}$ ; scan rate,  $20$   $\text{mV s}^{-1}$ ; initial oxidation state of PP, 0.005+.

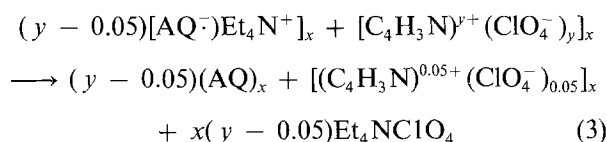
Table 1. Open circuit potentials of Pt|PAQ||Pt cells

$E_{\text{external}}$ (V)	$V_{\text{oc}}$ (PAQ/Pt) (V)	$V_{\text{oc}}$ (PP/Pt) (V)	Doping level	$V_{\text{oc}}$ (cell) (V)
1.3	-0.86	+0.31	0.13	1.17
2.1	-1.35	+0.68	0.24	2.03

and the cathodic discharge reaction is



The net discharge reaction is



When PAQ is charged to the  $\text{P}(\text{AQ}^{2-})$  state, the discharge cycle occurs via two one-electron steps.

The Pt/PAQ//PP/Pt cell was charged to varying degrees by an external source. The open circuit potentials of the cell,  $V_{\text{oc}}$ , and of the individual electrodes are shown in Table 1.

The voltage-time curves obtained when these cells are discharged through a given resistance are shown in Fig. 4. The curves associated with the discharge of  $\text{P}(\text{AQ}^-)$  are shown in Fig. 4a. The coulombic efficiencies for the charge/discharge cycle are 90.5, 96.7 and 95.5% for discharge through resistances of 100, 50 and 25 k $\Omega$ , respectively. The curve in Fig. 4b illustrates the discharge behavior when the anode is charged to  $\text{P}(\text{AQ}^{2-})$  state. A double plateau is obtained, evidence of the two one-electron discharge process. The coulombic efficiency is 89% when discharged through a 100 k $\Omega$  resistance. The cells were found to be stable for long periods of time. Twenty-five charge/discharge cycles did not affect the charge storage capabilities of the cell. Since the PAQ film is stable for extremely long periods of time, any loss of storage is expected to arise from irreversible oxidation of PP.

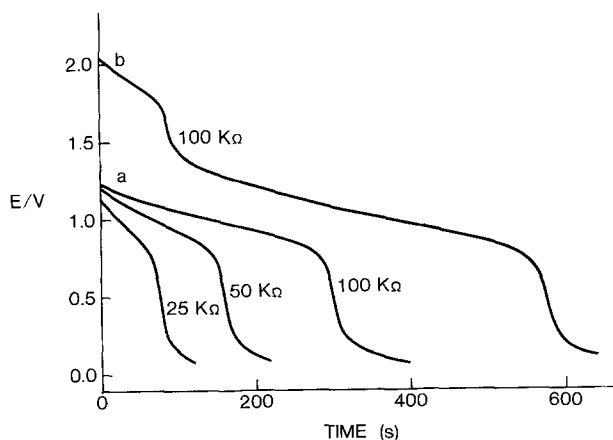


Fig. 4. Voltage-time discharge curves for Pt/PAQ//PP/Pt cells: (a)  $\text{P}(\text{AQ}^-)/\text{PP}^{y+}$ , (b)  $\text{P}(\text{AQ}^{2-})/\text{PP}^{y+}$ . External resistances of the cell as inscribed. Electrolyte, 0.1 M TEAP/ $\text{CH}_3\text{CN}$ ; electrode areas,  $0.18\text{ cm}^2$ .

The theoretical electricity storage densities (ESD) of PAQ, based on the molecular weight of the repeat unit and on the mass of the charge balancing counter ion, are 46 and 75  $\text{Ah kg}^{-1}$  when reduced to  $\text{P}(\text{AQ}^-)$  and  $\text{P}(\text{AQ}^{2-})$ , respectively. These values yield electricity storage densities (ED) of 45 and 70  $\text{Ah kg}^{-1}$  for the PP film.

The experimental ESD of the cell includes the masses of both polymer films.  $\text{ESD}_{\text{cell}}$  values are 7 and 14  $\text{Ah kg}^{-1}$ , from which energy densities of 8.4 and 28  $\text{Wh kg}^{-1}$  were calculated. The experimental ESD and ED values for the cell are very much lower than those reported for other polymer based systems [14]. This is a consequence of poor electron propagation through thick PAQ films. As shown previously, only 18% of the PAQ film is electroactive. The magnitude of the ESD and ED would be dramatically increased with complete reduction of the PAQ film. The electricity storage density of the cell would theoretically increase to 58 and 78  $\text{Ah kg}^{-1}$  since an increase in the number of AQ groups reduced produces a corresponding increase in the oxidation state of the PP film. As a result, the energy density of the cell increases to theoretical values of 99 and 171  $\text{Wh kg}^{-1}$ . The values are comparable to, or larger than, those values reported for cells based on other polymeric materials.

It is appropriate to use the condition of 100% reduction of the PAQ film to exemplify the charge storage properties of redox polymer films. PAQ is not a suitable material for the design of high energy storage cells due to the poor charge storage capacity. It is evident however, that with correct choice of redox polymer, a rechargeable cell of greater or comparable energy density to polyacetylene cells can be achieved. The advantage of redox polymer systems lies in the extensive choice of redox couple and polymer backbone, and in the diversity of film forming techniques.

The major problem with these systems is, at present, the limitation of film thickness and the consequent low storage capacity. In this aspect, conductive polymers are much superior to redox polymers. It is evident that the polymer chains in thick films lack flexibility for site-site collision. Electronic accessibility of redox

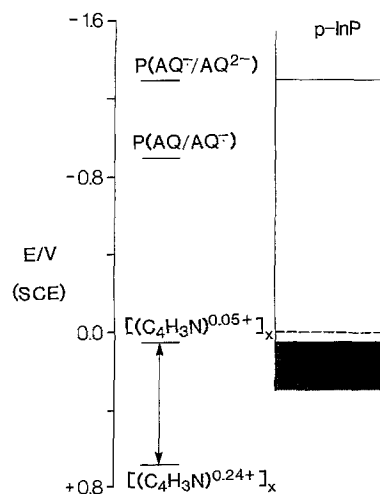


Fig. 5. Energy level diagram for  $p\text{-InP}/\text{PAQ}/\text{PP}/\text{Pt}$  cells.

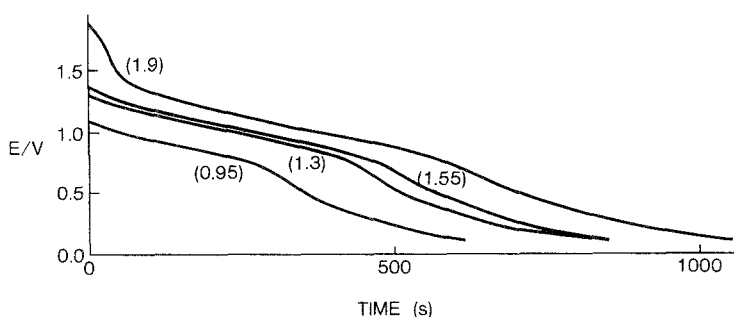


Fig. 6. Voltage-time discharge curves for *p*-InP/PAQ//PP/Pt cells. The external voltages used for cell charging are given in brackets. Electrolyte, 0.1 M TEAP/CH<sub>3</sub>CN. Electrode areas: *p*-InP = 0.296 cm<sup>2</sup>, Pt = 0.18 cm<sup>2</sup>.

sites can be improved substantially by incorporating the electroactive unit into a conductive matrix. Bidan and coworkers have recently reported the preparation of conducting PP films incorporating electroactive redox centres of Ru, ferrocene, paraquat, nitro-oxides and 9,10-anthraquinone [41, 42]. Alternatively, the accessibility of redox sites in a polymer film may be enhanced by blending with a conductive medium, e.g. carbon black, graphite powder [30].

### 3.3. *p*-INP/PAQ//PP/Pt rechargeable cells

The flat band potential of *p*-InP in 0.1 M TEAP/CH<sub>3</sub>CN was estimated as  $-0.05$  V from impedance measurements. Estimations of the redox energy levels of PAQ and the various oxidation states of PP allows construction of the schematic energy diagram shown in Fig. 5. The energy level of the P(AQ/AQ<sup>•-</sup>) couple is below the conduction band energy level of *p*-InP. The processes involved in the charging of the *p*-InP/PAQ//PP/Pt cell are essentially the same as that previously described except that reduction of PAQ occurs via photogenerated conduction band electrons. In the absence of irradiation neither of the polymer films are charged. The open circuit potential of the charged cell, and of the individual electrodes are shown in Table 2.

The discharge curves for these cells through a 100 kΩ resistance are shown in Fig. 6. Coulombic efficiencies were 82–90%.

It is evident from Table 2 that the reduction of PAQ and simultaneous oxidation of polypyrrole can be driven uphill by illuminated *p*-InP electrodes, albeit to a small degree. The photovoltage generated by the *p*-InP electrode is much lower than that theoretically calculated by  $|V_{fb}^- V_{redox}|$ , 0.85 V. This low value probably results from the injection of electrons from P(AQ<sup>•-</sup>) and P(AQ<sup>2•-</sup>) into InP surface states, leading to Fermi level pinning and constant band bending. This is supported by the fact that the generated photovoltage remains constant at  $\approx 0.2$  V when PAQ is extensively

reduced to the AQ<sup>•-</sup> or AQ<sup>2•-</sup> state ( $E_{external} = 0.95$  and 1.9 V, respectively).

For maximum efficiency of solar conversion and storage, the energy level of the redox couple must be located just below the conduction band, or just above the valence band, for *p*- and *n*-type semiconductors, respectively. The selection of suitable PEC systems is limited by the number of available electroactive redox polymers. In this aspect conductive polymeric films appear promising, since their oxidation state or doping level changes as a function of potential and can, therefore, be adjusted to suit the semiconductor energy levels.

We extended our study of photoassisted rechargeable cells to *n*- and *p*-Si/PP//PP/Pt systems. However, photovoltages were again low. A detailed study on the Si/polypyrrole interface showed that the band edges of the semiconductor change substantially with a change in the oxidation state/electrochemical potential of polypyrrole leading to loss of photovoltage (Fermi level pinning) [43].

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Table 2. Open circuit potentials of *p*-InP/PAQ//PP/Pt cells

$E_{external}$ (V)	$V_{ox}$ (PAQ/InP) (V)	$V_{oc}$ (PP/Pt) (V)	Doping level	$V_{oc}$ (cell) (V)
0.95	-0.81	+0.36	0.145	1.17
1.3	-0.88	+0.50	0.165	1.38
1.3 (25 cycles)	-0.87	+0.59	0.21	1.46
1.9	-1.25	+0.84	0.31	2.09

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