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Workshop on Nanoscience for Solar Energy Conversion

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Photoelectrochemical Solar Energy Conversion Based on Conducting Polymers

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Photoelectrochemical Solar Energy Conversion based on conducting polymers

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Outline

1. Background
   - PEC
   - Materials
2. Solid-State PECs Based on
   - Conducting Polymer
   - Conducting Polymer/Fullerene
3. Liquid-State PECs Based on
   - Conducting Polymers
   - Conducting Polymer/Inorganic Semiconductor
4. Conclusions

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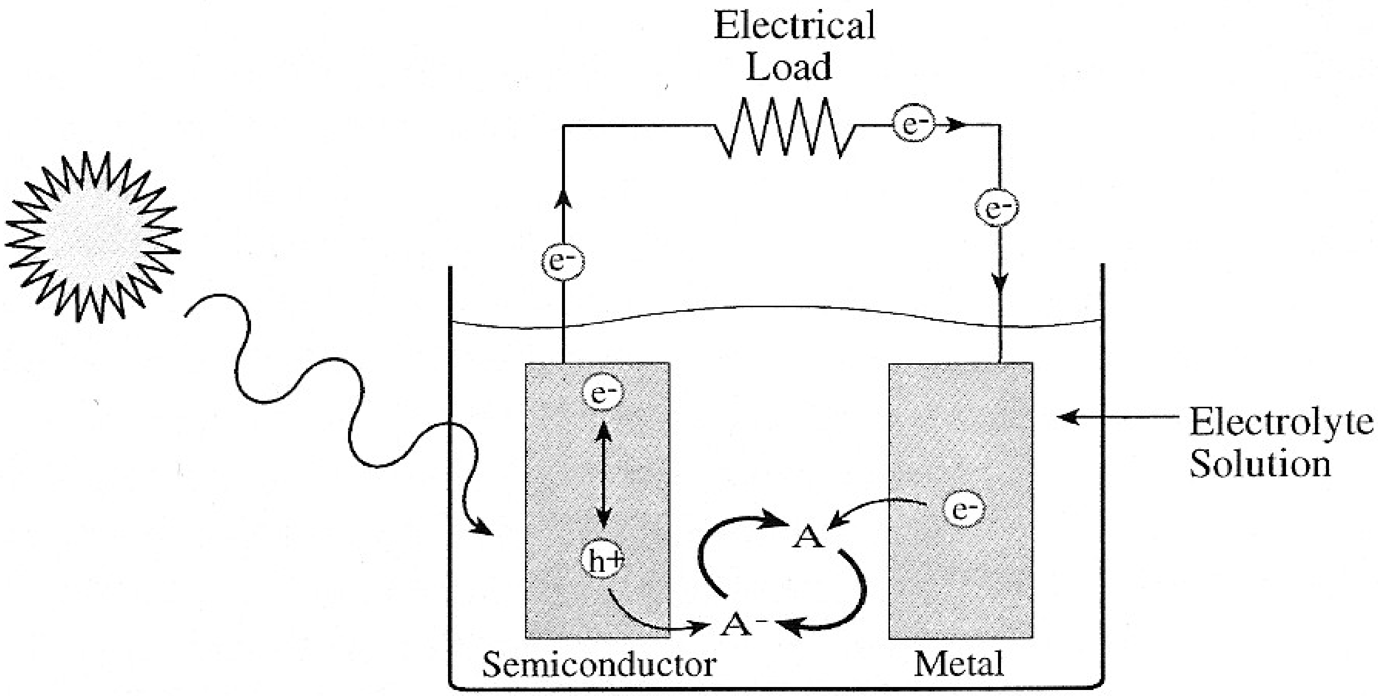
What are PECs?

PECs convert energy from the sun to electrical energy or to storable energy (chemical fuel)



Basic structure of the PECs

Conti...

- Absorption of light by the semiconductor electrode creates electron and hole pairs
- The electron-hole pairs separate by the electric field created at the junction
- A voltage can be created as the electrons move towards the unilluminated (counter) electrode.
- The mediator is the electrolyte solution which allows the flow of electrons to proceed completing the circuit.
- Electron and holes drive chemical reactions.
- Light energy is converted into electrical energy or Chemical fuel.

Conti...

- Narrow band-gap semiconductors whose photo-response matches the solar spectrum are in general unstable in contact with electrolytes.

- When a hole reaches the interface an oxidation reaction occur with the semiconductor itself. This is an example of photocorrosion.

- One of the earlier application of conducting polymers was photocorrosion prevention.

- Wide band-gap semiconductors are more stable but absorb only the small portion of the solar radiation.

Materials

Photoactive materials: Semiconductors with appropriate band gap and high absorption coefficient

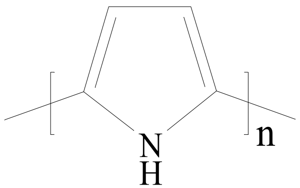
- **Inorganic Semiconductor:**
  - Si, Ge, CdS, GaAs, CdTe, TiO_2, $CuInSe_2$, etc.
- **Organic Semiconductors:**
  - **Small molecules**
    - phthalocyanines, porphyrins, etc.
  - **Conducting polymers**
    - Polythiophenes, polypyrrole, polyaniline, poly(p-phenylene), etc.

Our work is based mainly on **conducting polymers**.

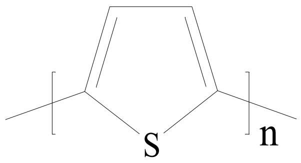
Synthesis: Chemical or electrochemical

Electronically Conducting Polymers

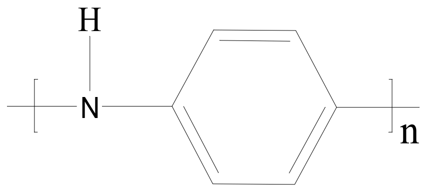
Chemical structures of some conjugated polymers



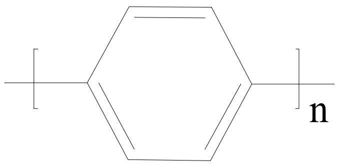
polypyrrole



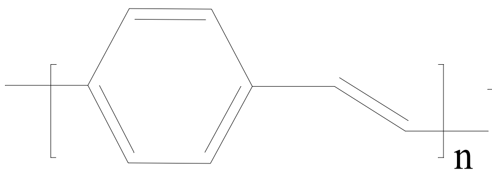
polythiophene



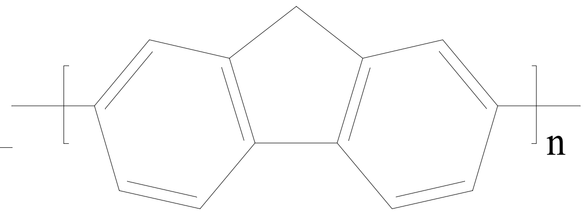
polyaniline



poly(*p*-phenylene)



poly(*p*-phenylenevinylene)



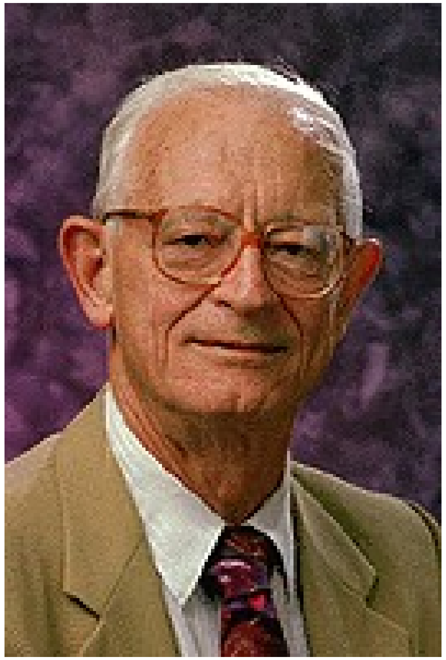
polyfluorene

Nobel Prize in Chemistry 2000

"For the Discovery and Development of Conductive Polymers"

Alan Heeger
University of California
at Santa Barbara

Hideki Shirakawa
University of Tsukuba



Alan MacDiarmid
University of
Pennsylvania

Ion-Conducting Polymers

Electrolyte: liquid or polymer electrolytes

Polymer electrolytes: Ion conductors by solvation of salts in polymer matrix.

<u>Polymer matrix:</u>

– Poly(ethylene oxide)

– Poly(propylene oxide)

– Poly(ethylene imine)

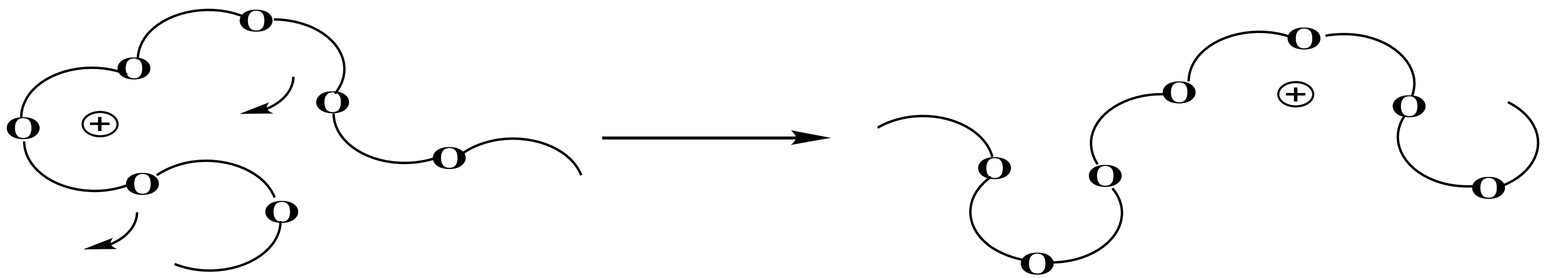
– Polysiloxane, ...

<u>Ions:</u>

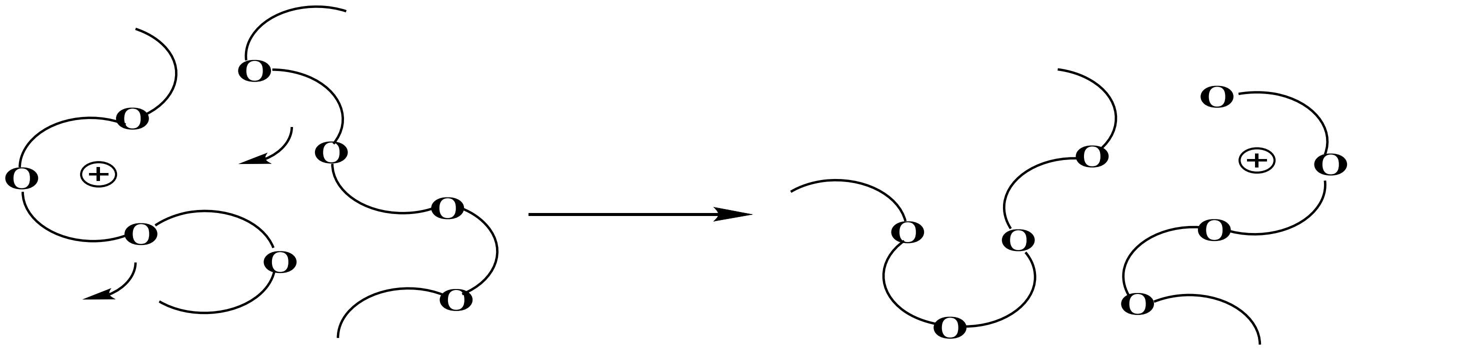
– Li, Na, K, ... salts with counter-ions: I^-, ClO_4^-, $CF_3SO_3^-$, ...

– NH_4^+ salts

Ionic Motion in Polymer Electrolytes



Intrachain hopping



Interchain hopping

- Cation motion coupled with segmental motion of polymer chain
- Anion is more mobile than cation

Redox couple & Counter Electrode

Redox couple

- Iodide/triiodide
- Eu^{3+}/Eu^{2+}
- Sulphide salt/sulphur
- $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$
- etc.

Counter electrode: Electrochemically stable materials

Usually: ITO, Au, Ag, etc.

Advantages

PECs are attractive because

- they can be used to store energy in the form of chemical fuels in addition to converting light to electricity

- are less expensive

- The band-bending characteristics of the semiconductor can be conveniently varied by suitable choice of redox couple or concentration of the redox couple

- no solid-state junctions unlike the case of photovoltaic devices

- etc.

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Solid-State PECs

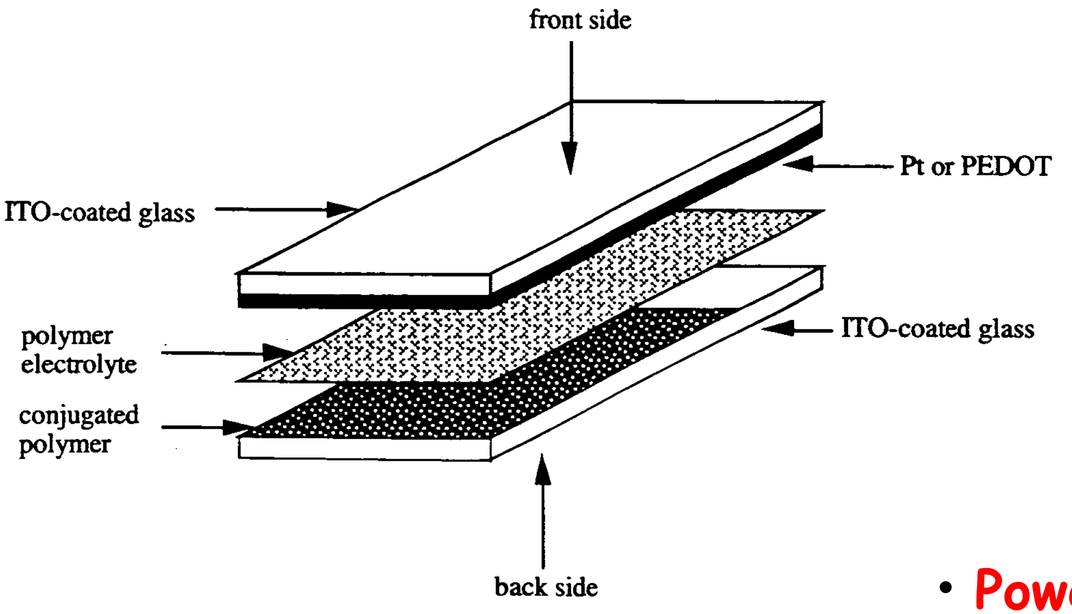
Two classes of polymeric materials:

- electronically conducting polymers
- ion-conducting polymers
- possibilities for application of both classes of material in combination with each other.

Eliminate problems encountered in liquid–junction PECs such as:

- Packaging
- Leakage
- Portability
- handling

Device Structure and Experimental Set-up



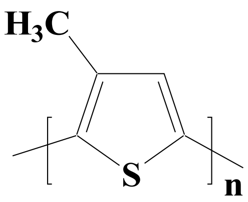
Conjugated Polymers:
P3MT, P3HT, P3OT, POPT, PTOPT, PANI, MEH-PPV, Co-polymers...

Polymer Electrolyte:
$-(CH_2O[CH_2CH_2O]_9\ )-$

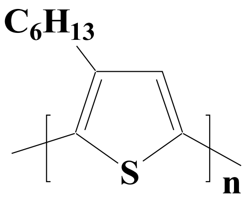
Redox Couple: I_3^-/I^-

- Power Supply
- Lamp housing
- Monochromator
- Sample holder
- Out-put measuring instrument

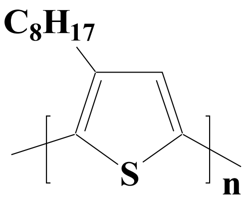
Semiconductor Polymers



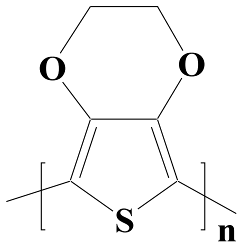
(I)



(II)

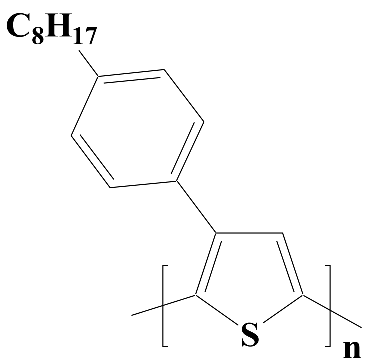


(III)

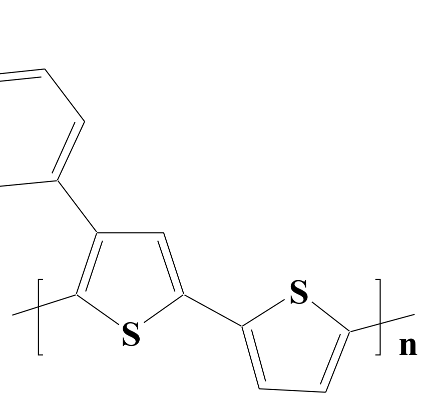


(IV)

- Chemical Synthesis
- Electrochemical synthesis



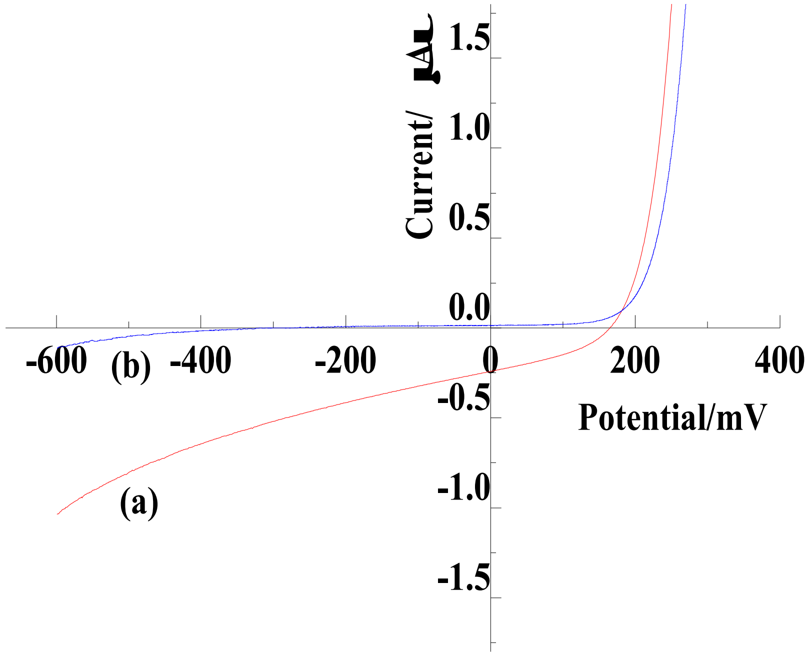
(V)



(VI)

I.	P3MT
II.	P3HT
III.	P3OT
IV.	PEDOT
V.	POPT
VI.	PTOPT

Current-Voltage Characteristics

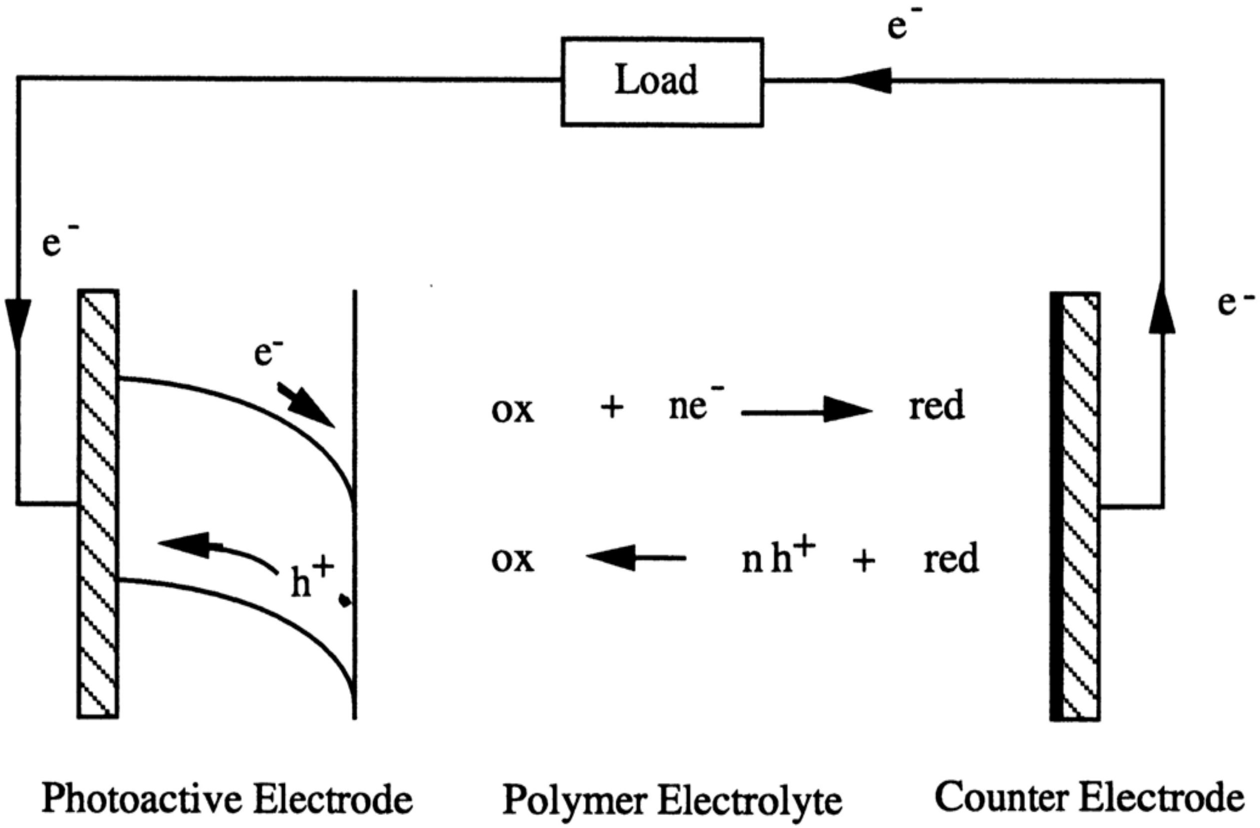


I_{SC} = 0.21 μA/cm²
V_{OC} = 165 mV

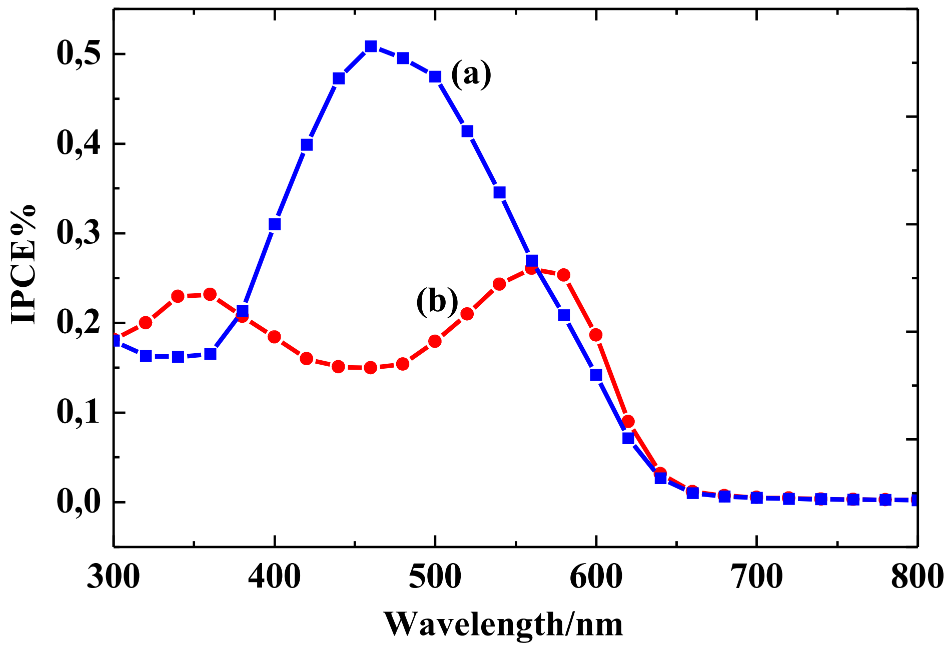
Tesfalidet Lemma and Teketel Yohannes, *J. Braz. Chem. Soc.*, 18 (2007) 818.

Current density-voltage Characteristics of ITO│ poly(3-MT-co-3OT)│ POMOE:I_3^-/I^-│ PEDOT│ITO in the dark and under illumination

Operation Principles of the Solid-State PECs



Spectral Response

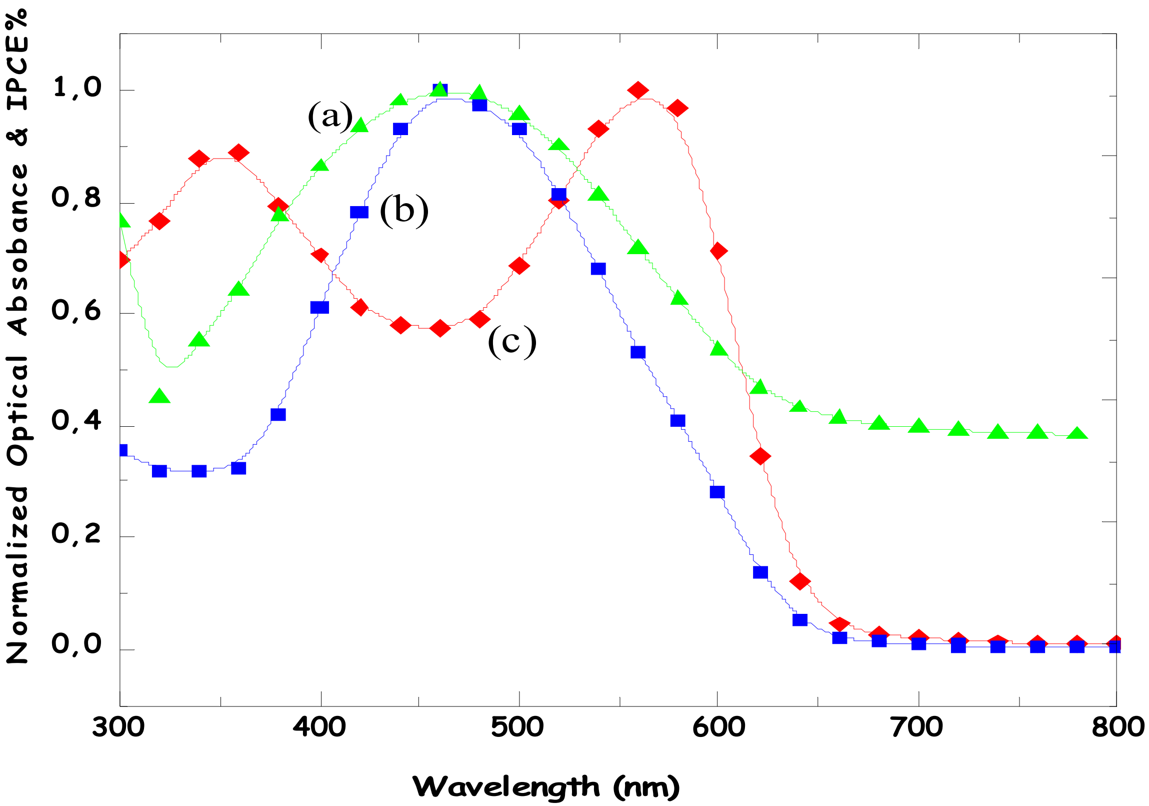


$$IPCE(\%) = \frac{1240 I_{SC}(\mu A/cm^2)}{\lambda\ (nm) I(W/m^2)}$$

Tesfalidet Lemma and Teketel Yohannes, *J. Braz. Chem. Soc.*, 18 (2007) 818.

Photocurrent action spectrum of ITO/ poly(3-MT-co-3OT) /I_3^-/I^-/PEDOT/ITO for illumination through a) front side b) back side.

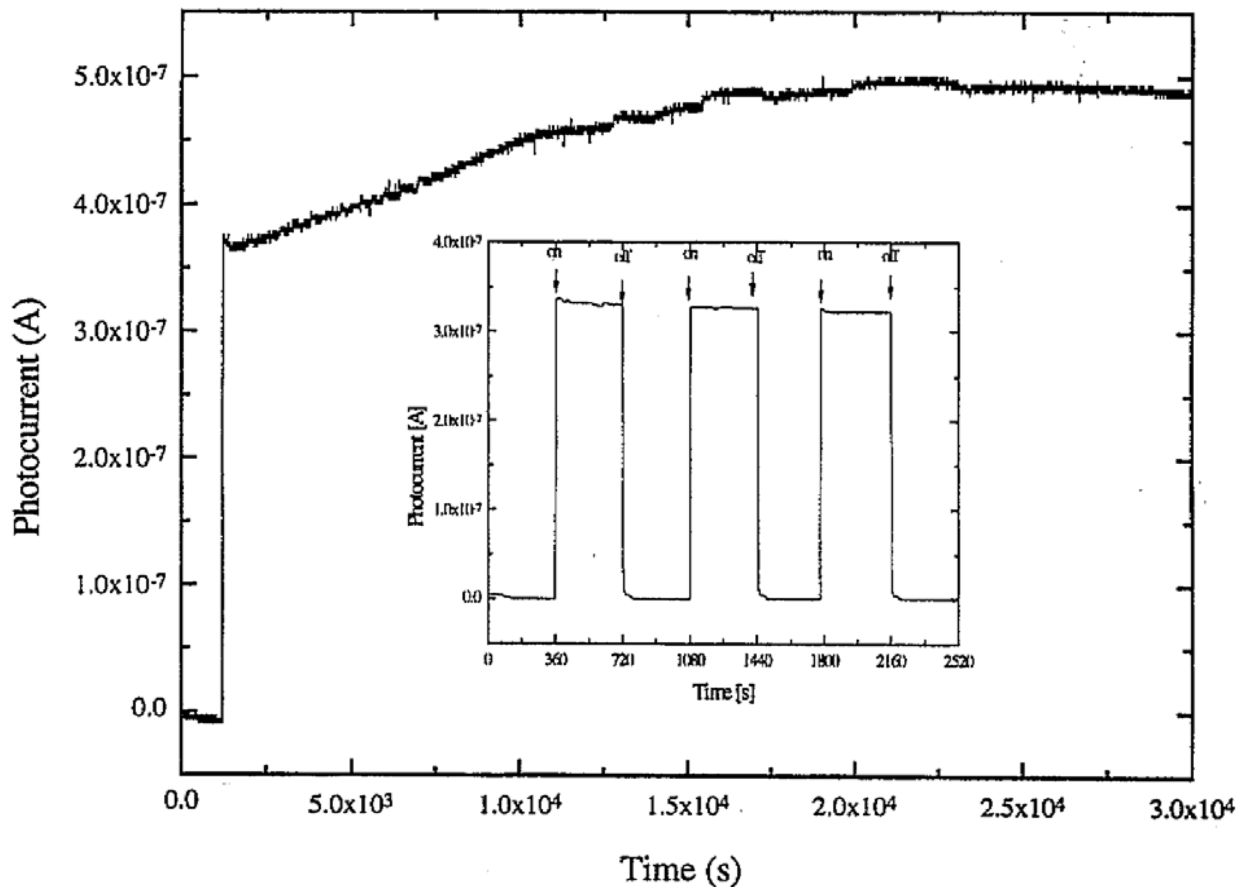
Spectral Response



Tesfalidet Lemma and Teketel Yohannes, *J. Braz. Chem. Soc.*, 18 (2007) 818.

a) Normalized optical absorption spectrum of poly(3-MT-co-3OT) deposited on ITO and normalized action spectrum of ITO/poly(3-MT-co-3OT)/I_3^-/I^-/PEDOT/ITO for illumination through b) front side c) back side.

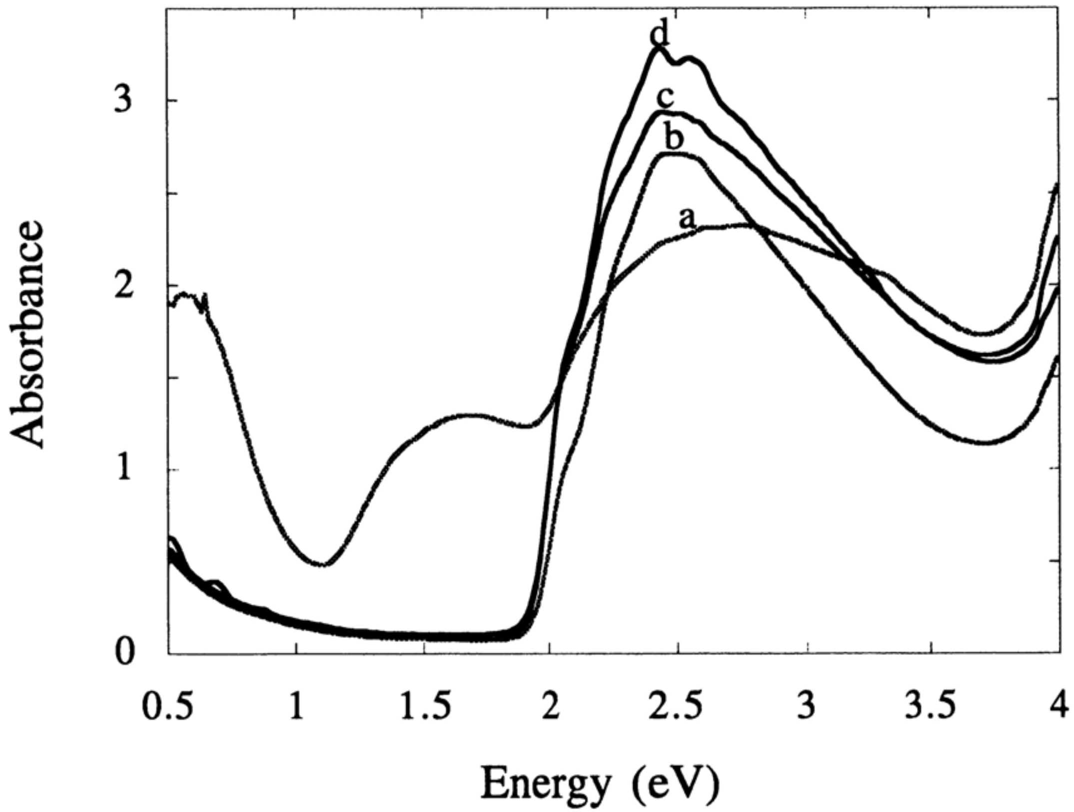
Transient and Steady State Photocurrent



ITO/P3MT/POMOE, I_3^-/I^-/Pt/ITO

Teketel Yohannes, Theodros Solomon, O. Inganäs, *Synth. Met.*, 82(1996)215.

Effect of Redox Couple Concentration

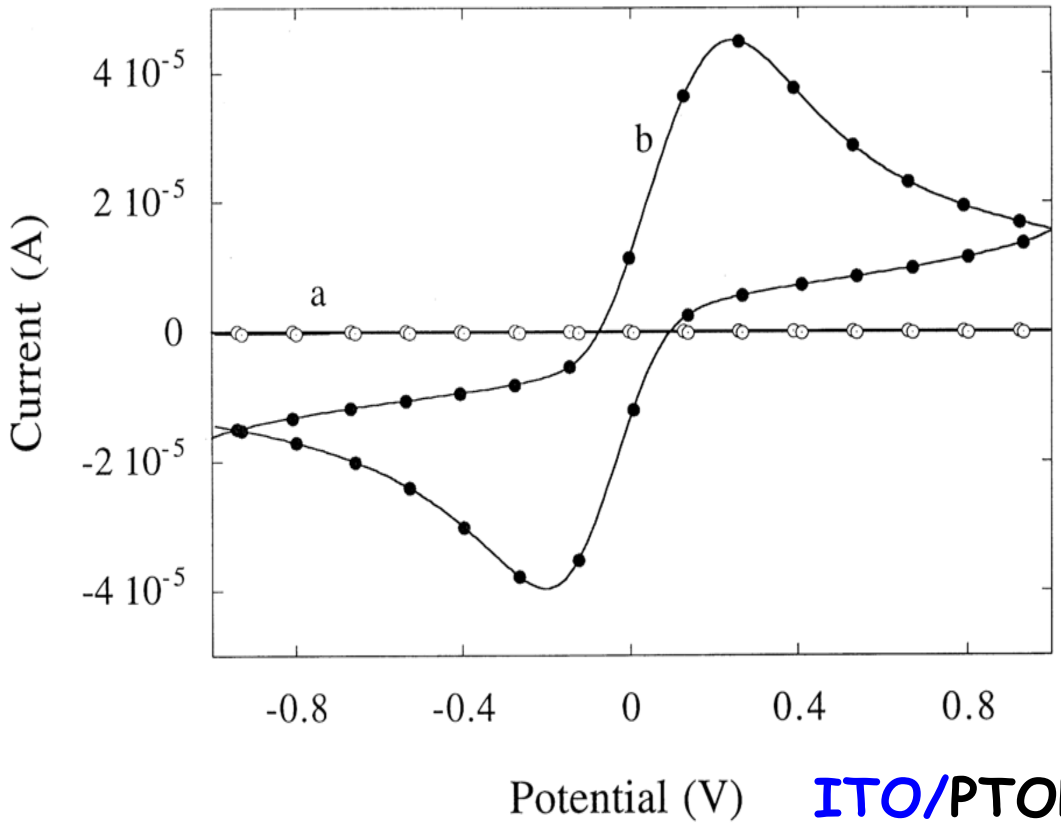


$[I_3^-]/[I^-]$	V_{oc} (mV)	I_{sc} (nA/cm²)
10	-	-
1.0	223.0	53.3
0.1	250.0	31.0
0.01	523.3	32.3

ITO/P3OT/POMOE, I_3^-/I^-/Pt/ITO

Teketel Yohannes, O. Inganäs, *J. Electrochem. Soc.*, 143 (1996) 2310.

Effect of Redox Couple



Eu^{2+}/Eu^{3+} redox couple

CV of ITO/POMOE/ITO a) no redox couple and b) POMOE complexed with $EuCl_3$.

Teketel Yohannes, O. Inganäs, *Synth. Met.*, 107 (1999) 97.

ITO/PTOPT/POMOE, .../Pt/ITO

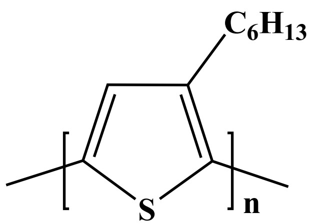
Redox couple	V_{oc} (mV)	I_{sc} ($\mu A/cm^2$)
I_3^-/I^-	250	0.04
Eu^{2+}/Eu^{3+}	600	0.10

I_{sc} and V_{oc} of the Various Solid-State PECs Studied

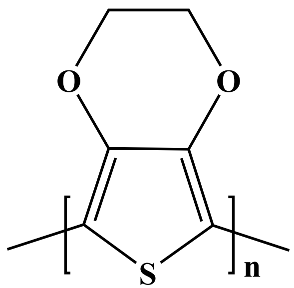
Solid-state PEC	I_{sc} (μA/cm²)	V_{oc} (mV)	Ref.
ITO/P3MT/POMOE, I_3^-/I^-/Pt/ITO	0.35	140	[1]
ITO/P3OT/POMOE, I_3^-/I^-/Pt/ITO	0.04	250	[2]
ITO/POPT/POMOE, I_3^-/I^-/PEDOT/ITO	0.20	166	[3]
ITO/PTOPT/POOE, I_3^-/I^-/PEDOT/ITO	0.40	240	[4]
ITO/P3HT/POMOE, I_3^-/I^-/PEDOT/ITO	0.47	130	[5]
ITO/P3HT:C_{60}/POMOE, I_3^-/I^-/PEDOT/ITO	7.28	98	[6]
ITO/poly(3MT-co-3OT)/POMOE, I_3^-/I^-/PEDOT/ITO	0.21	165	[7]
ITO/MEH-PPV/POMOE, I_3^-/I^-/PEDOT/ITO	0.14	310	[8]

[1] Teketel Yohannes, Theodros Solomon, O. Inganäs, *Synth. Met.*, 82(1996)215.
[2] Teketel Yohannes, O. Inganäs, *J. Electrochem. Soc.*, 143 (1996) 2310.
[3] Teketel Yohannes,, O. Inganäs, *Solar Materials and Solar Cells*, 51(1998) 193.
[4] Teketel Yohannes, O. Inganäs, *Synth. Met.*, 107 (1999) 97.
[5] Mosissa Adi, Teketel Yohannes, Theodros Solomon, *Solar Mater. and Solar Cells*, 83 (2004) 301.
[6] Ushula Mengesha, Teketel Yohannes, *Solar Materials and Solar Cells*, 90 (2006) 3508.
[7] Tesfalidet Lemma and Teketel Yohanness, *J. Braz. Chem. Soc.*, 18 (2007) 818.
[8] Ashenafi Asrat, Assefa Sergawie, Teketel Yohannes, *SINET: Ethiopian J. Sci., In Print, (2008)*

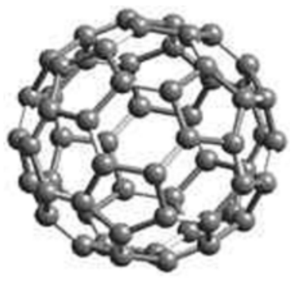
Solid-State Conducting Polymer/C_{60} PEC



(a)

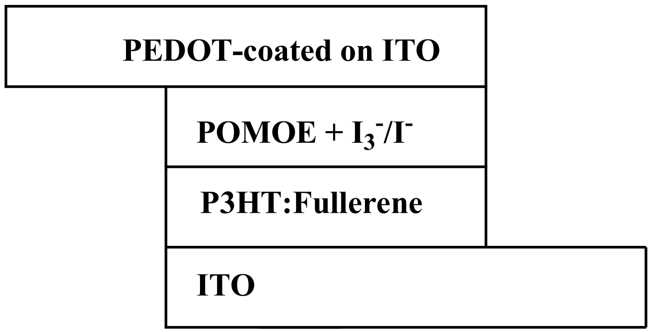


(b)



(c)

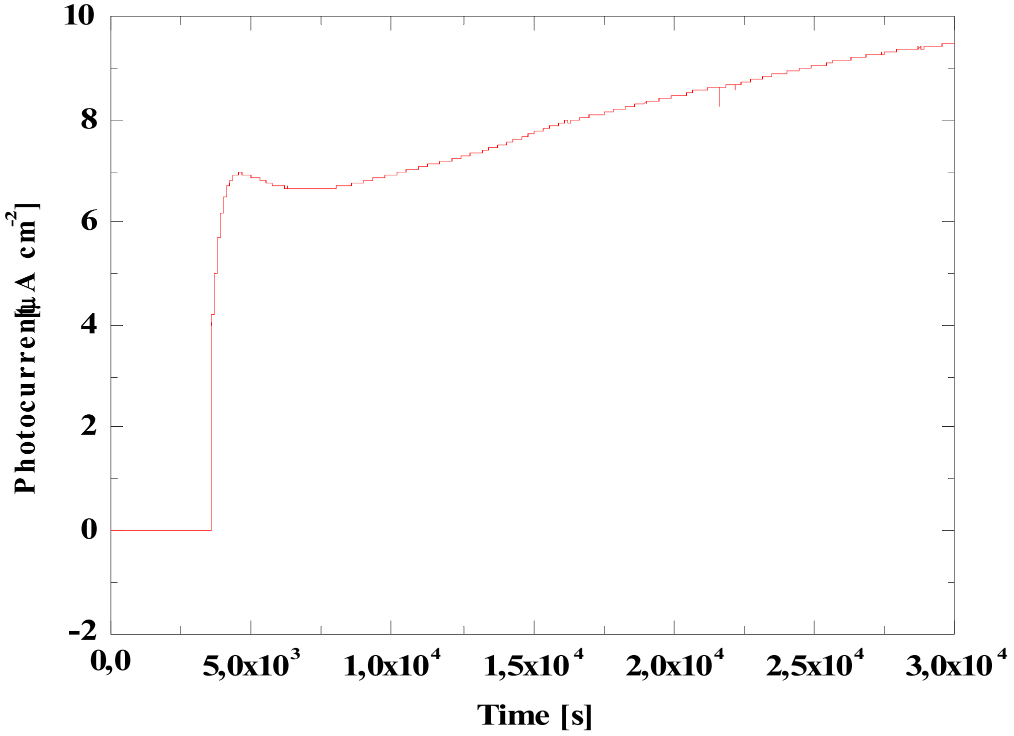
$-(CH_2O[CH_2CH_2O]_9)-$



(d)

The chemical structure of (a) poly(3-hexylthiophene). P3HT, (b) poly(3,4-ethylenedioxythiophe), PEDOT, and (c) fullerene, C_{60}, and (d) the basic structure of the solid state PEC.

Solid-State Conducting Polymer/C_{60} PEC



Photocurrent response to continuous illumination with light intensity of 100 mW/cm² for P3HT:C60 based solid-state PEC

Ushula Mengesha and Teketel Yohannes, Solar Energy Materials and Solar Cells, 90 (2006) 3508.

Photoactive layer	V_{oc} (mV)	I_{sc} (μA/cm²)
Pure P3HT	130	0.47
P3HT:C_{60}	98	7.28

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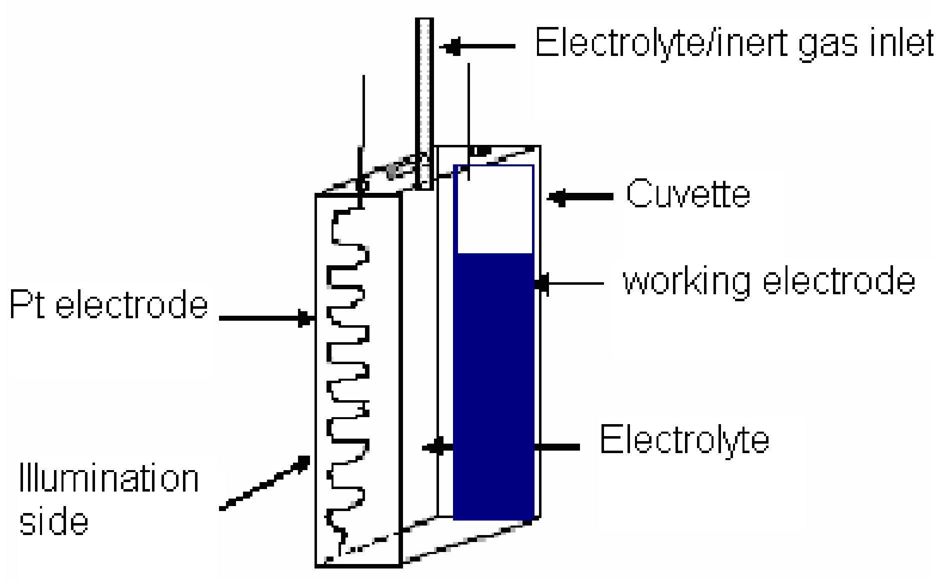
Liquid State Organic/Inorganic PECs

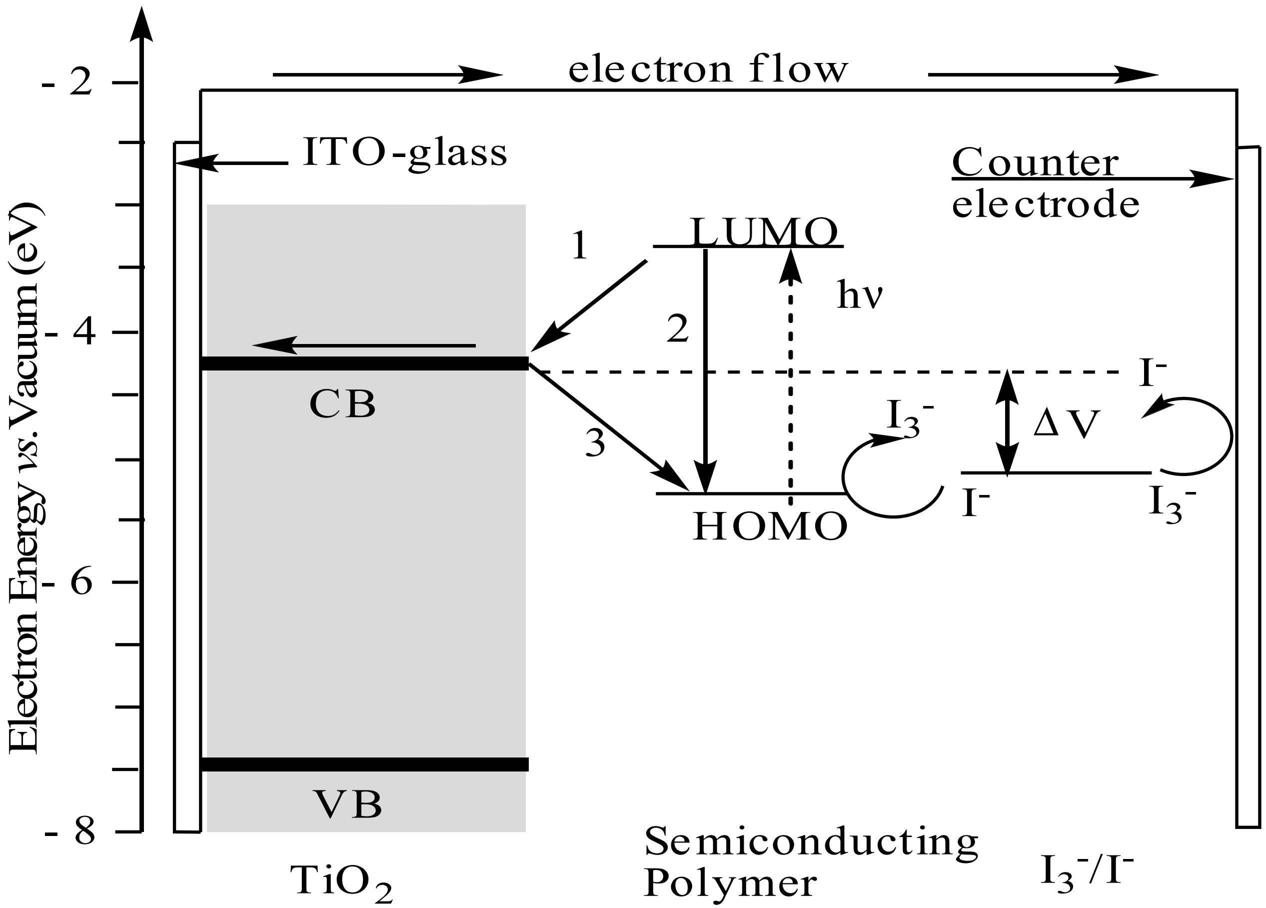
The device structure of the liquid-state PEC

Working Electrode:
ITO/Polymer
or
ITO/TiO_2/Polymer



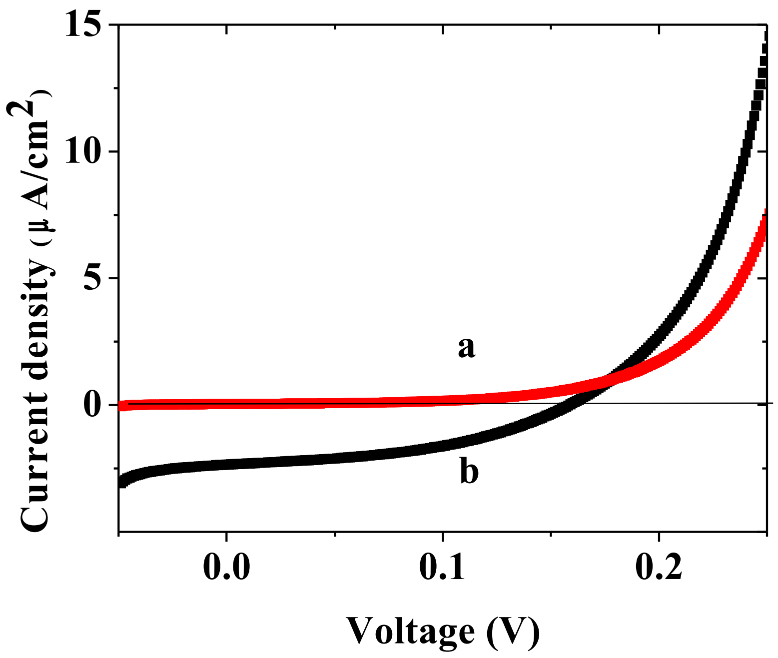
•A。 Sergawie, Teketel Yohannes, S. Guenes, H. Neugebauer, and N. S. Sariciftci, , *J. Braz. Chem. Soc.*, 18(2007) 1189.
•A。 Sergawie, S。 Admassie, W。 Mammo, Teketel Yohannes and T。 Solomon , *Synth. Met.*, 158 (2008) 307.
•A。 Sergawie, Teketel Yohannes and T。 Solomon, *Synth. Met.* 157 (2007) 75.
•A。 Sergawie, Teketel Yohannes and 。T。 Solomon, *Bull. Chem. Soc. Eth.*, 21 (2007) 281.
•A。 Sergawie, S。 Admassie, W。 Mammo, Teketel Yohannes and T。 Solomon, *Bull. Chem. Soc. Eth.,*, 21 (2007) 405.

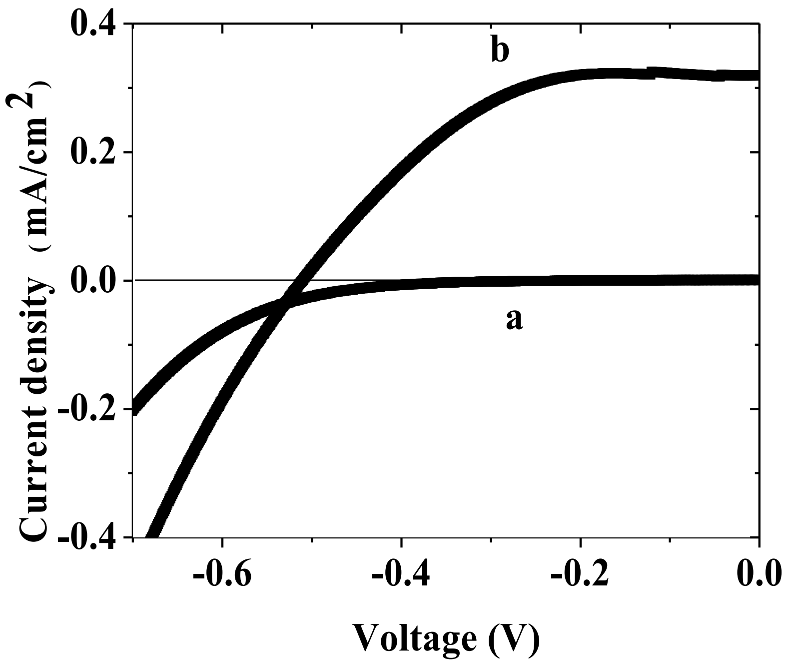
Operation Principle



Current-Voltage Characteristics

Chemically synthesised P3HT





ITO/P3HT **ITO/TiO_2/P3HT**

A。 Sergawie, Teketel Yohannes, and T。 Solomon, Synth. Met. 157 (2007) 75.

Devices Parameters: TiO_2/P3HT *Versus* P3HT

The photoelectrochemical devices parameters containing P3HT and TiO_2/P3HT photoactive electrodes. Light intensity of 100 mW/cm^2.

A。 Sergawie, Teketel Yohannes and T。 Solomon, Synth. Met. 157 (2007) 75.

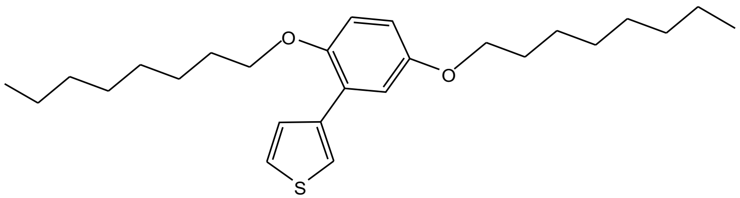
Photoactive layer	I_{sc} ($\mu A/cm^2$)	V_{oc} (mV)	FF	η (%)
P3HT	2.4	160	0.42	1.6×10^{-4}
TiO_2/P3HT	320	510	0.51	0.1

Electrochemical Synthesis

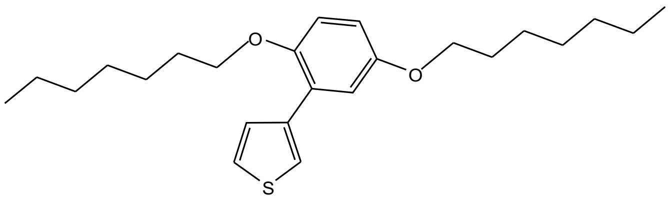
Monomers:

a) 3-(2′,5′-dioctyloxyphenyl)thiophene, DOOPT
b) 3-(2′,5′-diheptyloxyphenyl)thiophene, DHOPT
c) 3-(2′,5′-dibutyloxyphenyl)thiophene, DBOPT

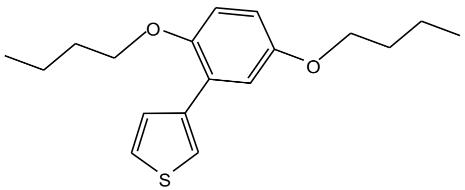
(a)



(b)



(c)



Method: cyclic voltammetry

Substrates: ITO-glass, TiO_2 coated ITO-glass and glassy carbon in a three-electrode cell.

Electrodes: RE (quasi) = Ag/AgCl, CE = Pt

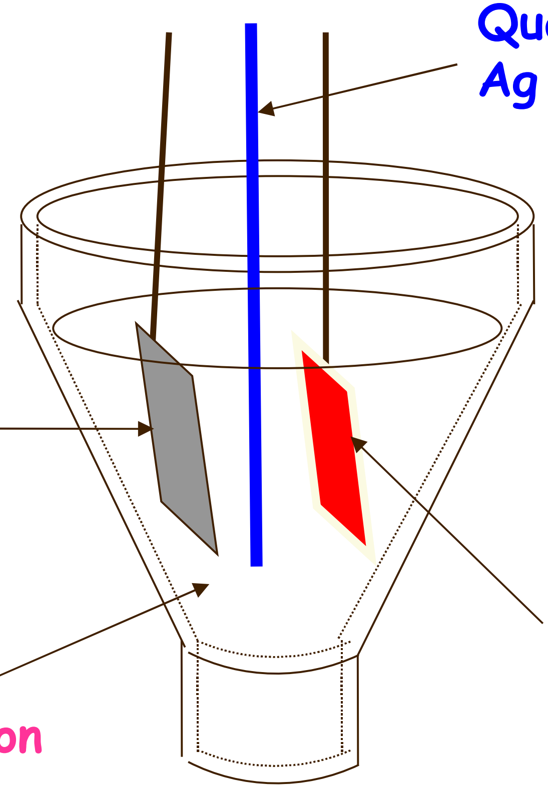
Solution: 1 mM of the monomers in 0.1 M $LiClO_4/CH_3CN$.

For solar cell applications, the polymers were dedoped to their neutral states.

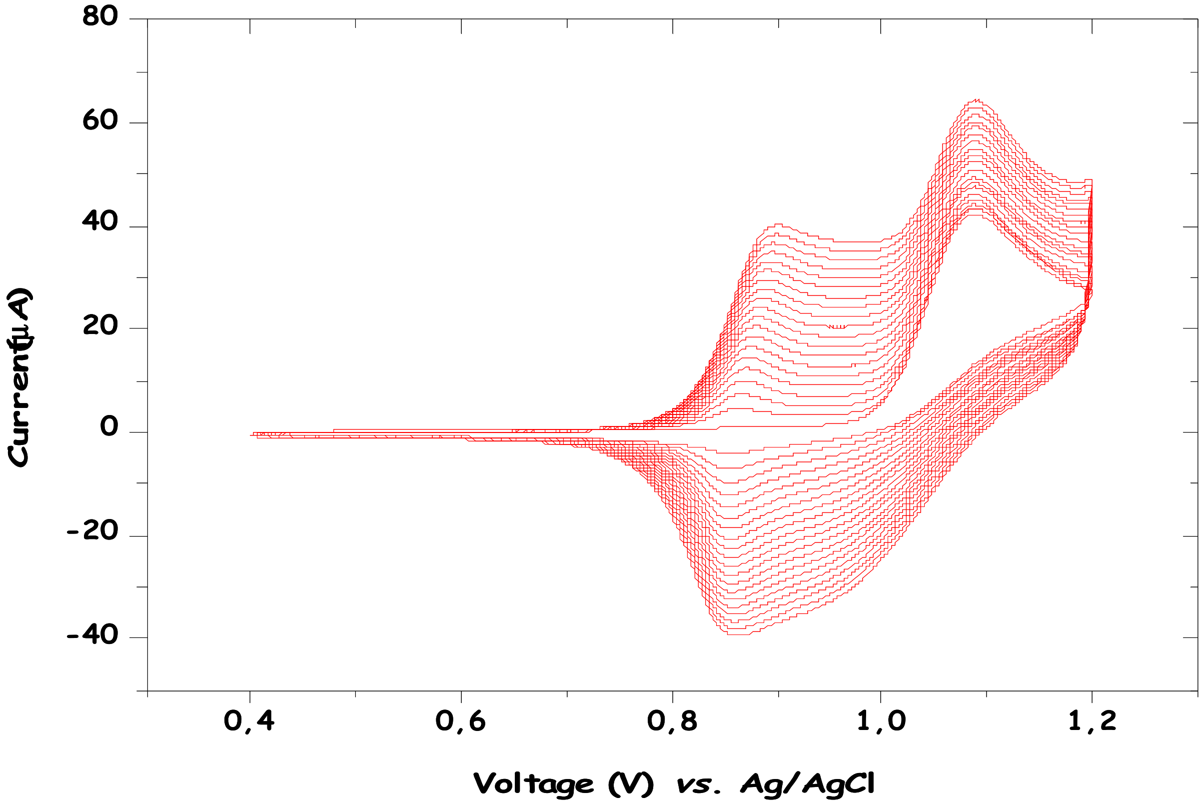
Electrochemical Cell

Electrochemical synthesis of polymers:

- PDOOPT
- PDHOPT
- PDBOPT

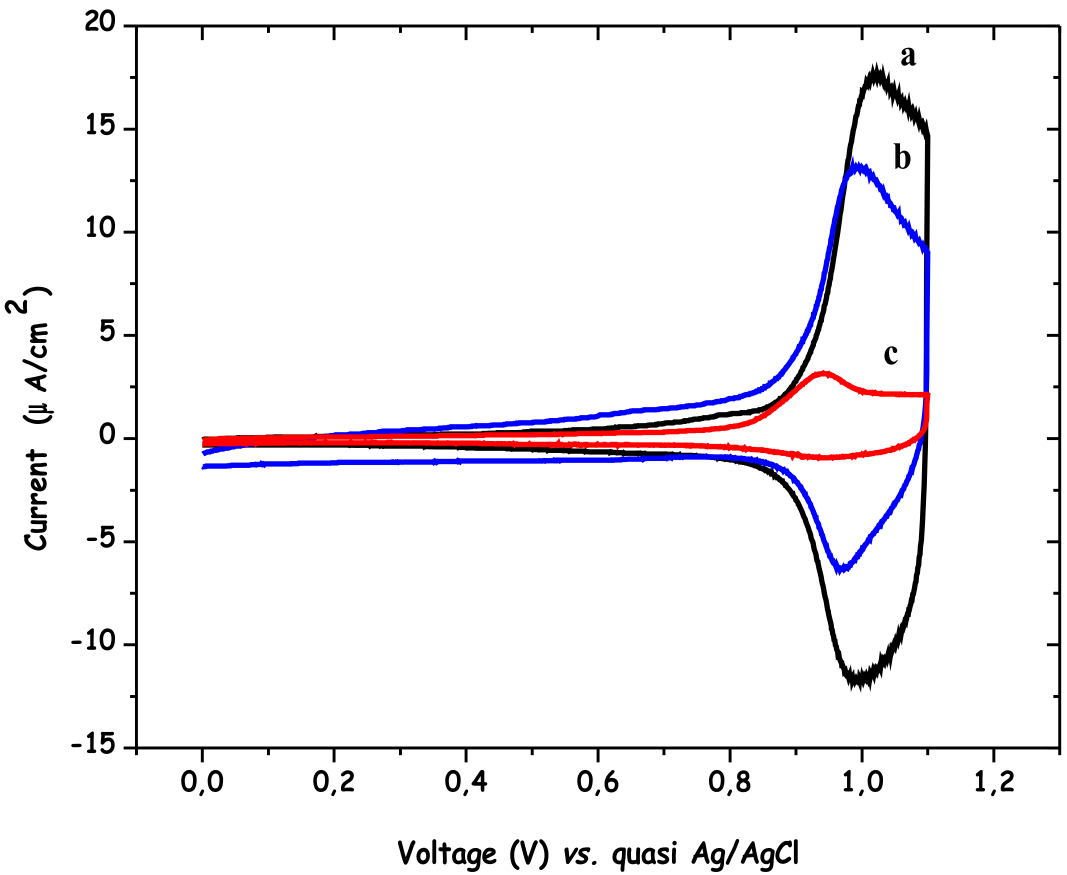


Cyclic Voltammogram of Monomer Oxidation



Cyclic voltammogram for the electropolymerization of DHOPT on glassy carbon disk electrode in CH_3CN solution containing 1 mM of the monomers and 0.1 M of TEATFB recorded at a scan rate of 10 mV/s.

Cyclic Voltammogram of Polymers

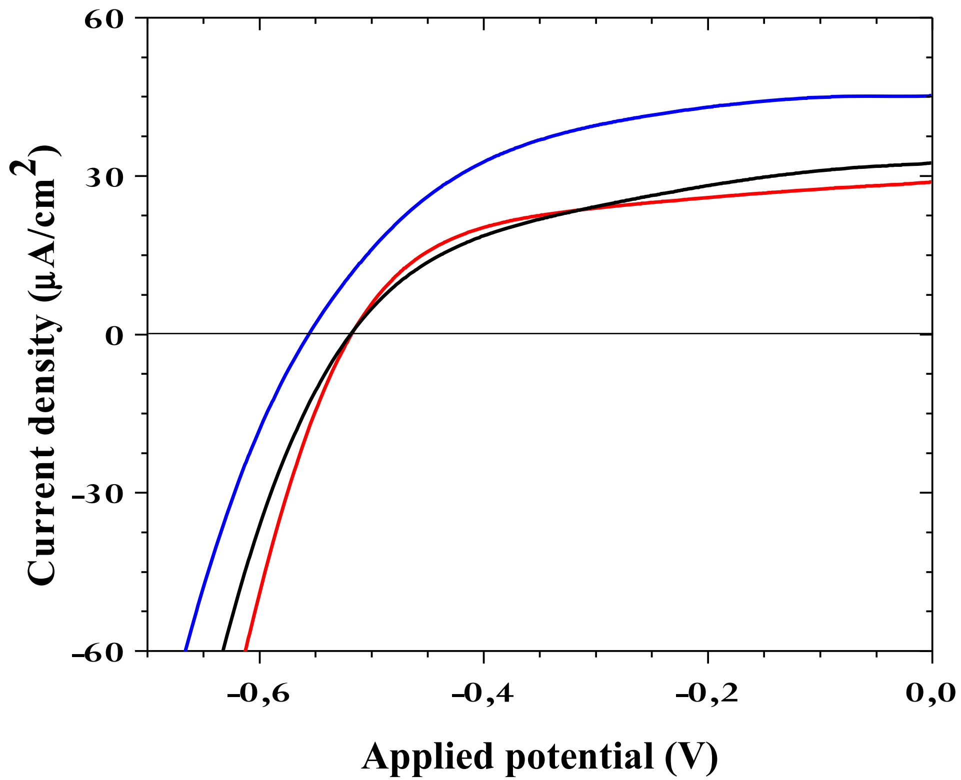


Cyclic voltammogram of
(a) PDOOPT
(b) PDHOPT and
(c) PDBOPT

On glassy carbon disk electrode recorded in a 0.1 M TEATFB/CH_3CN solution at a scan rate of 10 mV/s.

A. Sergawie, S. Admassie, W. Mammo, Teketel Yohannes and T. Solomon, *Synth. Met.*, 158 (2008) 307.

Current-Voltage Characteristics



I-V characteristics of the polymer/TiO_2 based PEC under white light illumination from the backside with light intensity of 80 mW/cm^2:

PDHOPT (Blue line), PDOOPT (Black line) and PDBOPT (Red line).

A。 Sergawie, S。 Admassie, W。 Mammo, Teketel Yohannes and T。 Solomon, *Synth. Met.*, 158 (2008) 307.

PEC Performance Parameters

PEC performance parameters of PDOOPT/TiO_2, PDHOPT/TiO_2 and PDBOPT/TiO_2 based devices

Photoactive Electrode	V_{oc} (mV)	I_{sc} ($\mu A/cm^2$)
PDOOPT/TiO_2	-520	32
PDHOPT/TiO_2	-520	28
PDBOPT/TiO_2	-560	45

Conclusions

- Solid-State PEC: prevent problems encountered in liquid state PEC such as leakage, packaging etc.
- Fullerene: improves PEC performance
- Conducting polymers: possible sensitizer

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