

PHOTOELECTROCHEMICAL CELL AND ITS APPLICATION

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&

BIO-TECH

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MARCH 2021

(I)

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CANDIDATE'S DECLARATION

We (**AAYUSH KHERA 2K20B1577 AND VIREIN HARJANI 2K20B1579**) students of bachelor of technology (**ENVIROMENTAL AND BIOTECH**) hereby declare that the dissertation titled "**PHOTOELECTROCHEMICAL CELL AND ITS APLPLICATIONS**" which is submitted by us to the Department of Applied Physics, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Bachelor of Technology, is original and is not copied from any source without proper citation. This work has not previously formed the basis of any award of any degree, diploma associateship, fellowship or any other similar title or recognition.

Place:Delhi

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CERTIFICATE

I, hereby certify that the project dissertation named **PHOTOELECTROCHEMICAL CELL AND ITS APPLICATIONS**” which is submitted by Aayush Khera(2k20b1577)

& Virein Harjani(2k20b1579) , Delhi Technological University, Delhi in complete fulfilment of the requirement for the award of the degree of the Bachelor of Technology, is a record of the project work carried out by the students under my supervision. To the best of my knowledge, this work has not been submitted in part or full for any degree or diploma to this University or elsewhere.

Place: Delhi

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ABSTRACT

This report is a study based on PHOTOELECTROCHEMICAL CELL, its modern application and its significance in Optoelectronics. Photoelectrochemical cell is used to convert light energy into electricity with efficiencies competing with silicon based photovoltaics. This report will focus on the area of photoelectrochemical cell and its application is optoelectronics ie electrochemical photovaltic cells, dye sensetized solar cells and light emitting cells. Most recent advances in the above area are included in the report. The report also cites information from an [Article in International Journal of Electrochemical Science](#) .

December 2007 by **GEHAN AMARATUNGA** UNIVERSITY OF CAMBRIDGE

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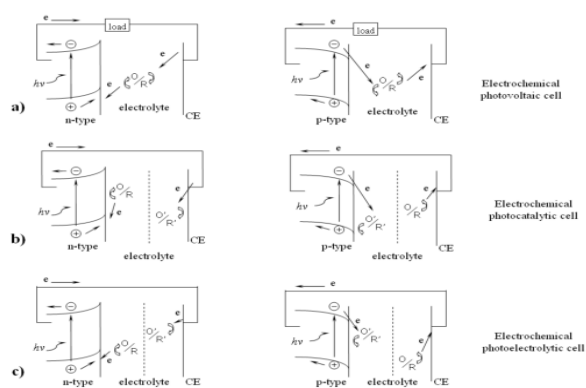
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INTRODUCTION

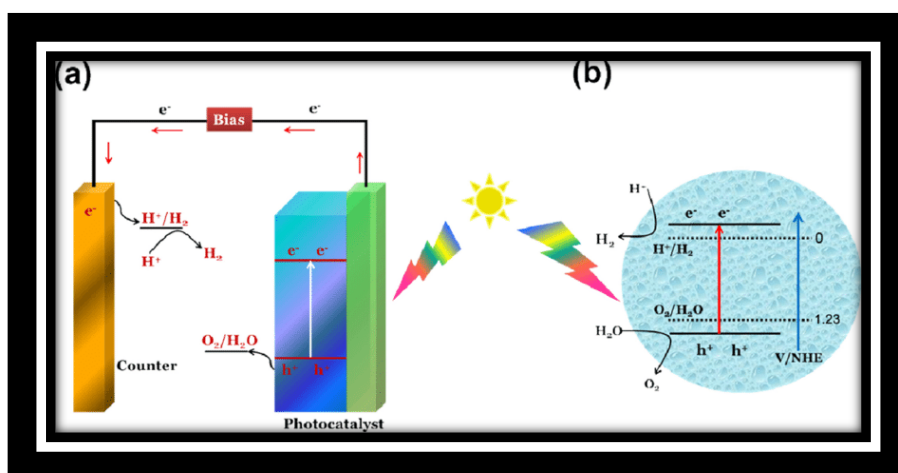
The first photovoltaic cell ever designed was also the first photoelectrochemical cell. It was created in 1839, by Alexandre-Edmond Becquerel, at age 19, in his father's laboratory. A typical type of the photocurrent-generated device has a semiconductor in contact with an electrolyte, and this is often referred as photoelectrochemical cells. A photoelectrochemical cell consists of a photoactive semiconductor working electrode (either n- or p-type) and counter electrode made of either metal (e.g. Pt) or semiconductors. Both electrodes are immersed in the electrolyte containing suitable redox couples. In a metal-electrolyte junction, the potential drop occurs entirely on the solution site, whereas in a semiconductor-electrolyte junction, the potential drop occurs on the semiconductor site as well as the solution site. The charge on the semiconductor side is distributed deep in the interior of the semiconductor, creating a space charge region. If the junction of the semiconductor-electrolyte is illuminated with a light having energy greater than the bandgap of the semiconductor, photogenerated electrons/holes are separated in the space charge region. Photogenerated majority carriers accumulate at the backside of the semiconductor. With the help of a connecting wire, 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 photocurrent between two platinum electrodes immersed in the 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]. The interest in photoelectrochemistry of semiconductors led to the discovery of wet-type photoelectrochemical solar cells [3-5]. These studies showed electron transfer to be the prevalent mechanism for photoelectrochemical sensitization processes. Grätzel has then extended the concept to the dye sensitized solar cells (DSSC), which will be discussed further in the later part.



Scheme 1 Different types of photoelectrochemical cells with the working electrode (WE) made of semiconductor (n- or p-type) and the counter electrode (CE).

WORKING

Scheme 1 shows various types of the photoelectrochemical cells. When shining the light, oxidation reaction will happen on the surface of n-type semiconductors, whilst reduction reaction will happen on the surface of p-type semiconductors. In the electrochemical photovoltaic cell, which is based on a narrow bandgap semiconductor and a redox couple as shown in Scheme 1a, optical energy is converted into electrical energy without change of the free energy of the redox electrolyte ($G=0$). The electrochemical reaction occurring at the counter electrode (CE) is opposite to the photoassisted reaction occurring at the semiconductor working electrode. Thus, they are also called regenerative photoelectrochemical solar cells [6-9]. If the photogenerated energy is converted to chemical energy, the free energy of the electrolyte will have a change ($G \neq 0$). Depending on the relative location of the potentials of the two redox couples (O/R and O'/R' in Scheme 1 b and c), the photosynthetic cells containing two redox couples, can be further classified as photocatalytic cell ($G < 0$, Scheme 1b) where light merely serves to accelerate the reaction rate and photoelectrolytic cell ($G > 0$, Scheme 1c) where the cell reaction is driven by light in the contra-thermodynamic direction. Comparing with electrochemical photovoltaic cells, anodic and cathodic compartments need to be separated to prevent the mixing of the two redox couples in these types of cells. Titanium dioxide (TiO_2) has been favoured semiconductor for such studies [10]. As early as 1971, photoelectrolysis of water was reported in an electrochemical cell with a TiO_2 photoanode and a Pt cathode without an external source [11]. A novel microreactor for TiO_2 -assisted photocatalysis in a microfluidic electrochemical cell was designed recently with TiO_2 nanoparticles embedded in a gold electrode matrix [12]. The metal ions in aqueous solution can be determined by voltammetry after in situ photocatalytic digestion of interfering organic matter. This is very important for environmental analysis



(VIII)

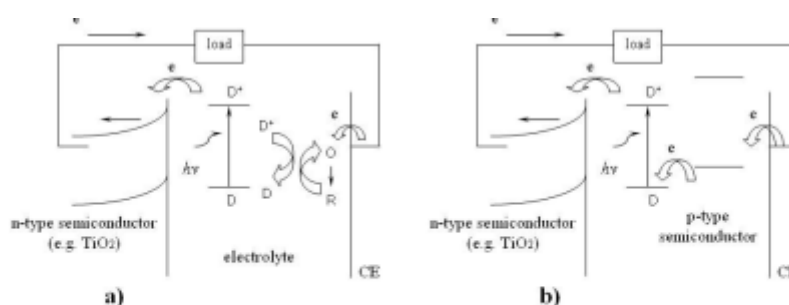
ELECTROCHEMICAL PHOTOVOLTAIC CELLS

1. Electrochemical photovoltaic cells without dyes

The most striking difference between a photoelectrochemical photovoltaic cell and the conventional 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. In electrochemical photovoltaic cells without dyes, both the semiconductor electrode and the counter electrode are immersed in the redox electrolyte. The incident light excites 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 as shown in Scheme 1a. In these kinds of cell, charge balance due to oxidation and reduction processes is maintained. However, the wet-type photoelectrochemical cells suffer from instability of semiconductor in aqueous media. Unsensitized photoelectrochemical photovoltaic cells can not replace the silicon based photovoltaics unless some photoelectrochemically stable semiconductor materials possessing band gap approximately 1.4 eV can be found.

2. Dye sensitized solar cells (DSSC)

A novel solar cell based on a dye sensitized porous nanocrystalline TiO₂ photoanode with attractive performance has been reported by Grätzel et al. [13-16]. Interest in porous semiconductor matrices permeated by an electrolyte solution containing dye and redox couples has been stimulated by their reports. The conversion efficiency of the dye sensitized solar cells (DSSC) has been currently improved to above 11% [15;17] since the first DSSC was reported with efficiency of 7.1% [16]. Even though silicon champion cells have attained 24%, the maximum conversion efficiency is approximately 30% for both devices [18]. Large-size DSSC has been prepared on silver grid embedded fluorine-doped tin oxide (FTO) glass substrate by screen printing method [19]. Under the standard test condition, energy conversion efficiency of active area was achieved to 5.52% in 5 cm×5 cm device, which is comparable to 6.16% of small-size cell prepared at similar condition. In DSSC, the initial photoexcitation does not occur in the semiconductor working electrode as the electrochemical photovoltaic cells in Scheme 1a, but occurs in the light absorbing dye as shown in Scheme 2. Subsequent injection of an electron from the photo-excited dye into the conduction band of semiconductors results in the flow of current in the external circuit. Sustained conversion of light energy is facilitated by regeneration of the reduced dye (D in Scheme 2) either via a reversible redox couple (O/R), which is usually I₃⁻/I⁻ (Scheme 2a) or via the electron donation from a p-type semiconductor. The need for DSSC to absorb far more of the incident light was the driving force for the development of mesoscopic semiconductor materials with an enormous internal surface....area....High photon to electron conversion efficiencies were reported based on the dye sensitized mesoporous TiO₂ solar cells [20]. The major breakthrough in DSSC was the use of a high surface area nanoporous TiO₂ 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. TiO₂ became the semiconductor of choice with advantage properties of cheap, abundant, and non-toxic.



Scheme 2 Operation mechanism of the dye sensitized electrochemical solar cell (DSSC). D: Dye, O: Oxidant (e.g. I₃⁻), R: Reductant (e.g. I⁻). a) Wet-type DSSC with redox couple in the liquid electrolyte b) Solid state DSSC with a p-type semiconductor to replace the electrolyte containing the redox couple.

(X)

3.Storage of electrochemical energy

It is also possible to make a rechargeable battery with in situ storage capability by using the photoelectrochemical cells.

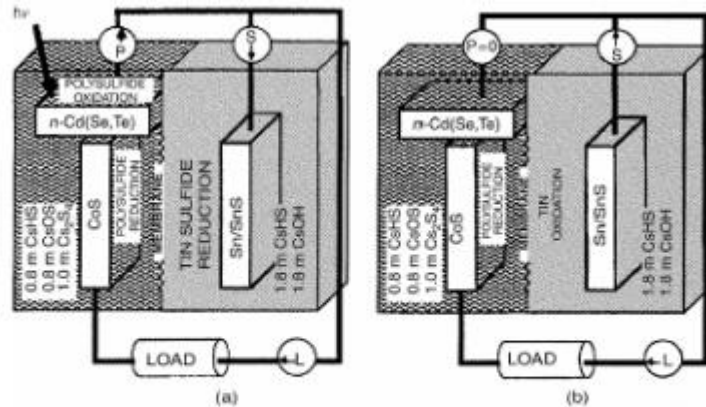


Figure 2. Schematic of a photoelectrochemical solar cell combining both solar conversion and storage capabilities. (a) under illumination, (b) in the dark. [77] Reproduced by kind permission from Nature.

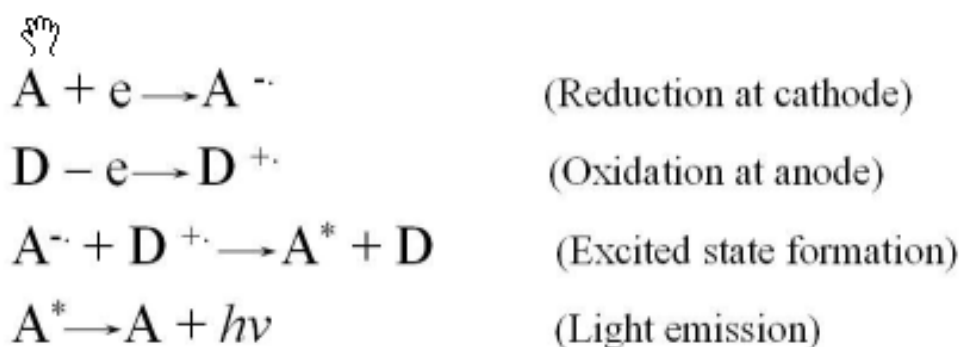
Fig. 2 presents the configuration of a photoelectrochemical cell combining in situ electrochemical storage and solar conversion capabilities and it provides continuous output insensitive to daily variations in illumination. A high solar to electric conversion efficiency cell configuration of this type was demonstrated in 1987 and used a Cd (Se, Te)/Sx conversion half cell and a Sn/SnS storage system, resulting in a solar cell with a continuous output [77]. Under illumination, as shown in Fig. 2a, the photocurrent drives an external load. Simultaneously, a portion of the photocurrent is used in the direct electrochemical reduction of metal cations (Sn^{2+}/Sn) in the device storage half cell. In darkness or below a certain level of light, the storage compartment spontaneously delivers power by metal oxidation (Sn/Sn^{2+}) as seen in Fig. 2b. This genius idea was further developed and the DSSC performance was improved significantly by using multi-band gap cells with storage.

ELECTROCHEMICAL LIGHT EMITTING CELLS

The reverse process of electrochemical photovoltaic cells is the electrochemical light emitting cells, which consists part of optoelectronics.

1. Electrochemiluminescence

Electrochemiluminescence (ECL) is the process where species generated at electrodes undergoes electron transfer reactions to form excited states that emit light. ECL is initiated and controlled by changing an electrode potential. Classic ECL involves the formation of an excited state as a result of an energetic electron transfer between electrochemically generated species (often radical ions) at the surface of an electrode. ECL reactions are localized spatially, temporally and controllable. A typical ECL system would involve a solution containing ECL precursors with supporting electrolyte in an electrochemical cell with either a single working electrode using an alternative potential, or more commonly two separated electrodes in close proximity to each other by holding one electrode at a reductive potential and the other at an oxidative potential. (XII)



Scheme 3. General mechanism of electrochemiluminescence.

A general ECL mechanism with two-electrode set up is shown in Scheme 3. Species A accepts one electron from the cathode to form A⁻, and species D loses one electron at the anode to form D⁺. When A⁻ and D⁺ diffuse away from the electrodes and come together, A⁻ transfers one electron to D⁺ to produce a neutral species D and the excited state A*. A* immediately emits light and returns to the ground state A. A and D could be the same species such as a polycyclic aromatic hydrocarbon. ECL is traditionally a very powerful analytic technique and has been widely used in many different areas. In this review, use of electrochemiluminescence in light emitting cells will be focused.

2. Polymer electrochemical light emitting cells

Device configurations for light emission from electroactive polymers and organic molecules have been described by many papers [92-99]. In these kinds of electrochemical light emitting cells (LEC), a *p-n* junction diode is created in situ through simultaneous *p*-type and *n*-type electrochemical doping on opposite sides of a thin film of conjugated polymer that contains added electrolyte to provide the necessary counterions for doping. Besides using liquid electrolytes, polymer electrolytes were also applied by complexation of an ionically conducting polymer, such as polyethylene oxide (PEO) with salts. In contrast to the traditional light emitting diodes (LEDs) where the active layer does not contain any ionic species, a polymer LEC is based on a mixed ionic/electronic conductor consisting of a solid state polymer electrolyte and a luminescent polymer. The polymer electrolyte contributes and transports free ions. Cyclic voltammetry studies have been carried out on polymer electrochemical LEC using poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH-PPV, as the active luminescent polymer [92]. The onset of electronic current in the LEC is coincident with the onset of electrochemical doping and the formation of a *p-n* junction. Blue, green, and orange emission have also been obtained with turn-on voltages close to the band gap of the emissive material [93]. Polymer electrochemical LECs possess many desirable device characteristics suitable for potential display applications. The operating mechanism of this type of LEC involves in situ electrochemical doping and the formation of a light emitting *p-n* junctions, which have been confirmed by the demonstrations and direct imaging of extremely large planar LECs with an interelectrode spacing up to 1.1 to 1.5 mm as shown in Fig. 4 [100-102]. When a large enough voltage is applied, electrons and holes are injected to the cathode and anode individually and subsequently compensated by the insertion of free cations and anions between the polymer chains in the vicinity of the electrodes. As a result, the luminescent polymer is electrochemically doped to *p* type on the anode side and *n* type on the cathode side. With time the *p* and *n* doped regions expand

towards the centre of the device until they make contact to form a p-n junction. The position of the light emitting junctions can be determined by direct optical probing of the doping progress and simultaneous recording of the current-time behavior [103]. The initial formation of a p-n junction triggers a sharp increase in both doping level and current flow. This is accompanied by the onset of electroluminescence in the vicinity of the junction, caused by the radiative recombination of the injected electrons and holes.

High resolution fluorescence imaging of the LEC structures reveals two fundamental problems for a conventional LEC. First, the luminescent polymer suffers significant photoluminescence quenching due to heavy doping throughout the polymer film. Second, the electroluminescence emission zone in an LEC is limited to less than 10% of the entire inter-electrode spacing. Both factors severely limit the ultimate electroluminescence efficiency of an LEC.

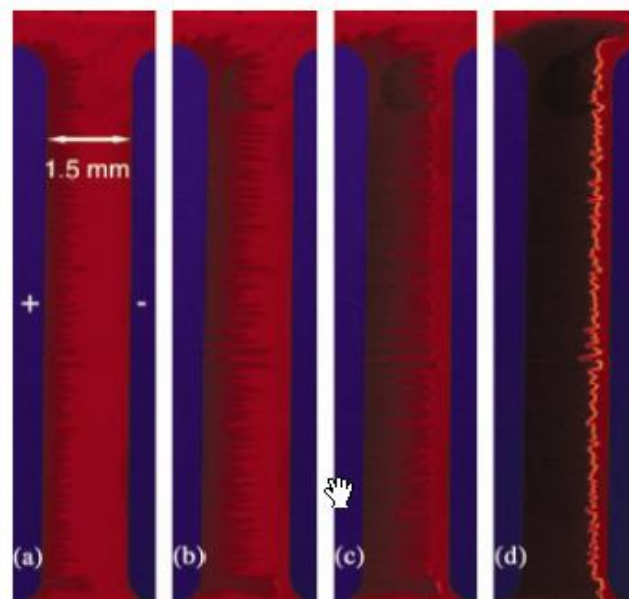
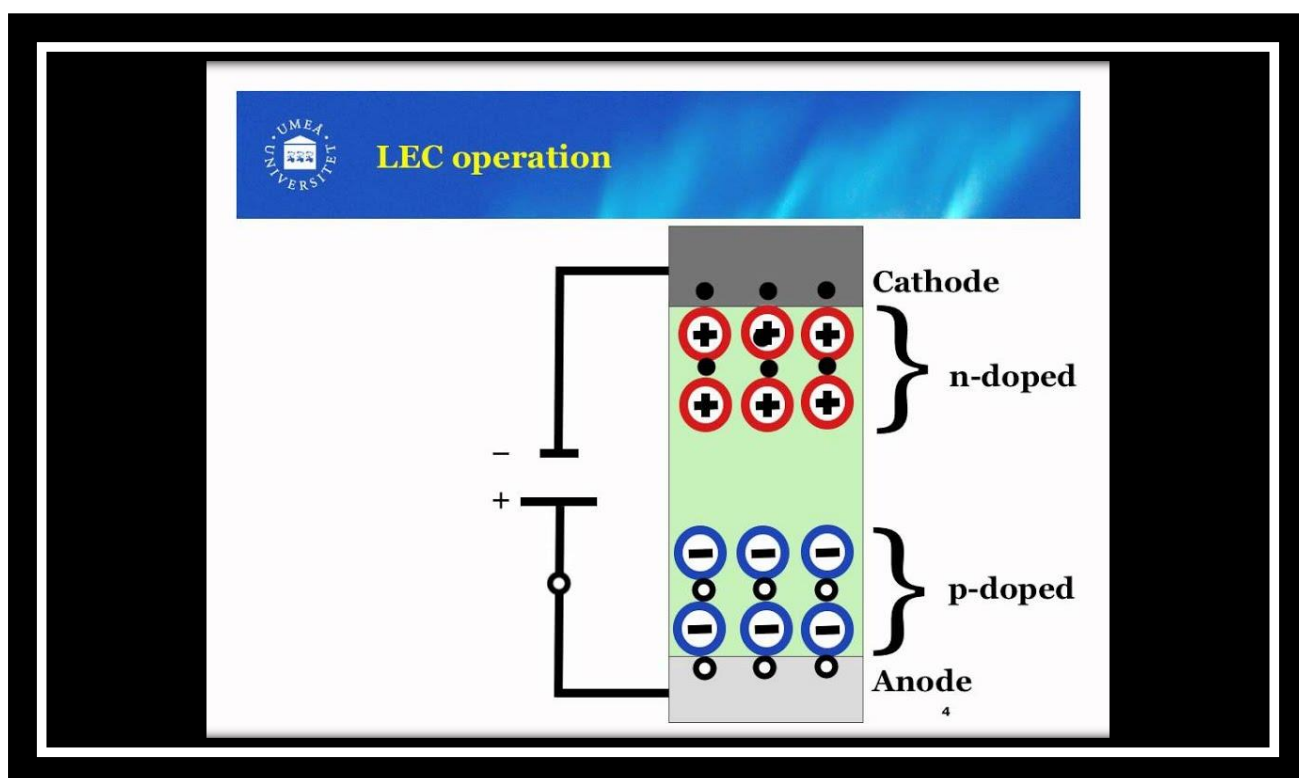


Figure 4. Colored photographs of a working 1.5 mm MEH-PPV polymer LEC under 365 nm UV illumination. The device was tested at 310 K under a voltage bias of 140 V. The electrode to the left is positively biased anode, denoted as '+' relative to the electrode to the right cathode, denoted as '-'. The photographs were taken at different time after the application of the voltage bias: (a) 8 min; (b) 13 min; (c) 18 min; (d) 43 min. [100] Reproduced by kind permission from American Institute of Physics.

3.OTHERS

Use of organic conjugated materials has also been exploited for the realization of electrochemically driven electrochromics . Recently, a photoelectrochromic cell is fabricated with a silver counter electrode and a transparent working electrode coated with a Ag-TiO₂ nanocomposite, which exhibits multicolour photochromism in an electrolyte containing silver ions. The photoelectrochromic cell operates in drawing mode (short circuit) and display mode (open circuit), and is initialized by polarizaton. The concepts of drawing and display modes are important to develop practical display devices based on the multicolour photochromism.



(XVI)

CONCLUSION

Effective photovoltaics, light emitting and photoelectrochromic cells can be realized by means of electrochemical methods. Solid state DSSC and electrochemical light emitting cells will have a promising future for the development of efficient and flexible optoelectronics. Although a long way to compete with the silicon based ones in markets, the subject of photoelectrochemistry is the fundamental and will be a vivid subject to realize the device design and technology transfer.

ELECTROCHEMICAL PHOTOVOLTICS VS SOLID PHOTOVOLTICS

One of the most important aspects in using solar energy is its conversion from solar radiation into electric energy.

Electrochemical photovoltaic cells have the following advantages comparing with the solid photovoltaics.

- A. It is not sensitive to the defects in semiconductors

- B. The solid/liquid junction is easy to form and the production price will be much reduced

- C. It is possible to realize the direct energy transfer from photons to chemical energy. Unlike conventional solid state photovoltaic cells, the potential of the working electrode can be varied with respect to the reference electrode by means of an external voltage source connected between working and counter electrode.

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