

Dye Sensitized Solar Cell

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ABSTRACT: The development of new types of solar cells is promoted by increasing public awareness that the earth's oil reserves could run out during this century. As the energy need of the planet is likely to double within the next 50 years and frightening climatic consequences of the greenhouse effect caused by fossil fuel combustion are anticipated, it is urgent that we develop a new kind of renewable energy to cover the substantial deficit left by fossil fuels. Since the prototype of a **Dye Sensitized Solar Cell (DSSC)** was reported in 1991, it has aroused intense interest owing to its low cost, simple preparation procedure, and benign effect on the environments. However, the potential problems caused by liquid electrolyte limit the long-term performance and practical use of DSSC. Therefore, much attention has been given to improving the light-to-electrical power conversion and replacing the liquid electrolytes by solid-state or quasi-solid-state electrolytes. This review will focus on progress in the development of improved electrolytes, especially quasi-solid-state electrolytes such as Titanium Dioxide (TiO₂) for DSSC's.

Keywords: dye-sensitized solar cells; liquid electrolytes; solid-state electrolytes; quasi-solid state electrolytes ; photoelectric performance; long-term stability.

I. INTRODUCTION

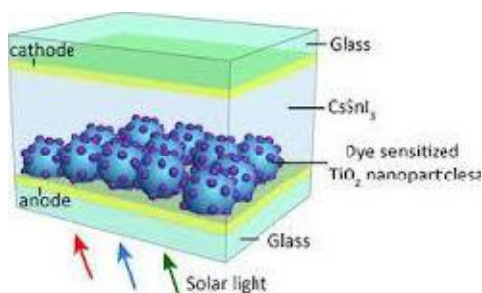
The prototype of a DSSC was reported in 1991 by M. Gratzel. In **Gratzel Cells** the functions of light absorption and charge-carrier transportation are separated. Although the solar power conversion efficiencies of DSSCs are lower than that of classical crystalline silicon cells. In DSSCs based on liquid electrolytes, a photoelectric conversion efficiency of 11 % has been achieved. However, the potential problems caused by liquid electrolytes, such as the leakage and volatilization of solvents, possible desorption and photo-degradation of the attached dyes, and the corrosion of Platinum counter electrode, are considered as some of the critical factors limiting the long-term performance and practical use of DSSCs. It is believed that quasi-solid-state electrolytes, especially those utilizing thermosetting gels, are particularly applicable for fabricating high photoelectric performance and long-term stability of DSSC in practical applications.

Here we describe a photo voltaic cell created from low to medium purity materials through low cost processes, which exhibits commercially realistic energy conversion efficiency. The device is based on a 10µm thick, optically transparent film of Titanium dioxide particles a few nanometres in size, coated with a mono layer of a charge- transfer dye to sensitize the film for a light harvesting. Because of a high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux(46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current(>80%). The overall light-to-electric energy conversion yield is 7.1-7.9% in simulated solar light and 12%N in diffuse daylight. The large current densities (>12mAcm⁻²) and exceptional stability (sustaining at least 5million turnovers without decomposition), as well as the low cost, make practical applications feasible.

II. STRUCTURE AND PRINCIPLES OF DSSC

DSSCs include a substrate of fluorine-doped SnO₂ conducting glass (FTO), a porous nano-crystalline semiconductor oxide (TiO₂) film sensitized by a dye for absorbing visible light, a redox electrolyte (usually an organic solvent containing a redox system, such as iodide/tri-iodide couple) layer for deoxidizing oxidized dye, and a platinised cathode to collect electrons and catalyse the redox couple regeneration reaction. The light-to-electricity conversion in a DSSC is based on the injection of electron from the photo excited state of the sensitized dye into the conduction band of TiO₂. The dye is regenerated by electron donation from iodide in the electrolyte. The iodide is restored, in turn, by

the reduction of tri-iodide at the cathode, with the circuit being completed via electron migration through the external load.



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|---|----------------------|
| 1. $\text{TiO}_2 \text{S} + h\nu \rightarrow \text{TiO}_2 \text{S}^*$ | Excitation |
| 2. $\text{TiO}_2 \text{S}^* \rightarrow \text{TiO}_2 \text{S}^+ + e^-_{(\text{cb})}$ | Injection |
| 3. $\text{TiO}_2 2\text{S}^+ + 3\text{I}^- \rightarrow \text{TiO}_2 2\text{S} + \text{I}_3^-$ | Regeneration |
| 4. $\text{I}_3^- + 2e^-_{(\text{Pt})} \rightarrow 3\text{I}^-$ | Reduction |
| 5. $\text{I}_3^- + 2e^-_{(\text{cb})} \rightarrow 3\text{I}^-$ | Recaption |
| 6. $\text{TiO}_2 \text{S}^+ + e^-_{(\text{cb})} \rightarrow \text{TiO}_2 \text{S}$ | Recombination |

The electrolytes employed in DSSCs can be classified as liquid, solid-state, or quasi-solid-state.

Several aspects are essential for any electrolytes in a DSSC.

(1) The electrode must be able to transport the charge carrier between photo anodes and counter electrode. After the dye injects electrons into the conduction band of TiO_2 , the oxidized dye must be reduced to its ground state rapidly. Thus, the choice of the electrolyte should take into account the dye redox potential and regeneration of itself.

(2) The electrode must be able to permit the fast diffusion of charge carriers (higher conductivity) and produce good interfacial contact with the porous nano-crystalline layer and the counter electrode.

For liquid electrolytes, it is necessary to prevent the loss of the liquid electrolyte by leakage and/or evaporation of solvent.

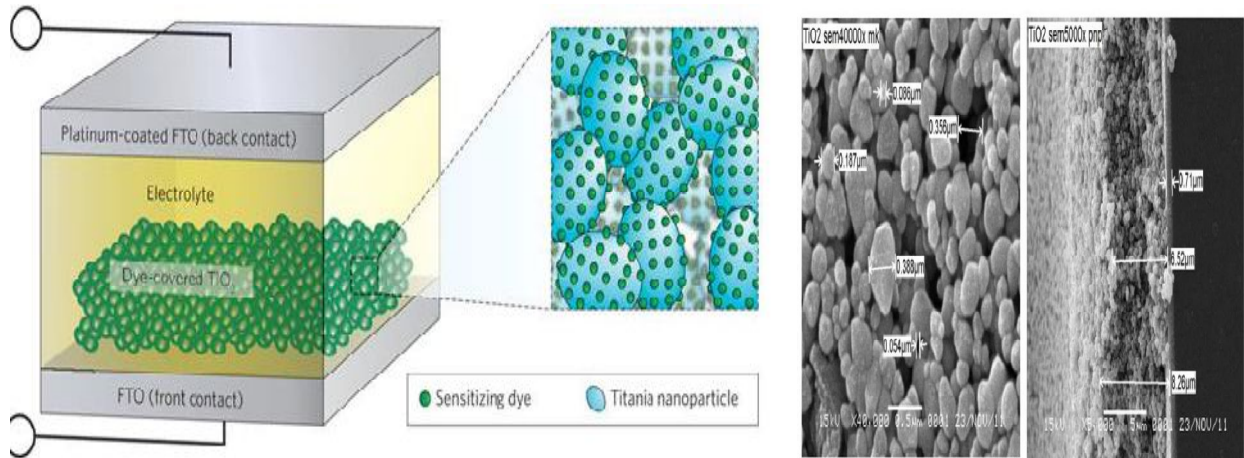
(3) The electrolyte must have long-term stability, including chemical, thermal, optical, electrochemical, and interfacial stability, which does not cause desorption and degradation of the dye from the oxide surface.

(4) The electrolyte should not exhibit a significant absorption in the range of visible light. For the electrolyte containing I^-/I_3^- redox couple, since I_3^- shows colour and reduces the visible light absorption by the dye, and I_3^- ions can react with the injected electrons and increase the dark current. Thus, the concentration of I^-/I_3^- must be optimized.

III. QUASI-SOLID-STATE ELECTROLYTES

The quasi-solid state, or gel state, is a particular state of matter, neither liquid nor solid, or conversely both liquid and solid. Generally, a quasi-solid-state electrolyte is defined as a system which consists of a polymer network (polymer host) swollen with liquid electrolytes. Owing to its unique hybrid network structure, quasi-solid-state electrolytes always possess, simultaneously, both the cohesive property of a solid and the diffusive transport property of a liquid. Namely, quasi-solid-state electrolytes show better long-term stability than liquid electrolytes do and have the merits of liquid electrolytes including high ionic conductivity and excellent interfacial contact property. These unique characteristics of quasi-solid-state electrolytes have been actively developed as highly conductive electrolyte materials for DSSCs, lithium secondary batteries, and fuel cells. Quasi-solid-state electrolytes are usually prepared by incorporating a large amount of a liquid electrolyte into organic monomer or polymer matrix, forming a stable gel with a network structure via a physical or chemical method. The quasi-solid-state electrolyte formed via physical cross-linking is called "entanglement network", which is thermo-reversible (thermoplastic). By contrast, chemical or covalent cross-linking leads to the formation of thermo-irreversible (thermosetting) gel electrolyte.

DSSC Based On Colloidal TiO₂ Films:



Dye-sensitized cells differ from the conventional semiconductor devices in that separate the function of light absorption from charge carrier transport. In the case of TiO₂, current is generated when a photon absorbed by a dye molecule gives rise to electron injection into the conduction band of the semiconductor. To complete the circuit the dye must be regenerated by electron transfer from a redox species. The monochromatic current yield.

$$J_i(\lambda) = LHE(\lambda) \times \phi_{inj} \times \eta_e$$

Where Light Harvesting Efficiency (LHE) is the fraction of the incident photons that are absorbed by the dye, ϕ_{inj} is the quantum yield for charge injection and η_e is the efficiency of collecting the injected charge at the back contact.

Although attempts to use dye sensitized photo electrochemical cells in energy conversion have been made before, the efficiency of such devices of such devices have been low. One problem is that poor light harvesting. On a smooth surface, a monomolecular layer of sensitizer absorbs less than 1% of incident monochromatic light. The remaining option is to increase the roughness of the semiconductor surface so that a larger number of dye molecules can be absorbed directly to the surface and can simultaneously be in direct contact with the redox electrolyte. By using semiconductor films consisting of nanometre sized TiO₂ particles, together with newly developed charge transfer dyes, the efficiency and stability of solar cell has been improved.

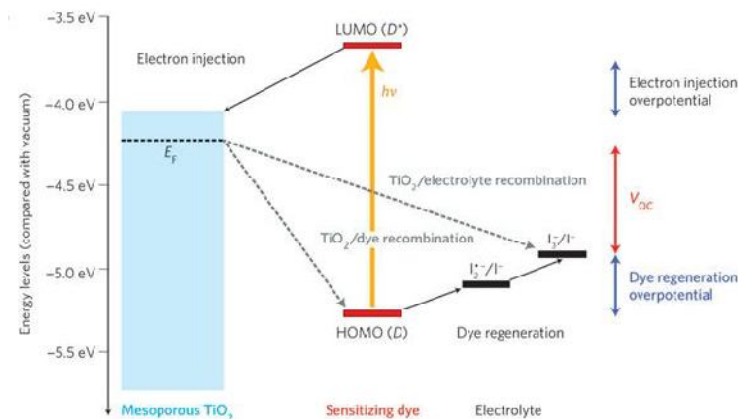
High surface area TiO₂ films were deposited on a conducting glass sheet from colloidal solutions. Electronic between the particles was produced by brief sintering at 450 °C. The size of the particles and pores making up the film is controlled by the size of the particles in the colloidal solution. The internal surface area of the film is determined by the size of the particles and the thickness of the films. These parameters were optimized to obtain efficient light harvesting while maintaining a pore size large enough to allow the redox electrolyte to diffuse easily. Films of 10µm thickness consisting of particles with an average size of 15nm gave linear photocurrent response up to full sunlight and were used throughout.

As each dye molecule occupies an area of 1nm², the inner surface of the film is 780cm² for each 1cm² of geometric surface. Thus, the roughness factor is 780, which is smaller than the predicted value of 2000.

The loss mechanisms such as recombination, normally encountered in semiconductor photo conversion, have been minimized. The role of semiconductor in dye-sensitized device is merely to conduct the injected majority charge carriers. There are no minority carriers involved in the photo conversion process. Therefore, surface and bulk recombination losses due to lattice defects, encountered in conventional photovoltaic cells, are not observed in such a device.

The long term stability of cell performance was tested by illuminating the thin TiO₂ film loaded with visible light for 2 months. The change in the photocurrent was less than 10% over this period, during which a charge of 62,000 C cm⁻² was passed through the device, corresponding to a turnover number of 5x10⁶ for the sensitizer. This implies that if any degradation had occurred its quantum yield is less than 2x10⁻⁸.

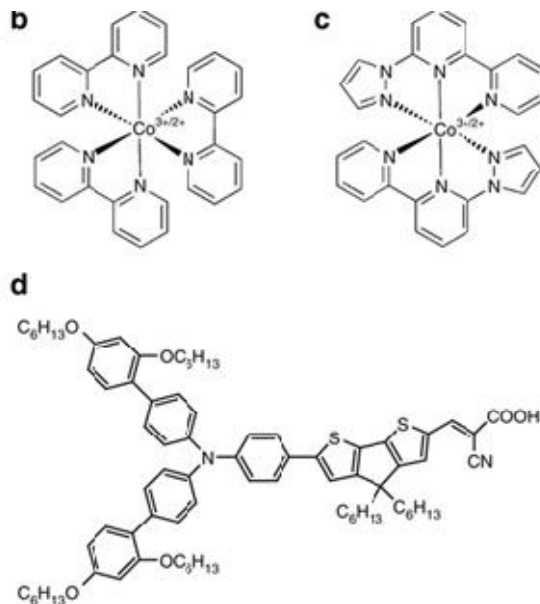
As $\Phi_{dec} = k_{dec}/\Sigma k$, the rate constant, $K_{dec} S^{-1}$, for excited state decomposition must be at least 10⁻⁸ times smaller than Σk , the sum of rate constants for all channels of dye deactivation. Because charge injection is the predominant channel, this sum is practically equal to the rate constant for charge injection which exceeds 10¹²S⁻¹. Therefore, the upper limit for k_{dec} is 2x10⁴S⁻¹, which agrees with the known photo physics of this class of transition metal complexes. The very fast electron injection observed with dyes such as, combined with high chemical stability, renders these compounds very attractive for practical development.



Thermoplastic Gel Electrolytes (TPGEs):

The formation of the TPGE is based on physical cross-linking of gelators to form an “entanglement network” to solidify liquid electrolyte. The main characteristic of this kind of gel electrolyte is the gel-sol-state reversible conversion with the change of temperature, which is a benefit of deep penetration of the electrolyte into mesoporous dye-coated nano-crystalline TiO₂ film. The interfacial contact between the electrolyte layer and nano-crystalline TiO₂ film or counter electrode is one of the most important factors influencing the photovoltaic performance of DSSCs besides the ionic conductivity of the gel electrolyte.

The TPGE contains gelator and liquid electrolyte, the liquid electrolyte consists of organic solvent, Redox couple, additive, or IL electrolyte system. The first thermoplastic polymer gel electrolyte used in DSSCs was reported. The electrolyte was composed of poly (acrylonitrile) (PACN), EC, PC, AcN and NaI. The light-to-electricity conversion efficiency of this DSSC was lower in comparison with that of the DSSC based on liquid electrolytes, due to the unoptimized components and the difficult penetration of the PACN network into nano-crystalline TiO₂ film. The high photovoltaic performance and excellent stability of DSSC was obtained by using a TPGE containing poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) combined with MePN-based liquid electrolyte containing 1,2-dimethyl-3-propyl imidazolium iodide and iodide. The DSSC showed a similar photovoltaic performance as that of an analogous cell containing the same liquid electrolyte, which means that the polymer matrix has no negative effect on the performance of DSSC.



Characteristics of TPGE:

(1) PEG contains many ether groups and polyhydric side groups, two kinds of groups can keep complexation with alkali metal ions such as potassium ions, sodium ions. Because of the interaction between PEG and PC and alkali metal iodide salts, the iodide anions can be separated from Alkali cations to form free anions.

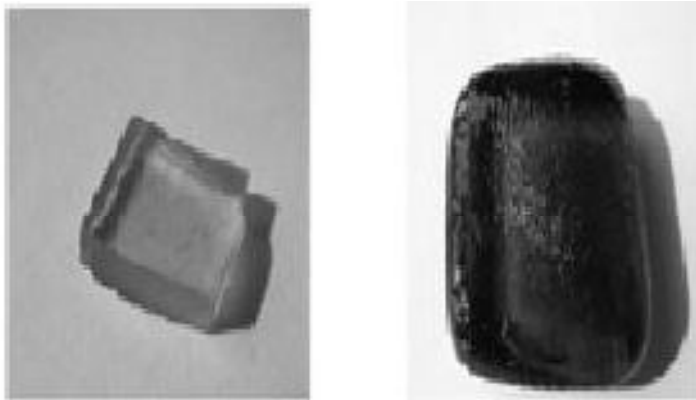
(2) The large amount of ether groups and polyhydric side groups on the PEG matrix can form a hydrogen bond with PC solvent, which hangs the molecule of solvent on the “entanglement network” of the polymer chain, and results in the formation of a stable thermo-reversible polymer gel electrolyte.

(3) The TPGE is in a solid state and shows the fluidity with a viscosity of 0.76 Pa s at a temperature higher than 50 °C, which makes for a deep penetration into the mesoporous dye-coated Nano-crystalline TiO₂ film, and forms a sufficient interfacial contact between electrolytes layer and nano-crystalline TiO₂ film and platinum counter electrode. Whereas at a temperature below 20°C, the TPGE is in a gel state with a viscosity of 2.17 Pa s. The reversible thermoplastic behaviour of the TPGE is very useful for sealing and assembling DSSCs.

The characteristic of the thermoplastic polymer gel electrolyte markedly depends on temperature. This is due to the fact that the increase of temperature causes a phase transfer from gel state to sol state, and a change of dominate conduction mechanism from Arrhenius type to Vogel–Tamman–Fulcher (VTF), which turns to the change of ionic conductivity of thermoplastic polymer gel electrolyte and photovoltaic performance of DSSC. The photovoltaic performance of DSSCs severely depends on the temperature, which is the typical characteristic of DSSCs based on this kind of polymer gel electrolyte.

**Thermosetting Gel Electrolytes (TSGEs):**

The TPGE is good for fabricating DSSCs. However, there is also a potential venture for actual application of DSSCs, which is the chemical instability, such as phase-separation, crystallization of iodide salts. Therefore, some more environmentally stable electrolytes are still needed. Among those optional methods, the TSGE is one of the good selections for high photovoltaic performance and good long-term stability of DSSCs. A high stable DSSC based on a TSGE containing ureasil precursors and organic liquid electrolyte containing iodide salts was prepared. The unique structure of this thermosetting Organic–inorganic hybrid gel electrolyte leads to the high quality of DSSC, which maintains 5–6 % light-to-electricity conversion efficiency even after preserving for several years.

**IV. CONCLUSIONS**

In this review, we introduce on Quasi-solid-state electrolytes for DSSCs. Although a light- to-electricity conversion efficiency of 11 % for DSSCs containing liquid electrolytes has been achieved, the potential problems caused by liquid electrolytes, such as leakage and volatilization of organic solvents, are considered as some of the critical factors limiting the long-term performance and practical use of DSSCs. Solid-state electrolytes overcome the disadvantage of fluidity and volatility for liquid electrolytes, however, poor interface contact property and lower conductivity for solid-state electrolytes lead to lower light-to-electricity conversion efficiency for DSSCs. Quasi-solid-state electrolytes, especially TSGEs, possess liquid electrolyte's ionic conductivity and interface contact property and solid-state electrolyte's long-term stability, it is believed to be one kind of the most available electrolytes for fabricating high photoelectric performance and long-term stability of DSSCs in practical applications.

International Journal of Innovative Research in Science, Engineering and Technology

An ISO 3297: 2007 Certified Organization

Volume 3, Special Issue 2, April 2014

Second National Conference on Trends in Automotive Parts Systems and Applications (TAPSA-2014)

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