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ORIGINAL CONTRIBUTION

SOLID STATE ELECTROLYTE BASED DYE SENSITIZED SOLAR CELL: STABILITY AND DEVICE PERFORMANCE

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ABSTRACT

Dye sensitized solar cells are facing challenging issue due to low stability, high cost and degradation of liquid electrolyte. Due to high mesoporous structure, TiO₂ is more appropriate compared to other metal oxide like ZnO and SnO₂. In case of TiO₂ based solar cell, the bandgap edge levels are suitably adjusted with respect to the Dyes and electrolytes. The significant movement considering the higher efficiency, lower cost and better scalability prospects, it is the right time to replace the expensive liquid-based materials to relatively cheaper solid-state materials that involve the use of perovskites-CH₃NH₃PbX₃ (X = Br, I) (sensitizers that can replace dye) and spiro-MeOTAD (solid-state electrolyte that can replace liquid electrolytes). In this paper, DSSC with different types of electrolytes combination along with the device performance, future prospective will be discussed.

KEYWORDS: Mesoporous TiO₂, Solid-State Electrolyte, Redox Electrolyte, Hole Transporting Material, PV-Performance.

1. INTRODUCTION

In DSSC, low-bandgap material will be directly activated by visible light, and photo-generated electron-hole pair can immediately recombine, that is one of the major drawbacks of DSSC solar cell. When UV photons excite TiO₂ directly, 99% of the electron-hole pairs recombine. In TiO₂ based dye sensitized solar cell, due to its mesoporous structure TiO₂ is more appropriate for dye adsorption and surrounded by dye molecules.. These dye instantly absorb the sunlight, immediately injects a charge into TiO₂ that creates instant charge separation between the TiO₂ and the dye. This is the mechanism to protect the semiconductor not to occur the charge recombination. The semiconductor only has majority carriers, and no recombination can occur in i) suitable band adjusts for electron injection from most successful commercial dyes, (ii) high surface area for higher dye loading, as any MOS will serve as a scaffold for dye anchoring, and high electronic mobility for photo-generated electron collection. The

photo-generated voltage mainly depends on band bending mechanism.

A typical Dye Sensitized Solar Cell (DSSC) consists of three major components: semiconductor, sensitizer and electrolyte between two electrodes. The device generates electric power without suffering any permanent chemical transformation. In the 1991 Nature paper, Graätzel and O'Regan reported a breakthrough work on electrolyte based Dye Sensitized Solar Cell. The composition of the electrolyte was adjusted using lower concentrations of lithium or potassium iodide, a conversion efficiency of 7.9% was achieved and after more than 15 years of intense research, remarkable progresses are achieved in devices performance but question exists in terms of stability and long term sustainability. Dye Sensitized Solar Cell (DSSC) technology has attractive market in Energy harvesting particularly for indoor applications, where rapid growth has started recently. Indoor energy harvesting market includes applications

such as power supplies for various sensors (temperature, humidity, CO₂ concentration, etc.), remote control units, charging devices and information management in a smart home or a large warehouse. In fact, the first commercialized DSC based products were flexible keyboards and portable battery chargers. Next challenge of DSSC technology is to grab the area of Building integrated photovoltaic (BIPV) and low-light driven consumer electronics applications. On-grid or utility-scale generation is not on the radar at the moment; however, this can change if any technological breakthrough manages to significantly improve the long-term stability of DSSCs in outdoor conditions. In this paper, we will highlight the different types of alternative solid state electrolyte and device architecture with updated PV-performances.

2. DEVICE ARCHITECTURE AND WORKING PRINCIPLE

The basic structure and working principle of DSSC is shown in Figure 1. Light absorption is performed by a monolayer dye absorbed chemically at the semiconductor surface.

A charge separation process in a DSSC consists of the following steps [1]. (i) Photoanode absorbs incident solar energy. Upon absorption of photo energy, the electrons in the dye become excited from ground state to the excited state. (ii) Due to the difference in energy levels of the electronic states, electrons from the excited state are injected to the conduction band of the semiconductor. As a result the dye becomes oxidized.

(iii) The electrolyte, which is in contact with the dye, then donates electrons to the dye restoring it to the initial state. (iv) Electrolyte then diffuses towards the catalytic electrode where the reduction reaction takes place and electrolyte restores its initial state by accepting electrons from the external circuit.

(v) In addition to these forward charge transfer processes, backward charge transfer processes also occur in one complete cycle. These backward electron transfer processes drastically reduce the efficiency of DSSCs. These include the following:(a)transfer of electrons from the semiconductor to the oxidized dye, (b) recombination of injected electrons with the electrolyte (dark current), (c) transfer of electrons from the dye in its excited state to the dye in the ground state.

The electrode must have the following features: a) high electrical conductivity and low viscosity for faster electron diffusion b) good interfacial contact with the nanocrystalline semiconductor and counter electrode c) no tendency to induce the desorption of the dye from the oxidized surface or the degradation of the dye d) no absorption of light in the visible region.

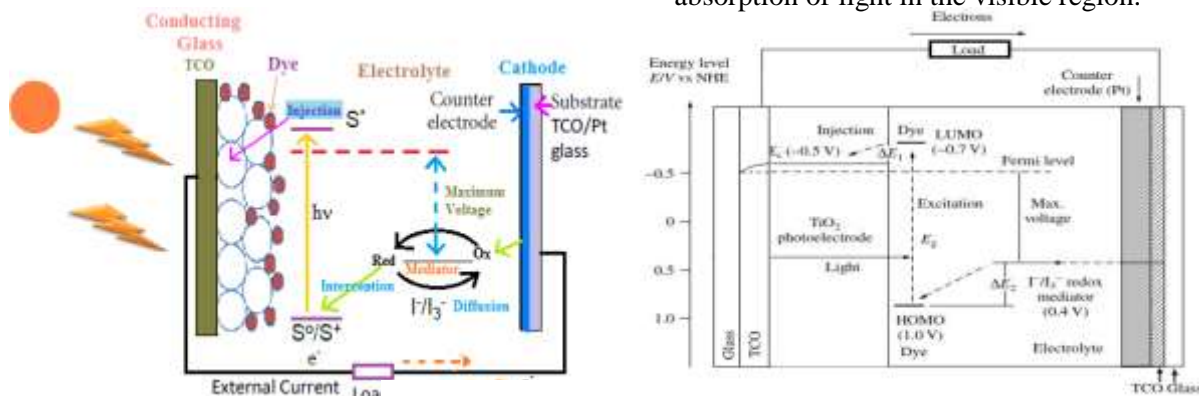


Fig.1-The structure and working principle of DSSC

3. ELECTROLYTE

The efficiency and stability of DSSCs do not depend on a single factor, also depends on many factors such as transparent conducting substrate, nanocrystalline semiconductor oxide film electrode, Dye sensitizers, Electrolytes, and Counter electrode. There must be trade off among different factors to improve the performance of DSSCs. Redox electrolytes in DSSCs function as the medium to transfer electrons from the counter electrode to the oxidized dye. The solubility and ionic mobility of a redox couple in organic medium, driving force for the dye regeneration, and fast electron transfer kinetics with a minimal over potential at the counter electrode are crucial for an effective redox electrolyte. On the basis of physical state, electrolytes can be roughly divided into three categories: liquid electrolyte, quasi-solid electrolyte, and solid-state electrolyte.

Liquid electrolyte:

Basically liquid electrolyte used in these cells such as the redox couple, solvent, acrylonitrile (AcN), ethylene carbonate (EC), propylene carbonate (PC), 3-methoxypropionitrile (MePN), and N-methylpyrrolidone (NMP) and additives affects the performance of DSSCs. A liquid electrolyte consists of a solvent, a redox couple and additives. The iodide-triiodide (I_3^-/I^-) electrolyte has been recognized as the most universal redox shuttle because of its satisfactory kinetic properties, such as fast oxidation of I^- at the photoanode/electrolyte interface for efficient dye regeneration and slow reduction of I_3^- at the electrolyte/counter electrode interface for high carrier collection, excellent infiltration, relative high stability, low cost and easy preparation. The function of the redox electrolyte or the hole transporting material, in the DSC is to shuttle electrons from the counter electrode to the photo-oxidized dye molecule. A liquid electrolyte of I_3^-/I^- [2], bipyridal cobalt (III/II)-complexes [3], $(SCN)_2/SCN$ [4], $(SeCN)_2/SeCN$ [5] are to date the most efficient electrolyte systems in DSC. Most of them researchers are used

acetonitrile/valeronitrile as electrolyte and the efficiency of this cells shows a better results such as 9.1% and 10% respectively [6]. Different dye and electrolyte combination shows the different efficiency, latest efficiency of DSSCs attained 15% with organic dye, which is still low for commercial applications [7]. Redox electrolytes are ionic conductors in which charges are transported via diffusion (concentration controlled) or by migration (electric field controlled). In the DSC the ionic conduction mainly takes place by diffusion, a process which occurs because the reduction-oxidation cycles at each electrode deplete and replenish the redox active species at each interface. Other types of liquid electrolytes have successfully been tried in the DSSC configuration such as ferrocene and disulfide/thiolate.

Although covalent electrolytes show record efficiency, they have a high evaporation rate due to high volatility. High evaporation rates and leakage limit the long-term stability of DSSCs based on covalent electrolytes. In order to minimize these problems, room temperature ionic liquids (RTIL) have been employed successfully. They are a group of organic salts containing cations such as pyridinium, imidazolium, and anions from the halide or pseudohalide family [8]. They act simultaneously as an iodine source and as a solvent. The most commonly used ionic liquid (IL) for DSSC applications is N, N' bis-alkyl-substituted imidazolium iodides.

The liquid based (organic & ionic) DSSCs have been attained the highest efficiency though Leakage is a key problem in liquid-electrolyte based DSSCs, which drastically reduce the long-term stability of solar cells.

Quasi-solid electrolyte:

As alternative of liquid electrolyte efforts have been directed toward alternatives to liquid electrolytes, that is, quasi-solid-state electrolytes and solid-state electrolytes. Ionic liquids (e.g. 1-propargyl-3-methylimidazolium iodide, bis(imidazolium) iodides and 1-ethyl-1-methylpyrrolidinium) and polymer gel (e.g. poly(ethylene oxide), poly(vinylidene fluoride) and polyvinyl acetate) containing redox

couples are commonly used as quasi-solid-state electrolytes to overcome the volatilization and leakage problems of liquid electrolytes. Latest PCEs of DSSCs based on quasi-solid-state electrolytes have reached 8–9% [9–10]. However, because of their thermodynamic instability under high temperature, quasi-solid-state electrolytes still suffer from solvent leakage, and thus also require careful sealing treatment when used in high temperature environments [11].

Solid State Electrolyte:

In order to improve the performance and stability, solid state electrolytes have been developed [12]. Consequently, solid-state electrolytes will be the major focus for DSSC electrolyte research and industrialization in the future. In case of Solid state DSSC basically two types of electrolytes are used such as hole transport materials (HTM) and a I_3^-/I^- redox couple as medium. Due to low power conversion efficiency organic and inorganic electron HTMs are not used as a transport material in DSSCs. To avoid the leakage and evaporation of liquid electrolytes inorganic hole conductor, organic conducting polymers and organic hole conductors have been tested in DSSCs.

Dye Sensitized Solar Cells (DSSCs) based on liquid electrolytes, already established power conversion efficiency of 11 % has been reported. But, the followings are the important drawbacks of liquid electrolytes those play the critical role in limiting the long-term performance and practical use of DSSCs:

Leakage and volatilization of solvents, Possible desorption and photo-degradation of the attached dyes, Corrosion of Pt counter electrode.

They replace the liquid electrolyte with a p-type semiconductor or a hole transfer material (HTM). The band gap structure of the p-type semiconductor must be compatible with the HOMO level of the photo-sensitizer and the conduction band of the n-type semiconductor (TiO_2) [13]. Copper based compounds such as CuI, CuBr, and CuSCN have been employed as inorganic HTMs because of their good conductivity [14]. An

ionic liquid-based electrolyte is one of the most attractive charge mediators used in DSSCs for practical applications. Solidification of the liquid state electrolytes may be necessary in DSSCs, especially when considering applications for matching different architectural constructions. Quasi- or solid-state electrolytes can be realized by mixing the liquid electrolytes with polymers, inorganic silica nanoparticles, and low molecular weight organic gelators. There exist some reports on the solidification of volatile organic solvent-based electrolytes in DSSCs in order to prevent the solvent leakage and evaporation, expected to improve the device stability. It should be noted that the solidification only affects their macroscopic fluidity, and cannot radically solve the issue of evaporation and leakage in the DSSCs, especially under thermal stress. This is due to the solidification not being able to significantly improve boiling points of the solvents used in the electrolytes. CsSnI₃ electrolyte-based devices have yielded a PCE of up to 10.2% for SS-DSSC in 2012 [15]. Spiro-MeOTAD is much better than other types of organic HTMs [16], and in 2013 produced a high PCE of 15% when used in perovskite-based SS-DSSCs [17]. However, low hole mobility and high manufacturing costs still inhibit the application of spiro-MeOTAD in SS-DSSCs. Good diffusion of HTMs into photoanode films and high conductivity for effective hole transfer are key issues for solid-state electrolytes in high-performance SS-DSSCs.

4. LATEST PERFORMANCE

In May 2013 Dyesol announced that Dye Solar Cell technology has achieved a technical breakthrough by achieving a solid-state DSSC (ss-DSSC) efficiency of 11.3% at full sun [18]. Currently, the official accredited World Record Efficiency is 14.1% however efficiencies exceeding 15% are being achieved in the laboratory using perovskites, and experts are forecasting well beyond 20% as achievable not too distantly". A new two-step deposition process is appropriate to create the light harvesting pigment for solid-state dye solar

cells. Cells fabricated using this technique and incorporating Dyesol's key DSC input materials and specially formulated 18NR-T Titania Paste have established a new world record efficiency of 18% for a solid-state Dye Sensitized Solar Cell (ssDSSC). DSSC Technology is in the R&D phase of development and not yet available for purchase in the mass market. However, Dyesol currently produces high purity sensitizing dyes; titania pastes & platinum pastes; electrolytes; sealants for use in flexible and rigid devices; substrates and silver Inks.

5. FUTURE PROSPECTS

Low efficiency and low stability are the major challenges for the commercial deployment of DSSCs. The following factors are responsible for the low efficiency and stability of DSSCs: (i) non-optimized dark current, (ii) poor performance of dyes in the NIR region, (iii) poor contact between the electrodes, (iv) low volatility and high viscosity

of electrolytes, (v) degradation of electrolyte properties due to UV absorption of light.

The following steps can be recommended in order to enhance the efficiency and stability of DSSCs: (i) improvement in the morphology of semiconductors to reduce the dark current, (ii) improvement in the dye design to absorb radiation in the NIR region, (iii) developing low volatile and less viscous electrolytes to improve the charge transfer rate, (iv) improvement in the mechanical contact or adhesion between the two electrodes, (v) use of additives for dyes and electrolytes that enhance their properties.

6. CONCLUSIONS

In future the DSSC technology can cover the wireless society (mobile communications) remote sensing-transmitters, building management sonobuoys and also the road lane makers. In Deutsch e-Newsletter EPFL scientist shows expected efficiency 18-20% of DSSC will reach within the year of 2018.

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References

- [1].L. Andrade, H.A.Ribeiro and A.Mendes, "Dye-sensitized solar cells: an overview," in Encyclopedia of Inorganic and Bioinorganic Chemistry, pp.1-20, 2011.
- [2]. Hara K et al., Sol. Energy Mater. Sol. Cells 70, 151-161 (2001).
- [3].S. A. Sapp, C. M. Elliott, C. Contado, S. Caramori and C. A. Bignozzi, J Am Chem Soc, 124 (37) (2002) 11215-11222.
- [4].B. V. Bergeron, A. Marton, G. Oskam and G. J.Meyer, J Phys Chem B, 109 (2) (2005) 937-943.
- [5].G. Oskam, B. V. Bergeron, G. J. Meyer and P. C. Searson, Inorg Chem, 105 (29) (2001) 6867 - 6873.
- [6]. A highly efficient organic sensitizer for dye-sensitizer Solar cells-Suyoung Hwang, Jung Ho Lee, Chanmoo Park, Hoinglac kim, Chiyoung Park, Mi-Hyeon Lee, Wanin Lee, Jihee Park, Kyungkon Kim, Nam-Gyu Park, And Chulhee Kim. Chem Commun, 2007, 4887-4889.
- [7].Dye-Sensitized Solar Cells Achieve Record Efficiency Of 15% July 15th, 2013 by James Ayre .
- [8].S.M.Zakeeruddin and M.Gratzel, Solvent free ionic liquid electrolytes for mesoscopic dye-sensitized solar cells," Advanced Functional Materials, Vol.19,no.14,pp.2187-2202,2009.
- [9] M.B. Achari, et al. Phys. Chem. Chem. Phys. 15 (2013) 17419-17425.
- [10] X. Wang, et al. ACS Appl. Mater. Interfaces 5 (2012) 444-450.
- [11] D. Li, et al. Energy Environ. Sci. 2 (2009) 283-291.
- [12].B.Li, L.Wang, B.Kang, P.Wang and Y. Qiu, " Review of recent progress in solid state dye sensitized solar cells," Solar Energy Materials & Solar cells, Vol.90,no.5,pp.549-573,2006.

- [13].J.Gong , J. liang and K.Sumathy, “Review on dye-sensitized solar cells(DSSCs):fundamental concepts and novel materials ,” Renewable and sustainable Energy Reviews, Vol 16,no.8,pp.5848-5860,2012.
- [14].J.Wu, Z.Lan, S.Hao et al, ‘ Progress on the electrolyte for dye sensitized solar cells, “ Pure and Applied Chemistry, vol.80,no.11,pp.2241-2258,2008.
- [15] I. Chung, et al. Nature 485 (2012) 486–489.
- [16] J.H. Heo, et al. Nat. Photonics 7 (2013) 486–491.
- [17] J. Burschka, et al. Nature 499 (2013) 316–319.
- [18]. Deutsche Newsletter Juli 2013dyesol.com.