Dye Sensitized Solar Cells Consisting of Ionic Liquid and Solidification

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Two crucial research items on dye sensitized solar cells (DSC), increasing photovoltaic performances and solidification of liquid electrolytes, are reported. A direction to increasing photo-voltaic performances of DSCs is proposed. An interface between TiO_2 /dye and an electrolyte layer is focused on. It is proved that better coverage of TiO_2 layers with dye molecules increases photovoltaic performances. The results are discussed by using electron diffusion coefficient and electron life time in TiO_2 layers. Another crucial research item is solidification. Liquid electrolytes are quasi-solidified without decreasing the parent liquid type DSCs, where Gröthuss type mechanism are introduced to the solidified electrolytes. Because of this, charge carrier can move swiftly even in the hard clay like electrolytes.

Keywords: Dye sensitized solar cell, diffusion, nano, TiO_2 , CO_2 super critical, PEDOT-PSS, electron life time, dark current, Gröthuss mechanism, ionic liquid

1. Introduction

Dye sensitized solar cells (DSC) are expected to be one of the future solar cells, because the procedure of the cell preparation are composed of simple coating and heating process [1]. These simple processes are completely different from conventional Si based solar cells requiring vacuum processes. Because of this, DSCs have a potential to provide low cost solar cells. The efficiencies reached 10-11 % which is much higher than those for other solar cells consisting of organic molecules [2,5b]. However, increases in the efficiency are still needed in order to catch up the preceding Si based solar cells [3].

Solidification of liquid electrolytes is the other item to be solved. Solidification often retards ion-diffusion in electrolytes and decreases photo-voltaic performances. Solidification methods without decreasing the photovoltaic performance are desired. In this report, a direction to increasing photovoltaic performances and a new solidification method are discussed.

2. Dye sensitized solar cell -structure and mechanism-

DSC consists of the following staffs (Figure 1). (1) transparent conductive oxide glass (F-doped SnO_2 glass (F/SnO_2)), (2) Nanoporous TiO_2 layers (diameter: 15-20 nm), (3) dye monolayer bonded to TiO_2 nano-particles, (4) electrolytes consisting of I^- and I_3^- redox species, (5) platinum, (6) a counter electrode a (transparent conductive oxide glass (F/SnO_2)).

The mechanism is summarized in Figure 2 [4]. Dye molecules are photoexcited (11) and electrons are injected into TiO_2 layers (12). These electrons diffuses in TiO_2 layers (13) and collected in F/SnO_2 layers (14). On the counter electrode, I_2 (I_3^-)

Figure 1 Dye sensitized solar cell - structure-

Figure 2 Mechanism of generation of electricity molecules are reduced to I^- , catalyzed with Pt(15). These I^- diffuses in organic solvents(16) to give electrons to the oxidized dye molecules(18). I^- is oxidized to I_2 (I_3^-) molecules and diffuse again back to the counter electrode (17).

Efficiency (Eff) is described as the following equation.

$$\text{Eff}(\%) = V_{oc} \times J_{sc} \times FF \quad (1)$$

V_{oc} : open circuit voltage, J_{sc} : short circuit current, FF: fill factor, where FF is described as follows.

$$FF = V_{max} \times I_{max} / V_{oc} \times J_{sc} \quad (2)$$

V_{max} and I_{max} are defined as voltage and current at which maximum electric power is obtained. V_{oc} , J_{sc} and FF have to be increased in order to increase Eff. In order to increase photovoltaic performances, new dye molecules whose absorption is extending into near-IR region [5], TiO_2 light scattering layer [6], transparent conductive layers [7] and core-shell particles [8] have been reported. In this report, focus is put on TiO_2 surfaces.

3. Interface between TiO_2 /dye molecules and electrolytes

Maximum V_{oc} obtained theoretically is the difference between quasi-Fermi level of TiO_2 layers and I/I_3^- redox potential (Figure 2). Considering that the most negative quasi-Fermi level corresponds to the flat-band potential of TiO_2 (-0.7 V vs. SCE), the highest theoretical V_{oc} is 0.95 V (the difference between the flat band potential of TiO_2 (-0.7 V) and I/I_3^- redox potential (+0.25 V)). The V_{oc} is also affected largely by the back electron transfer reaction from TiO_2 to I_3^- , the route 19 in Figure 2. The back electron transfer decreases V_{oc} largely.

Figure 3 Electron diffusion in TiO_2 layers and back electron transfer from TiO_2 layers

One of the methods to increase V_{oc} is to retard the back electron transfer [4].

J_{sc} is affected by linear electrical resistance such as resistance in F/SnO_2 , TiO_2 , an electrolyte layer and interfaces between a counter electrode and an electrolyte layer. These resistances have to be reduced.

The interface between TiO_2 /dye molecules and an electrolyte layer is very important for V_{oc} and J_{sc} , because the interface is associated with both of back electron transfer and electron diffusion in TiO_2 layers (Figure 3). Electrons diffuse in TiO_2 layers by hopping the trapping sites and occur swiftly when the amount of traps decreases. Since TiO_2 nano-particle size is 15-20 nm, the surface traps are much more pronounced. Because of this, the amount of the surface traps has to be reduced. It has been reported that the surface traps are the center for electrons to leak to I_3^- (back electron transfer) and decrease V_{oc} [9]. In addition, it has been reported that the modification of TiO_2 surfaces with molecules bearing carboxylic acids decreases the surface traps and increases electron diffusion coefficients in TiO_2 layers [10]. In order to prepare TiO_2 particles covered better with dye molecules,

Figure 4 Schemes for dye adsorption on TiO_2 particles by dipping (A) and pressurized CO_2 process (B)

pressurized CO₂ process (a kind of super critical fluid) was used. It has been reported that diffusions of molecules are promoted in CO₂ super critical fluids [11]. The authors expected that swift diffusions of dye molecules in nano-pores occur and TiO₂ nano-particle surfaces facing narrow spaces between nano-particles can be covered sufficiently with dye molecules (Figure 4).

Figure 5 I-V curves for dye sensitized solar cells prepared by dipping (A) and CO₂ process (B)

Electrolyte: LiI:500mM, TBuPy:500mM, I₂:50mM, MP11:600mM in Acetonitril, Solaronix Ti-Nanoxide D, N3 dye, Supercritical fluid: 0.234cm³, Liquid phase: 0.258cm³, 100mW/cm² (AM1.5)

Figure 5 shows the relationship between photocurrent and photovoltage for cells prepared by dipping and CO₂ process. The cell prepared by a CO₂ process had better Jsc and Voc than that prepared by a dipping process. Figure 6 shows the relationship between the amount of dye adsorption of a TiO₂ layers and the treated time when the cells were prepared by a dipping and a CO₂ process. In the case of a CO₂ process, dye adsorption occurred more swiftly than that in the case of a dipping process. The amount of adsorbed dye molecules was higher than that prepared by a dipping process. This suggests that TiO₂ prepared by a CO₂ process had better coverage than that prepared by a dipping process. Dark current (current associated with back

Figure 6 Dye adsorption on TiO₂ layer by dipping (A) and CO₂ process (B)

Figure 7 I-V curves for dye sensitized solar cell

Electrolyte: LiI:500mM, TBuPy:500mM, I₂:50mM, MP11:600mM in Acetonitril, Solaronix Ti-Nanoxide D, black dye, 100mW/cm² (AM1.5)

electron transfer from TiO₂ to I₃⁻, a process 14 in Figure 2) was -0.21 mA/cm² which was lower than that prepared by a dipping process (-0.44 mA/cm²). Electron life time is affected by the easiness of the back electron transfer from TiO₂ to I₃⁻. The electron life time is longer when the back electron transfer is retarded. Electron life time of TiO₂ layers was calculated by Intensity Modulated Photovoltaic Spectroscopy [12]. The electron life time in TiO₂ layers prepared by a CO₂ process was 0.24 s which was longer than that prepared by a dipping process. This also supports the explanation that back electron transfers are retarded for the cell prepared by the CO₂ process. Electron diffusion coefficient measured by Intensity Modulated Photoelectron Spectroscopy [12] for the cell prepared by a CO₂ process was 2.5 cm²/s (light intensity 4.5 W/cm²), which was higher than that for a cell prepared by a dipping process (1.8 cm²/s). The retardation of dark current, increase in electron life time, increase in electron diffusion coefficients and increase in the amount of dye adsorption support the explanation that better coverage of nano-porous TiO₂ surface decreases the amount of surface traps and increased electron diffusion in nanoporous TiO₂ layers and decreased the site for electrons to leak to I₃⁻ molecules. It was proved that the CO₂ process is a useful tool in order to stain nanoporous walls with dye molecules swiftly and effectively. One of the best results is shown in Figure 7.

3. Solidification of liquid electrolytes

Solidification of electrolytes is one of the crucial research items for DSCs. Solidification retards ionic diffusions (16 and 17 in Figure 2) and decreases photo-voltaic performances for DSCs. The decrease in the photovoltaic performances becomes serious when the content of electro-inactive gelators increases in order to reach all solid type DSCs. The authors solved the problem by fabricating ion-paths in the solidified electrolytes which have structures similar to proton-conductive films (Nafion) (Figure 8) [13]. The films are composed of phase-separated fluoropolymers and side chains where SO_3H groups are bonded. The film consists of bulk water layers and water layers adsorbed tightly on SO_3H groups. Protons are pushed and released through three dimensional hydrogen bonding of the tightly adsorbed water layers. The mechanism is different from mere diffusions of protons and is called Gröthuss mechanism. The authors proposed a new hard gel electrolyte in which I^-/I_3^- species move by Gröthuss mechanism. Photovoltaic performance does not decrease even when gel electrolytes looks like hard gels.

Figure 8 Proton conducting films and I^-/I_3^- conducting gels

The gel electrolyte consists of ionic liquid type electrolytes and gelators. Ionic liquids were employed because of the low volatility. Nano-particles were employed as the back bone material which corresponds to fluoropolymer backbone for Nafion film. The electrolyte was filled with nano-particles whose surfaces were modified with C12 (Fig. 8 and 9). The ratio of the modified nano-particles against ionic liquid type electrolytes was 1:1 (wt %), which looked like hard

Figure 9 DSCs prepared by surface modified nano-particles and ionic liquid type electrolytes

clay. Figure 10 shows I-V curves for cells before and after solidification. Photovoltaic performance did not change even after solidification with TiO_2 nano-particles modified with C12I. It is notable

Figure 10 I-V curves for cells before and after solidification

CEP-2000 AM1.5, N719 dye (Solaronix), Cell size 0.25cm^2 , Masking, Particle content: 83wt%, Ionic liquid electrolyte: ionic liquid containing methylpropylimidazolium iodide and methylethylimidazoliumtricyanomethanide (7:3), IL 300mM, LiI 580mM, t-butylpyridine 500mM

that I^-/I_3^- carried charges sufficiently even in hard clay type gel electrolytes (Figure 10, insertion). On the contrary, solidification using bare TiO_2 nano-particle decreased the photovoltaic performance largely, suggesting that the surface modification with C12I is critical. It seems that C12I was aligned on the porous TiO_2 wall because of the self-organization of long alkyl groups. Endothermic (68°C) and exothermic peaks (39°C) corresponding to melting and crystallization were observed by Differential Scanning Calorimetry. These thermal behaviors were not observed for TiO_2 nano-particles modified with shorter chains such as C3, C6 and C8 in Figure 11, suggesting that these shorter chains are not aligned on TiO_2 nano-particles. In addition, photocurrent increased with an increase in the carbon chain length. These facts suggest that self-organization of alkyl moieties and the alignment of methylimidazolium moieties are critical. The

Figure 11 Surface modified TiO_2 nano-particle

aligned methylimidazolium iodide moiety would form ion-paths for I^-/I_3^- species, where hopping of I^- and I_2 (Gröthuss mechanism) is expected, because I_2 was adsorbed and concentrated on the surface-modified TiO_2 walls (Figure 12). When 30 wt % of nano-particles modified with C12 was added into methylethylimidazolium iodide containing 300 mM of I_2 , 1830 mM of iodine was concentrated on the TiO_2 surfaces. The value was only 900 mM when bare TiO_2 nano-particles were used. Because I_2 was concentrated highly on the surface modified TiO_2 wall, formation of I_5^- species (long chain of iodide and iodine) was confirmed by Raman spectroscopy [14]. Because of the

Figure 12 Gröthuss mechanism (A) and diffusion mechanism (B) for I^-/I_3^-

fabrication of the ion paths, apparent diffusion coefficients of I_3^- and photovoltaic performances were kept high after the solidification. I_3^- diffusion in unmodified TiO_2 nanopores was $3.0 \times 10^{-7} \text{ cm}^2/\text{s}$, which increased to $3.9 \times 10^{-7} \text{ cm}^2/\text{s}$ after TiO_2 surface was modified with C12.

The authors found that Gröthuss type mechanism of I^-/I_3^- ion path can be fabricated in the gel consisting of surface modified nano-particles, where nano-particles correspond to phase-separated fluoro-polymers for proton-conductive nafion films and methylimidazolium iodide bearing long alkyl chains corresponds to side chain bearing SO_3H groups. Solar cell performance was maintained even

in hard clay type solidified electrolytes.

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