CHAPTER VIII

CTAB MODIFIED SODIUM-BENTONITE SOLIDIFIED LIQUID ELECTROLYTE FOR DYE-SENSITIZED SOLAR CELLS

8.1 Abstract

Gel electrolyte from CTAB-modified Na-bentonite (CB) and commercial laponite RD (L-RD) were scrutinized in terms of cell performance and cell stability. Two kinds of electrolytes, 3-Methoxypropionitrile based (Z646) and ionic based (Z655) liquid electrolyte were employed. The optimal amount of CB and L-RD is 20 wt.% in Z646 and the optimal amount of CB in Z655 is 13 wt. %. The UV-vis spectroscopy shows light scattering properties of both clays but they are not sufficient to enhance J_{sc}. The photovoltaic properties of both gels with Z646 are slightly lower than those of the standard cell. However, L-RD provides higher fill factor than CB. This is probably due to the fact that L-RD has smaller particle size than CB, which does not retard the ion diffusion much. In addition, non-modified laponite attenuates cell stability because its high basicity desorbed dye molecule from the TiO_2 surface by the acceleration of light and heat. The photovoltaic properties of CB gel electrolyte of ionic liquid Z655 are in the same trend with gel electrolyte of Z646. Nevertheless, the fill factor of the Z655 gel drops much during the stability test.

Keywords: Titanium dioxide; Modified clay; Gel electrolyte; Photovoltaic properties

8.2 Introduction

Dye-sensitized solar cell (DSSC) or Grätzel's cell has been developed widely since it is promising for clean and sustainable energy, i.e. environmentally friendly, low cost, and comparable energy conversion efficiency, in particular, indoor application. The Grätzel's cell is mainly composed of dye acting as light sensitizer or electron source, highly porous semiconductor for supporting dye which is usually TiO_2, p-type semiconductor or electrolyte, and catalyst (platinum, graphite, gold, etc.) for regenerating electron or reduced species at back electrode. All these components are equally necessary to provide a high efficient cell.

Sealing is one main problem of DSSCs. The evolution is started from volatile to non-volatile electrolyte and then ionic liquid electrolyte which seems to be the best solution. Nevertheless, it still needs electrolyte injecting hole leading to several leaking points on one panel and more difficult in large-scale manufacturing production. Moreover, it is hard to avoid liquid electrolyte touching edge of sealing at which there is some glue probably reacting with electrolyte.

A nanosized SiO_2 powder and Al_2O_3 have been used to form gel with liquid electrolyte as the study of Kay (1994). With about 10 wt.% nanosized SiO_2, he mentioned that gel matrix does not influence the ion diffusion in the electrolyte. Ten year later, Wang *et al.* (2004) also found that 5 wt.% fumed silica and PVDF-HFP do not significantly affect the cell performance. These researches have been interesting for applying other oxide to form gel in electrolyte, especially clay, alumino silicate mineral. Park *et al.* (2008) reported that 20 wt.% synthetic laponite with 100 nm of platelet size in MPN base electrolyte improved J_{sc} by 2.3 mA/cm^2. They attributed this improvement to light scattering effect of clay particle in electrolyte. In addition, some studies found that the addition of small amount of modified-surface clay (0.5 wt.%) (Lai *et al.*, 2009) or mica (3 wt.%) (Lai *et al.*, 2010) and could enhance ion exchange mechanism of PVDF-HFP gel electrolyte, which led to an increase in J_{sc} about 4 to 5 mA/cm^2. Surprisingly, Inoue *et al.* (2010) found that 10 wt.% synthetic monmorillonite with 10 nm of particle size could form gel in acetronitrile based electrolyte and rendered high efficiency to 10.3%.

Herein CTAB-modified bentonite prepared in our lab was employed as a liquid-electrolyte gelator and compared with commercial synthetic laponinite. To compromise between efficiency and stability of DSSCs, MPN based electrolyte (Z646) and ionic liquid electrolyte (Z655) were investigated.

8.3 Experimental

8.3.1 Materials

Na-bentonite, 70% purity was kindly supplied from Thai Nippon Chemical Industry Co., Ltd, Thailand. CTAB-modified Na-bentonite defined as CB was prepared by modifying surface of natural clay (500 nm - 2 μm size) with cetyl trimethylammonium bromide (CTAB) described in Muksing *et al* (2008). Laponite-RD defined as L-RD (~100 nm size) sample was supplied by Southern clay, Rockwood additive Ltd. All chemicals and materials were supported from Laboratory of Photonics and Interfaces, EPFL. Liquid electrolytes used were Z646 MPN-based (Kaung *et al.*, 2007), Z655 Ionic liquid (Kaung *et al.*, 2006) and sulfolane-based from G24 Innovations Limited, UK. Ru(4,4′-dicarboxy-2,2′-bipyridine)(4,4′-dinonyl-2,2′-bipyridine)$(NCS)_2$, Z907 was employed as sensitizer.

8.3.2 Gel Electrolyte Preparation

CB and L-RD was dried under vacuum at 120 °C for 3 h before use. Gel electrolytes were formed after homogenized the mixture of clays and electrolytes by using ultrasonic bath and ultrasonic homogenizer tip at room temperature.

8.3.3 Cell Fabrication

The 9 μm-thick transparent TiO_2 films prepared in Laboratory of Photonics and Interfaces were immersed in 0.3 mM dye solution in 1:1 volume ratio of acetonitrile and *tert*-butanol. The counter electrode was prepared by coated Pt solution on FTO, TEC 15 and annealed at 450 °C for 15 min. Gel electrolyte was spread on a photoanode and then the cell was seal with a 25 μm-thick transparent surlyne ring from Dupont at 150 °C for 16 min. Liquid electrolyte was injected through a predrilled hole in the counter electrode after two electrodes are sealed with melt-surlyne ring and then the hole was sealed with a surlyne sheet and a cover glass. Finally, double seal with epoxy glue was applied on the gap between two electrodes of all cells. The photoanode was masked by using metal mask with the open active area of 0.159 cm^2. The larger cells for UV-vis spectroscopy were fabricated. The gels were filled between two plates of glass slides within the internal space area of

2.5×2.0 cm^2 of 25 μm-thick surlyne and then the cell was sealed by heating. The reference or blank cell was filled with pure sulfolane through an injection hole.

8.3.4 Characterization and Measurement

The light scattering effect was characterized by a UV-vis spectrophotometer with integrating sphere. Sulfolane-based electrolyte was gelled with CB and L-RD. Since sulfolane has higher boiling point than MPN, this facilitates the sealing of large cell dimension by heating. The photovoltaic properties of the prepared DSSCs, i.e. short circuit current (J_{sc}, mA/cm^2), open circuit voltage (V_{oc}, V), fill factor (*FF*), and efficiency (η, %), were determined from the I–V curve obtained by using a digital Keithley model 2400 digital source meter (Keithley, USA) under an irradiation of a 450 W xenon light source (Oriel, USA) with an irradiance of 100 $mWcm^{-2}$ (the equivalent of one sun at AM 1.5).

8.4 Results and Discussion

8.4.1 Optical Properties

With 25 μm thickness of 20 wt.% CB gel electrolyte according to the thickness of surlyne ring, the gel looked transparent after heat sealing and then look translucent due to the crystallization of CTAB on bentonite surface during cooling. These crystalline packs would probably block ion diffusion, which were not good for the performance of the cell. These could be avoided by avoiding heat sealing method or cooling down cells quickly. Meanwhile, L-RD can efficiently provide clear gel of aqueous solution by agitating the mixture. Besides, other less polar solvent like acetonitrile or MPN could be gelled as well by applying more energy from ultrasonicator. It obtained opaque gel in the later case.

The transmittance and reflectance of gel electrolyte are shown in Fig. 8.1. The shift of total transmittance curve of CB to lower wavelength compared to the liquid one is possibly due to less film thickness of over-heating surlyne in CB cell. It is an error occurring from preparation process. However, the overall optical properties of two kinds of clay are not different much. It is clearly that liquid electrolyte do not show evidently light scattering effects. Nevertheless, the amount of light scattering in both clays is not enough to enhance light absorption and to increase J_{sc} significantly because it needs almost 100% total light reflectance. In addition, CB shows higher light scattering in red region of diffuse transmittance and diffuse reflectance, indicating to larger particle size or larger aggregates of CB. The low light transmittance and reflectance in UV region is owing to UV absorption of iodine in electrolyte.

8.4.2 Photovoltaic Properties

Various CB contents were investigated to find the optimal clay content. Table 8.1 shows the photovoltaic properties of DSSCs at various clay contents. It was found that V_{oc} increase as the clay content reach 20 wt.%. This attributed to high recombination due to lower ion species and higher ion-transport resistivity which is in consistence with lower J_{sc}. Since at 20 wt.% the liquid electrolyte is gel and provides the maximum cell performance, this is in accordance with the study of Park *et al.* (2008) that 20 wt.% synthetic L-RD in liquid electrolyte was the minimum content to gel liquid electrolyte and render the highest conductivity.

Table 8.2 and Fig. 8.1 compare between photovoltaic properties of CB and those of L-RD. Interestingly, at the same J_{sc} of both types of clays, L-RD provides better fill factor. This could be ascribed to its small particle size which do not retard the charge transportation much, along with the influence from Grotthus-type exchange mechanism on the laponite surface (Zakeeruddin and Grätzel, 2009) or the enhancement of ion pair dissociation owing to the high dielectric constant of clay (Inoue *et al.*, 2010; Wang *et al.*, 2004). Nevertheless, the improvement of J_{sc} is not observed in our study. This agrees with the optical properties of its gel. Park *et al.* (2008) mentioned that the surface modified is needed only to enhance good compatibility between solvent and synthetic clay but L-RD in this study is not modified-surface laponite. This is probably a factor. However, the comparison between non-modified and modified surface of laponite should be investigated further.

The gel electrolyte of Z655 started forming at 13 wt.% CB. This is because of the higher viscosity of ionic liquid electrolyte. As Z646 the cell performance is decrease with the increase in clay content as shown in Table 8.4 and Fig. 8.3. At the gel point, 13 wt.% CB, the cell performance drops a little bit since the fill factor significantly decrease. This is in consistence with the results of Z646.

8.4.2 Stability Test

Before beginning the stability test, cells of Z646 were kept in the dark for 1 week. V_{oc} of all cells with both gels from two kids of clays are lower rapidly and finally equal to or lower than that of the standard cell (Fig. 8.4), compared to that of the standard cell which has lower V_{oc} (Table 8.2). The reason why shoot up of V_{oc} of the fresh cell with these gels has not been clear but eventually their V_{oc} are down back quickly to meet a new equilibrium point. The normal phenomena in stability test of DSSCs occurs in both standard and 20 wt.% CB cells, namely the slightly decrease in V_{oc} and fill factor but increase in J_{sc}. It is the proton adsorption on TiO_2 surface induced by light and then causing the band edge movement, leading to the lower V_{oc} and higher J_{sc} (Chen *et al.*, 2009a, Chen *et al.*, 2009b). On the contrary, the stability test of DSSCs with 20 wt.% L-RD gel electrolyte under sun simulation test showed rapidly increase in V_{oc} on first 24 h of testing and then reach the equilibrium at around 500 h while J_{sc} dropped continuously (Fig. 8.4). Its dye color fade out obviously compared to the standard cell or 20 wt.% CB at the same condition. This implies that some dye was desorbed from the photoanode film. This is attributed to some strong basic species generated from laponite which accelerated by light and heat during testing since 2 wt.% L-RD in water provides pH of 9.8. Therefore, non-modified clay was not good for the stability of DSSCs; however, modified surface of laponite could diminish strong negative charge.

In case of the stability of 13 wt.% CB in Z655, this content of clay did not affect much the DSSC performance in dark storage for 2 weeks apart from the increasing of V_{oc} and reducing of J_{sc} since its photovoltaic properties take time that viscous gel would reach the maximum point at equilibrium. After the cells was soaked under sunlight simulator, the performance of standard one was quite stable except for normally decrease in V_{oc} while the fill factor of 13 wt.% CB cell rapidly dropped at the first week in sun test and 0.1 different after 1000 h light soaking. It is presumed that the leak of surlyne in some points make channels between epoxy glue and gel electrolyte to exchange some reactive species and then take place a reaction in the gel electrolyte. These processes are catalyzed by light and heat. As epoxy glue could bleach the iodine color of some electrolytes, namely from dark yellow to colorless when they contact directly. This mean that all iodine species are changed to iodide permanently and this would result in the diffusion problem and then the fill factor. Even it is not seen the change of gel color of Z655 clearly, It is possible that the epoxy glue decrease iodine content in the electrolyte. Thus, apart from humidity proof, the double seal with epoxy glue is not good for the cell stability with first seal leaking.

8.5 Conclusions

CB was employed and compared to commercial L-RD as a gelator for liquid electrolyte. The optimal amount of CB and L-RD in Z646 is 20 wt.% and the optimal amount of CB in Z655 is 13 wt. %. The UV-vis spectroscopy shows light scattering properties of both clays but they are not sufficient to enhance J_{sc}. The photovoltaic properties of both gels with Z646 are slightly lower than those of the standard cell. Moreover, L-RD gives higher fill factor than CB. However, non-modified laponite destroys the cell stability. The photovoltaic properties of CB gel electrolyte of Z655 are in the same trend with gel electrolyte of the Z646 except for that the former takes longer time to reach the maximum V_{oc} and its fill factor drops much during the stability test.

8.6 Acknowledgments

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8.7 References

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Table 8.1 Photovoltaic properties of DSSCs with various CB contents in Z646 electrolyte

CB content (wt.% in liquid electrolyte)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η%
0	734	12.7	0.69	6.5
10	756	11.2	0.67	5.8
20	772	11.7	0.65	5.9
25	770	8.7	0.62	4.1
30	775	5.0	0.66	2.6

Table 8.2 Comparison of cell performance between DSSC with CB and DSSC with L-RD at full-sun light intensity

Type of clay	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	%□
None	734	12.7	0.69	6.5
CB	772	11.7	0.65	5.9
L-RD	766	11.8	0.68	6.2

Table 8.3 Stability testing of DSSCs with Z655 gel electrolyte compared to standard cell

Type of cells	Cell storage condition (time)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η%
Standard cell	2 day and 1 h light soaking*	714	11.3	0.68	5.6
	150 h in dark	736	10.7	0.64	5.0
	300 h in dark	736	10.4	0.63	4.8
	1000 h light soaking*	677	10.5	0.64	4.6
13wt.% CB	1 day and 1 h light soaking*	715	10.9	0.65	5.1
	150 h in dark	736	10.0	0.66	4.8
	300 h in dark	732	10.4	0.62	4.7
	1000 h light soaking*	658	10.3	0.52	3.6

* 60°C under 1.5 AM sun simulator

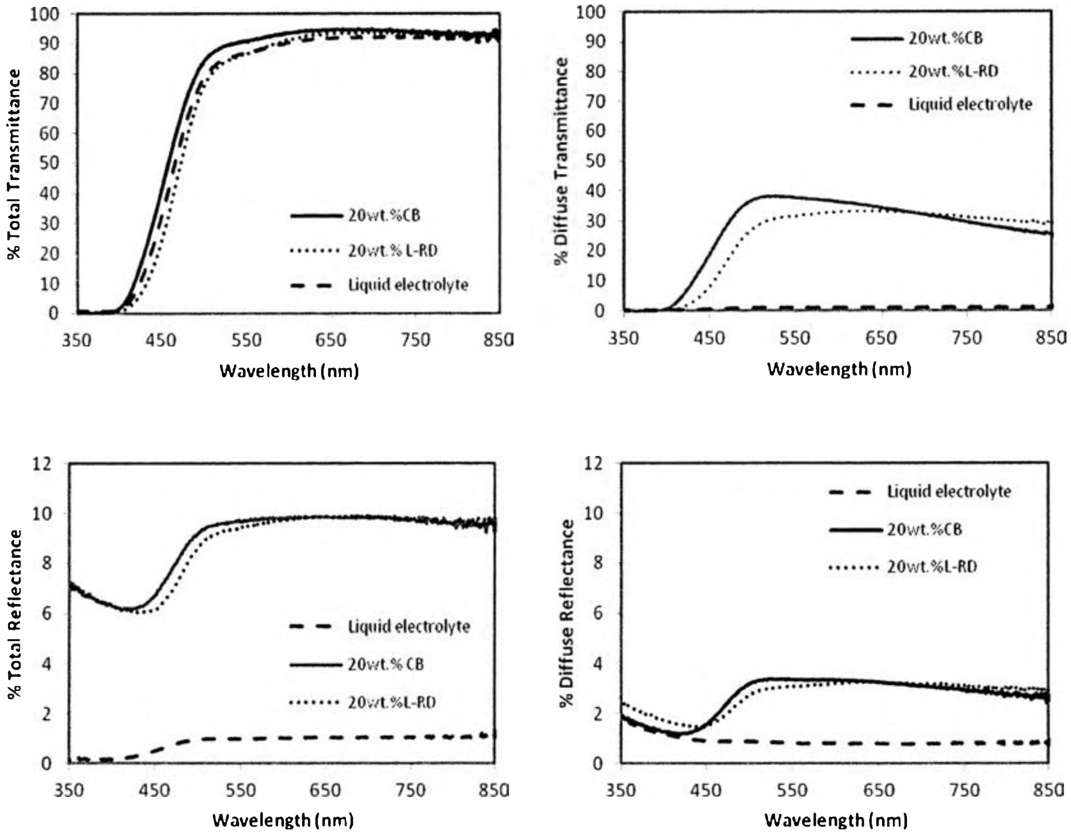

Figure 8.1 The optical properties of gel electrolyte containing CB and L-RD.

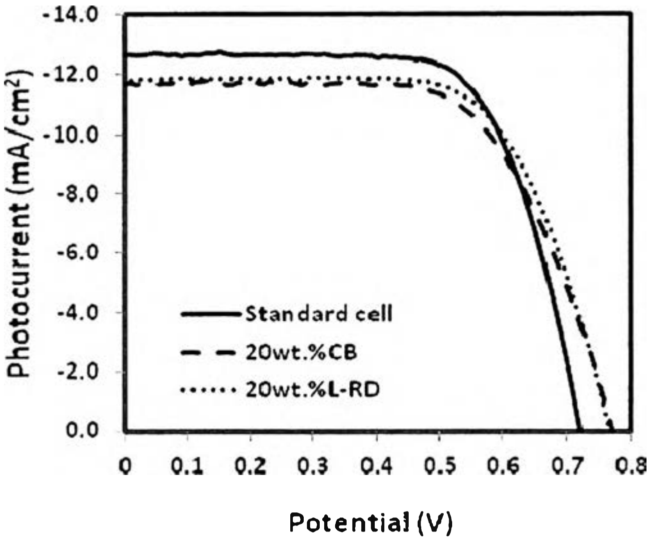

Figure 8.2 J-V curves for the DSSCs with Z646 liquid and its gel electrolytes.

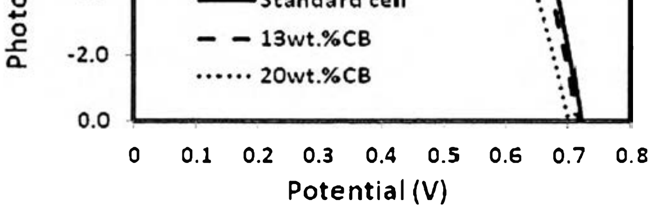

Figure 8.3 J-V curves for the DSSCs with Z655 liquid its gel electrolytes with various CB contents.

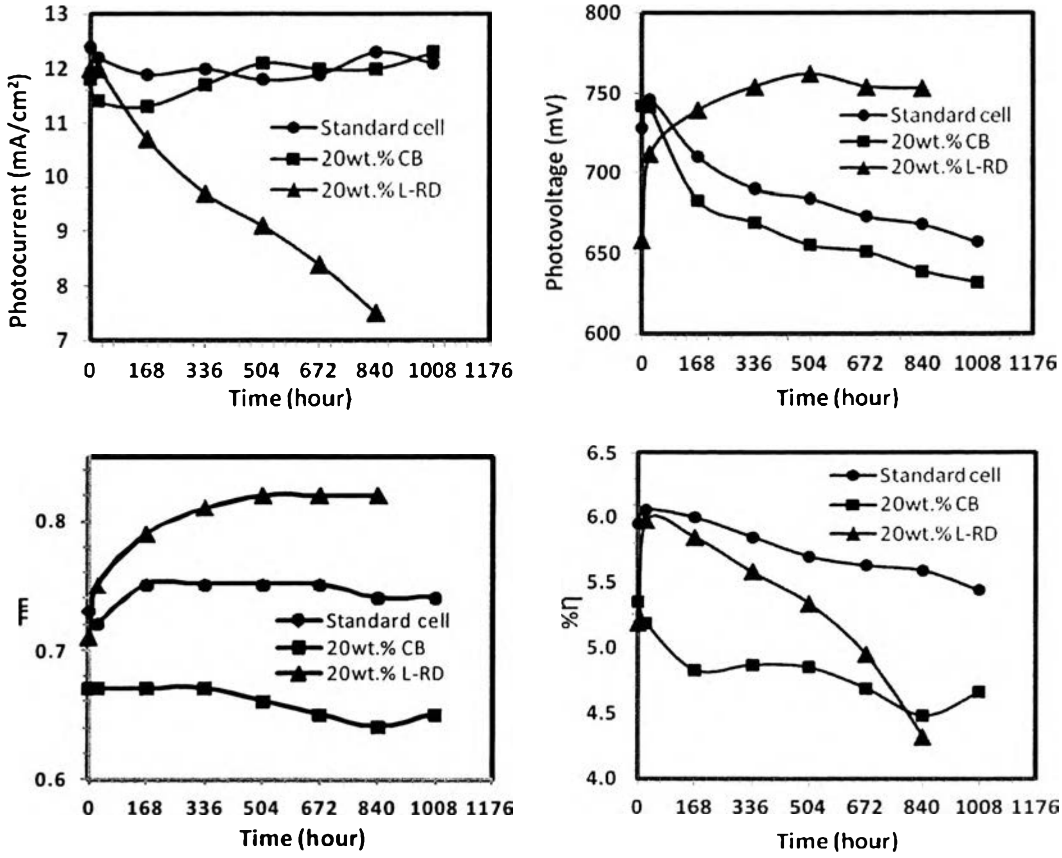

Figure 8.4 Stability test of standard cell and cells with gel electrolyte at 60°C under 1.5 AM sun simulator.