



Roles of layered titanates in ionic liquid electrolytes for quasi-solid state dye-sensitized solar cells

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ABSTRACT

Quasi-solid state dye-sensitized solar cells (DSSCs) were prepared by using gel-state ionic liquid electrolytes containing layered titanates as gelator. These gelators were prepared by intercalating organic materials into interlayers of layered titanates and then dispersed within ionic liquid electrolytes. As a result, the quasi-solid DSSCs showed the enhancement of current density from 3 (mA/cm²) to 4.5 (mA/cm²) although the viscosity of electrolytes increased. The improvement of current density is explained by an increase in dissociation of ionic species as well as scattering effect of layered titanates.

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1. Introduction

DSSCs are regarded as a regenerative low-cost alternative to traditional photovoltaic devices based on the *p-n* junction diode since reported by Grätzel in 1991 [1–3]. In spite of excellent photovoltaic efficiency [4], DSSCs employing liquid electrolytes have been known to have a doubtful stability due to a leakage and evaporation of the liquid solvents. Recently, in order to substitute liquid electrolytes, many research groups proposed several materials of quasi-solid electrolytes using polymer electrolytes [5–7], oligomer electrolytes [6], ionic liquid electrolytes [8,9], and hole transport materials [10]. Especially, ionic liquids including inorganic nanopartilces attract great attention due to their favorable thermal stability, negligible vapor pressure and low fluidity. Yanagida et al. has added carbon nanotubes, carbon nanopartilces, and TiO₂ nanoparticles individually in ionic liquid electrolyte [11]. Also, Jianbao et al reported a composite quasi-solid electrolyte by mixing layered α -zirconium phosphate [12].

In this study, we suggested a new-type gelator “layered titanate” which provides ion dissociation effect as well as scattering effect. The layered titanate composed of negative-charged sheets and interlaid potassium cations. In order to promote dispersion of layered titanates in ionic liquid electrolytes, tetrabutylamine (TBA) molecules were intercalated into interlayer of the layered titanate.

2. Experimental

The ionic liquid electrolytes consisted of 1M 1-methyl-3-propylimidazolium iodide, 0.1M iodine, and layered titanate. The layered titanate (K₂Ti₄O₉) was prepared by grinding titanium oxides (TiO₂,

Aldrich, anatase 99.9%) and potassium nitrate (KNO₃, Aldrich, 99%) together with a molar ratio of 2: 1 and then heating at 1000 °C for two days, as reported previously [13]. They were modified into a proton exchanged structure (H₂Ti₄O₉) and TBA-intercalating layered titanate successively [14]. Table 1 shows the sample codes varying the composition and cation species (potassium, proton or TBA) of layered titanates in ionic liquid electrolytes. The detailed procedures were presented in Supplementary material.

3. Results and discussion

The XRD patterns of layered titanates derived from K₂Ti₄O₉ are shown in Fig. 1. From the (200) reflection at $2\alpha = 10.1^\circ$, the basal spacing of 0.88 nm for the pristine layered titanate, K₂Ti₄O₉ was determined. After proton-exchange in the layered titanates, the basal spacing decreased to 0.78 nm, which was mainly attributed to the formation of H₂Ti₄O₉ [14]. Intercalation of TBA molecules into the interlayer space of the protonic titanate, H₂Ti₄O₉ resulted in the lattice expansion into 1.84 nm ($2\alpha = 4.8^\circ$), meanwhile some remaining H₂Ti₄O₉ were still found without the intercalation of TBA. Table 1 shows the various ionic liquid electrolytes applied for each DSSC depending on compositions and cation species in layered titanates. The layered titanates were kept at 25, 50, and 100 wt.% respectively relative to the weight of MPII. The electrolytes turned into gel or solid state after the gelators were mixed within ionic liquid electrolytes. The electrolyte B and C series nearly had no fluidity compared to the electrolyte A at room temperature. Since the electrolytes were kept at room temperature for 10 min, the phase separation has been initiated in the electrolyte B25. Consequently, the electrolyte B25 was completely separated into two phases after 24 h. The electrolyte C25 containing TBA-intercalating layered titanates showed almost no

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Table 1

Electrolytes applied for DSSCs as a function of compositions and cation species of layered titanate in ionic liquid electrolytes.

Codes	Gelator	
	Layered materials	
	Structure	wt.%
A	H ₂ Ti ₄ O ₉	0
B 25	H ₂ Ti ₄ O ₉	25
B 50	H ₂ Ti ₄ O ₉	50
B 100	H ₂ Ti ₄ O ₉	100
C 25	TBA/H ₂ Ti ₄ O ₉	25
C 50	TBA/H ₂ Ti ₄ O ₉	50
C 100	TBA/H ₂ Ti ₄ O ₉	100

phase separation up to a few months, of which ability to keep homogeneous is due to the good compatibility between the positive functional group $-N^+$ in the TBA molecules and the negative surface of layered titanates or iodide ion. The TBA-intercalating layered titanates in the electrolytes C series resulted in preventing aggregation of gelators by minimizing interfacial energy and providing efficient paths for ion moving. The detailed photovoltaic characteristics of DSSCs with complex ionic liquid electrolytes at AM 1.5 sunlight were summarized in Table 2. The short-circuit current density (J_{sc}) values of DSSCs with electrolyte B series were below 2.4, which was lower than those with pure ionic liquid electrolyte A without gelator (~3.0) and decrease gradually as the content of layered titanate became higher. It is mainly due to the poor mobility of the redox couples (I^-/I_3^-) in highly viscous and heterogeneous electrolyte B series, on which the overall performance of DSSCs strongly depends. Also, there is a problem for the quasi-solid electrolytes to enter to the mesoporous TiO₂ film because the used layered titanates were much larger than the pores of TiO₂ film even though the cell internal space was filled with gel electrolytes using a vacuum pump. In spite of these disadvantages in gel electrolytes, the J_{sc} and overall conversion efficiency (α) of DSSCs with electrolyte C showed increase up to 4.5 and 1.43%, respectively. We investigated their improved photovoltaic performance in terms of effective scattering and dissociation effects shown in IPCE and EIS measurements.

To compare the scattering effects, incident photon-to-current conversion efficiency (IPCE) values for each cell were normalized by the maximum value for DSSC with electrolyte A as a reference value [15]. As shown in Fig. 2, the enhancement in the normalized IPCE onset from 600 nm to 800 nm reflects the scattering effect in electrolyte B and C series. The better dispersion of layered titanate in electrolyte C leads to the higher IPCE, i.e., scattering effect in the

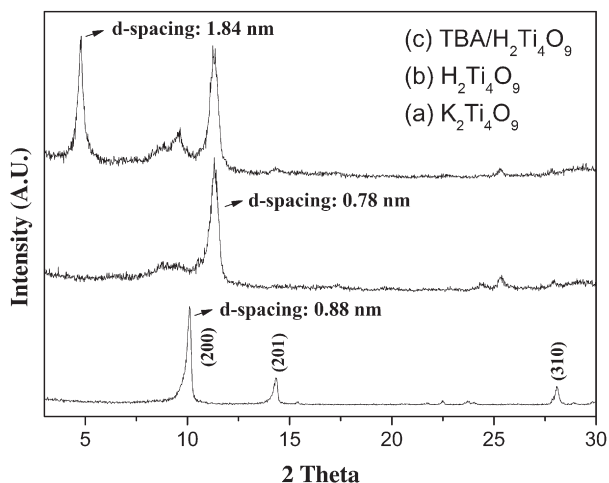


Fig. 1. XRD patterns of layered titanate: (a) K₂Ti₄O₉, (b) H₂Ti₄O₉, (c) TBA/H₂Ti₄O₉.

Table 2

Photovoltaic characteristics of dye-sensitized solar cells with ionic liquid electrolytes.

	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	η(%)
A	0.637	3.0	67.6	1.30
B 25	0.641	2.4	66.7	1.02
B 50	0.636	2.4	65.7	0.99
B 100	0.634	1.6	65.5	0.67
C 25	0.636	3.4	61.0	1.33
C 50	0.618	3.6	59.4	1.30
C 100	0.633	4.5	50.6	1.43

visible wavelength range, which results in the increase of J_{sc} in DSSCs. The scattering effect was increased gradually as the composition of layered titanate was higher within B or C series. Electrochemical impedance spectra (EIS) measurements were performed in order to investigate the role of gelators on the life-time of electron. According to the EIS model reported by J. Luther et al [16], the electron life-time (τ_e) in TiO₂ film can be obtained from the characteristic frequency (f_{mid}) in the mid-frequency regions (1–10³ Hz), which are attributed to the impedance based on charge-transfer process occurring at TiO₂/dye/redox(I^-/I_3^-) interface. Bode phase plots of DSSC with ionic liquid electrolytes under illumination are shown in Fig. 3. As compared with electrolyte A and B, f_{mid} of electrolyte C series shifted to lower frequencies. From the viewpoint of the electron life-time (τ_e), the maximum value was increased from 0.20 ms (A) to 0.63 ms (C100). The higher electron life-time could be explained by an increased amount of redox couples joining in electron transfer reaction due to the dissociation of ionic liquid species. The ionic interaction of ionic species with TBA-intercalating titanate hinders their self-aggregation and makes them dissociate freely. Accordingly, J_{sc} in DSSCs using electrolytes C series shows the remarkable increase.

Therefore, such higher α and J_{sc} of electrolyte C100 should be related to the simultaneous factors of the strong scattering behavior of gelators and the effective dissociation of ionic liquid even though it was less homogeneous and the concentration of ionic species of electrolyte C100 was lower than that of electrolyte C25. These results suggest that electrolyte C100 were successfully employed for a long-term stable and highly conductive electrolyte for DSSCs.

4. Conclusion

In summary, we prepared quasi-solid DSSCs using ionic liquid electrolytes containing layered titanate as gelator, which showed superior long-term stability and exhibit the higher J_{sc} and photovoltaic cell efficiency than those with pure ionic liquid electrolytes. We found that the TBA-intercalating layered titanates in ionic liquids play

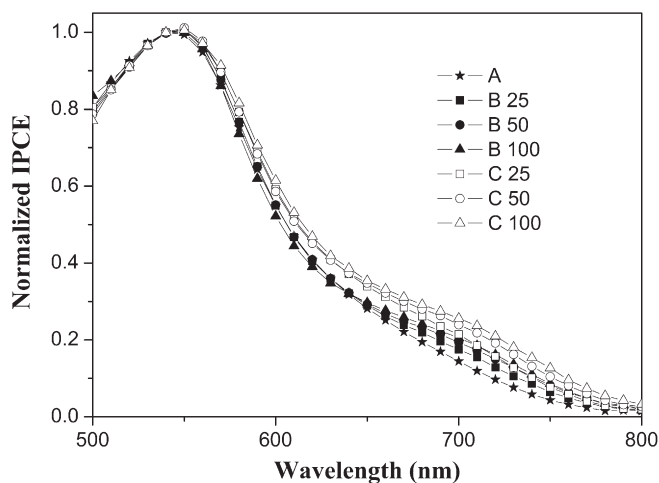


Fig. 2. Normalized IPCE of dye-sensitized solar cells with ionic liquid electrolytes.

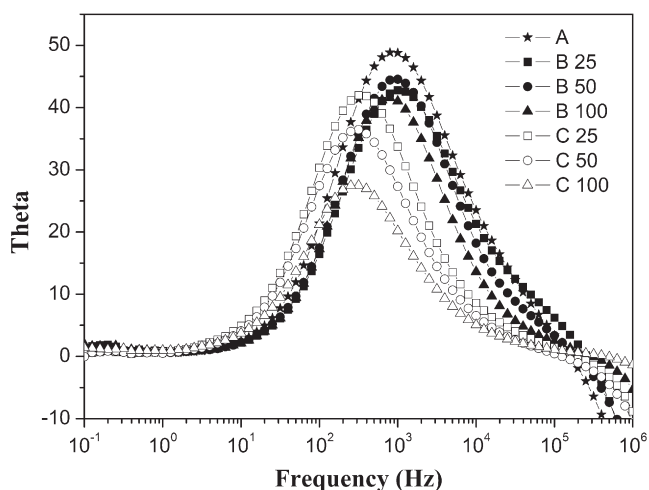


Fig. 3. Bode phase plots of dye-sensitized solar cells with ionic liquid electrolytes under illumination.

predominant roles in the scattering effect especially from 600 nm to 800 nm and the dissociation of ionic species in electrolytes. Consequently, they will be able to enable the high photovoltaic performance in quasi-solid state without leakage of electrolyte and the fabrication of excellent long-term durable and flexible device for practical applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.matlet.2009.03.042](https://doi.org/10.1016/j.matlet.2009.03.042).

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