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Quasi-solid dye sensitized solar cells solidified with chemically cross-linked gelators

Control of TiO_2/gel electrolytes and counter Pt/gel electrolytes interfaces

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Abstract

Dye sensitised solar cells (DSSCs) were solidified with chemically cross-linked gelators without losing the performance of DSSCs before gelation. The electrolytes contain ionic liquids (1-methyl-3-propylimidazolium iodide) solidified with polyvinylpyridine and 1,2,4,5-tetra(bromomethyl)benzene. The solidification was carried out by baking the cells after the gel electrolyte precursors were injected in the cells. This brought about sufficient physical contacts between gel electrolytes and TiO_2 nano-crystals in nano-porous TiO_2 electrolytes. Small amount of water was added in order to decrease initial viscosities for ionic liquid type gel precursors, which makes it possible for the gel precursors to impregnate into nano-pores in TiO_2 layers. The addition of water also has an advantage for decreasing charge transfer resistances between electrolytes and counter Pt. It was found that short circuit current (J_{sc}) and open crcuit voltage (V_{oc}) increased much, when TiO_2 layers with N3 dye were dipped in dilute carboxylic acid solutions and dried. Decreases in resistant of TiO_2 layers were observed after the carboxylic acid treatments were carried out. This method is useful for increase in performance DSSC containing ionic liquid type electrolytes.

Keywords: Dye sensitized solar cell; Gel; Ionic liquid; Cole–cole plot; TiO_2; Surface modification

1. Introduction

Dye sensitised solar cells (DSSCs) have been reported to exhibit high photo-current conversion efficiencies reaching 10% and are one of the promising candidates for the next generation of solar cells [1]. DSSCs contain liquid electrolytes diluted with volatile organic solvents such as acetonitrile, propionitrile, methoxyacetonitrile, propylene carbonate and so on. Because of their high volatilities, solvent losses occur during long-term operations, resulting in decreases in DSSC performances [2]. This is one of the most substantial problems to be resolved before DSSCs are put into practical uses. The use of gel electrolytes may solve the problem partially, but, solvent volatilities from gel electrolytes remain unsolved [3–9]. We focused on gel electrolytes filled with ionic liquids. Some results concerning ionic liquid type quasi-solid DSSCs have been reported [10–14].

Ionic liquids are non-volatile liquids having relatively high conductivities [15,16]. However, their viscosities are higher than those for conventional electrolytes containing organic solvents. This decreases the diffusion constant of I_3^- species by one or two orders of magnitudes [17]. In order to increase the limiting currents in electrolytes, 300 mM of iodine has to be added in the ionic liquid type electrolytes. The amount of iodine is one order of magnitude higher than that in case of organic solvent type electrolytes (30–50 mM). We suspected that the reason why PV performances for ionic liquid type solar cells are lower than those for organic

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solvent type solar cells may be partially explained by frequent back electron transfers from TiO_2 to $I_2(I_3^-)$ in ionic liquid type electrolytes, because the amount of $I_2(I_3^-)$ in ionic liquid type electrolytes is much higher than that in organic solvent type electrolytes. We tried to retard the back electron transfer reaction by modifying TiO_2 surfaces.

Two methods have been reported to retard back electron transfers from TiO_2 to $I_2(I_3^-)$. Kay and Gratzel have reported that open circuit voltage (V_{oc}) increased, but short circuit current (J_{sc}) decreased, when TiO_2 surface was covered with Al_2O_3, MgO and Y_2O_3 [18,19]. In this process, to begin with, TiO_2 is covered with metal oxides. After that, dye molecules are adsorbed. Dye molecules exist on metal oxide layers. Palomares et al. have reported that electron injection rates from dye molecules to TiO_2 decreased, but back electron transfer rates from TiO_2 to $I_2(I_3^-)$ decreased more, leading to increase in the PV performances. The other method is to fill the space among dye molecules with blocking molecules. The blocking molecules are adsorbed after dye molecules were adsorbed on TiO_2. They are directly bonded on TiO_2 surfaces. Gregg et al. filled spaces with polymers prepared by electro-deposition of phenols or by vapor deposition of silane coupling agents [20]. They have reported that the treatment was effective for ferrocene/ferrocenium redox electrolytes, but, was not effective for electrolytes containing $I_2(I_3^-)$. Hung et al. have reported that basic material such as *t*-butylpyridine and polyvinylpyridine adsorbed on TiO_2 retarded back electron transfers from TiO_2 to $I_2(I_3^-)$ in organic solvent type electrolytes [21]. They observed that V_{oc} actually increased, but, J_{sc} did not. In these reports, conventional electrolytes containing organic solvents such as acetonitrile have been employed. There is no report on blocking material on TiO_2 when ionic liquid type electrolytes are employed.

We aimed at blocking the TiO_2 surfaces with carboxylic acids. Because dyes are bonded directly to TiO_2 surfaces with simple dipping methods, small carboxylic acids should be also bonded directly to TiO_2 surfaces where dye molecules are not bonded accidentally. Kang et al. have reported that when acetic acid was added directly into organic solvent type electrolytes, they observed increase in J_{sc} and decrease in V_{oc} [22]. They concluded that the increase in J_{sc} may be associated with reduced surface electron traps by addition of acetic acid in the electrolytes [22]. We directly treated the TiO_2 surfaces and avoided the additional effects of acetic acids in electrolytes to evaluate the blocking properties of carboxylic acids. We found that the effect of carboxylic acid treatment was remarkable for ionic liquid type electrolytes and gel electrolytes than for acetonitrile-based-electrolytes.

2. Experimental

Electrolyte compositions are summarized in Table 1. Imidazolium iodides were purchased from Shikoku Kasei Co. and used without further purification. Ti-nanoxide D paste (Solaronix S.A.) was coated on SnO_2/F layered glasses (30 Ω/sq, Nippon Sheet Glass Co. Ltd.) by using a metal mask (t: 30 μm) and the plate was baked at 450 °C for 30 min. TiO_2 layers with 9 μm thickness were obtained by repeating the process three times. TiO_2 layers were immersed in *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) (N3) dye solutions (Kojima Kagaku Co.) in ethanol (0.1%) at room temperature over night. After TiO_2 electrodes were rinsed with ethanol, they were dried at room temperature in the dark. The TiO_2 electrolytes were further dipped in 1% acetic acid solution in toluene for 5 min followed by rinsed with toluene. The substrate was dried at room temperature in the dark. SnO_2/F layered glass substrates on which Pt was thermally deposited were employed as counter electrodes. Plastic sheets (Himilan 1702, 50 μm, DuPont-Mitsui Polymer Chemicals Co. Ltd.) were inserted between a TiO_2 electrode and a counter electrode as the spacer. Gel electrolyte precursors or ionic liquid type electrolytes were injected in the cell at room temperature. In case of gel electrolytes, these cells were heated at 80 °C for 5 min. The gelation is brought about by reacting PVP (Aldrich) with 1,2,4,5-tetra(bromomethyl)benzene B4Br (Aldrich) to make chemically cross-linked ionomer structures [14] (Scheme 1). Finally, the cells were sealed with epoxy resins. The cell area was 1 cm^2. Interfacial resistances were monitored by the method described in [2]. The symmetrical cells sandwiched with two thermally

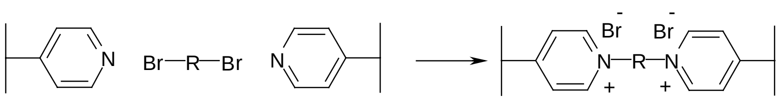
Table 1
Abbreviations and electrolyte compositions

Abbreviation	Electrolytes				Gelator	
	Ionic liquid or solvent[a]	LiI (mM)	I_2 (mM)	*t*-BuPy (mM)	PV[b] (wt.%)	B4Br[b] (wt.%)
Et1	MeEtImI	500	300	580	–	–
Pr1	MePrImI	500	300	580	–	–
Bu1	MeBuImI	500	300	580	–	–
Hex1	MeHexImI	500	300	580	–	–
Pregel1	MePrImI	–	300	–	2	2

MeEtImI: 1-methyl-3-ethylimidazolium iodide; MePrImI: 1-methyl-3-propylimidazolium iodide; MeBuImI: 1-methyl-3-butylimidazolium iodide; MeHexImI: 1-methyl-3-hexylimidazolium iodide; *t*-BuPy: *tert*-butylpyridine; B4Br: 1,2,4,5-tetra(bromomethyl)benzene; PV: polyvinylpyridine (M_w: 80,000).

[a] 5 wt.% of water is contained.

[b] wt.% to ionic liquids.



Scheme 1.

$$D \quad \frac{I\,\mathrm{lim}\times d}{2nFC}$$

D: Apparent diffusion coefficient
I lim: Limiting current
d: Cell gap
n: The number of electron(2)
F: Faraday constant
C: I_2 concentration

Scheme 2.

deposited Pt electrodes fabricated on the SnO$_2$/F layered glass substrates were employed. Interfacial resistances were estimated by using cole–cole plots. The diffusion constant for I$_3^-$ was measured by the method described in [2]. Symmetrical cells were prepared. The electrode was fabricated in the same method as that for photo-voltaic cell counter electrodes described in Section 2. The cell gap was controlled to be 50 μm. Electrolyte shown in Table 1 was inserted in the cell. The electrode size was 1 cm^2. The voltage was swept from 0 to +1 V. I$^-$ is oxidized to I$_2$(I$_3^-$) on an anode, and I$_3^-$ diffuses to cathode. I$_3^-$ is reduced to I$^-$ on cathode. When the voltage increased from 0 to 1 V, the current went up and reached a constant value corresponding to the limiting current. The difussion constant was calculated by using a formula shown in Scheme 2 [2]. Impedance spectra were recorded over frequency ranges of 0.01 Hz to 100 kHz by using Perkin-Elmer Model 283 Potentiastat/Galvanostat and Model 5210 Lock-in-Amplifier. Photo-electrochemical measurements were performed using solar simulator (YSS-50A, Yamashita Denso Co. Ltd.) furnished with a Xenon lamp(AM1.5, 100 mW/cm^2). The light intensity was monitored with a polysilicon illuminometer.

3. Results and discussion

3.1. Gel electrolyte precursors

Quasi-solid dye sensitized solar cells are fabricated by pouring gel electrolyte precursors into cell and by heating the cell to solidify. In order to achieve sufficient physical contacts between gel electrolytes and nano-crystalline TiO$_2$ surfaces in nano-pores, initial viscosities for the gel electrolyte precursors have to be low. Small amount of water addition is necessary to decrease the viscosity for precursors. Fig. 1 shows the relation between apparent diffusion constant and water content for Gel1. Before gelation, the apparent diffusion constant increased with an increase in water content [14]. However, after gelation, the apparent diffusion constant has a maximum value at 2% water addition. We have already reported that when the gelator is somehow phase-separated from ionic liquids, apparent diffusion constants are maintained even after solidification. Gel1 is the case. Gel1 is a opaque gel electrolyte and the gelator containing network polymers made with PVP and B4Br is somehow phase-separated. This phase separation retards the interaction between cations fixed on polymer matrixes and I$_3^-$ species [23]. Water addition may change the phase separation state. At 2% water addition, the phase separation may occur most. Namely, after water content exceeds 2%, the phase separation gradually disappears and becomes homogeneous. In homogeneous gel electrolytes, the interaction between cations fixed on polymer matrixes and I$_3^-$ species

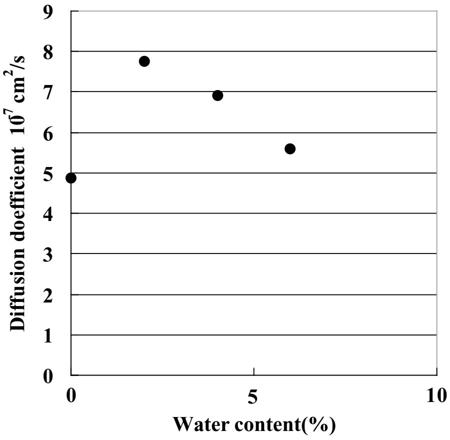


Fig. 1. Relationship between diffusion coefficient and water content electrolyte: MePrImI; iodine 300 mM.

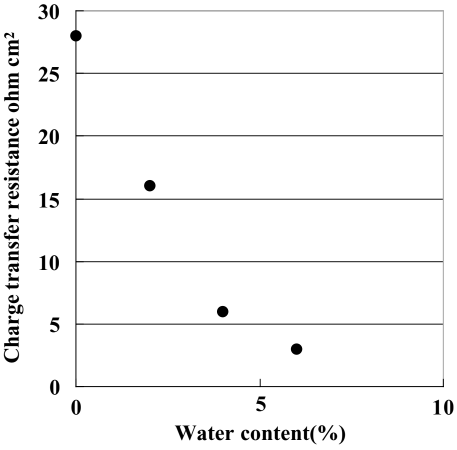


Fig. 2. Relationship between charge transfer resistance and water content electrolyte: MePrImI; iodine 300 mM.

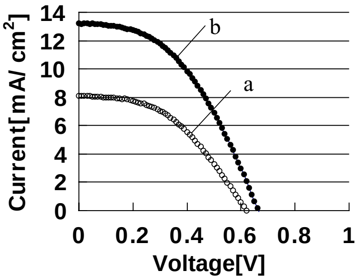


Fig. 3. *I–V* curves for DSSCs before and after acetic acid treatment: (a) after acetic acid treatment; (b) before acetic acid treatment electrolyte: Pr1, cell area: 1 cm^2, AM1.5, 100 mW/cm^2.

retards the diffuison of I_3^- species [23]. Therefore, performance for gel electrolytes is sensitive to electrolyte compositions. Another advantage of water addition is the decrease in charge transfer resistances between counter Pt electrodes and electrolytes [23–25]. This is also true for Gel1. The interfacial resistance decreased with an increase in water content as shown in Fig. 2.

3.2. Modification of TiO_2 surface

Fig. 3 shows the *I–V* curves for photo-voltaic cells before and after acetic acid treatment. V_{oc} increased from 0.62 to 0.69 V after acetic acid treatment. The J_{sc} of the DSSC before acetic acid treatment was 8 mA/cm^2 which increased largely to 13.5 mA/cm^2 after acetic acid treatment. The small increase in V_{oc} and large increase in J_{sc} after acetic acid treatment was also observed for DSSCs containing other ionic liquids as shown in Table 2, where alkyl groups of alkylmethylimidazoliumiodide were varied from ethyl to hexyl group. Increase in the photo-voltaic performance for DSSCs containing Pr1 was remarkable among them. Gel1 was obtained by solidifying Pregel1 in Table 1. Both J_{sc} and V_{oc} for quasi-solid dye sensitized solar cells increased after TiO_2 layers were treated with acetic acid. The increase in J_{sc} was also observed after TiO_2 was treated with other aliphatic and aromatic carboxylic acids such as hexanoic acid, lactic acid and benzoic acid as shown in Table 3. The chain length for aliphatic carboxylic acids did not change the photo-voltaic performances for DSSCs. We tried to treat TiO_2 surfaces with molecules having other active sites such as decanethiol, thiophenol, hexyltrichlorosilane, dihexyldicholorosilane. However, they did not increase J_{sc} at all.

Table 2
J_{sc} and V_{oc} for DSSCs before and after acetic acid treatment

Abbreviation	J_{sc} (mA/cm^2)		V_{oc} (mV)	
	After	Before	After	Before
Et1	7.8	3.6	0.58	0.58
Pr1	13.5	8	0.69	0.62
Bu1	8.1	3.8	0.69	0.63
Hex1	5.8	5	0.73	0.66
Gel1	10.8	9.7	0.63	0.52

Gel1 was obtained by quasi-solidifying Pregel1; cell area: 1 cm^2, AM1.5, 100 mW/cm^2.

Table 3
Treatments with carboxylic acids having various chain length

Carboxylic acids	V_{oc} (mV)	J_{sc} (mA/cm^2)
Hexanoic acid electrolyte (Pr1)	0.66	11.4
Lactic acid electrolyte (Pr1)	0.66	11.3
Acetic acid electrolyte (Pr1)	0.66	11.7
Non electrolyte (Et1)	0.56	6.4
Benzolic acid electrolyte (Et1)	0.62	9.4

Cell area: 1 cm^2, AM1.5, 100 mW/cm^2.

Hung et al. have reported that V_{oc} increased, but J_{sc} did not change after TiO_2 was treated with *t*-butylpyridine [21]. This contrasts with our results that large increase in J_{sc} was observed. Kang et al. have reported that photo-voltaic performance was stabilized by the addition of acetic acids into organic solvent type electrolytes [22]. In addition, they described that the addition of acetic acid increases J_{sc} at the expense of V_{oc}. We also observed the same phenomena, namely increase in J_{sc} and decrease in V_{oc} when acetic acid was added directly into ionic liquid type electrolytes without *t*-butylpyridine. This suggests that bonding of carboxylic acids on TiO_2 layers and washing out the unreacted acetic acids are substantial for the increase in both J_{sc} and V_{oc}. Another possible explanation for increase in both J_{sc} and V_{oc} is that our ionic liquid type electrolytes contain *t*-butylpyridines which may resists the decrease in V_{oc}. These cells were stable for 1 month exposure to Hg lamp (10 mW/cm^2). We did not observe decreases in J_{sc} and V_{oc}.

The treatment of TiO_2 with acetic acid was also effective for gel electrolytes containing ionic liquids as shown in Fig. 4. J_{sc} increased from 10 to 11 mA/cm^2 after the treatment. For comparison, photo-voltaic performance of DSSC where TiO_2 electrodes were treated with *t*-butylpyridine is also shown in Fig. 4. Large increase in V_{oc} and large decrease in J_{sc} were observed. (a) Fig. 4 has the following properties: I_{sc} 10.9 mA, V_{oc} 0.52 V, ff 0.42, eff. 2.4 (1 cm^2, AM1.5, 100 mW/cm^2). Apparently, the effect of acetic acid

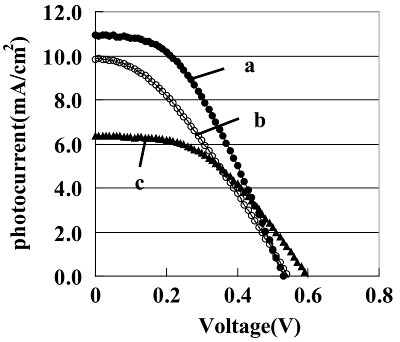


Fig. 4. Photo-voltaic performances for DSSCs containing Gel1: (a) acetic acid treatment; (b) no treatment (reference); (c) dye anchored TiO_2 electrode was treated with *t*-butylpyridine cell area: 1 cm^2, AM1.5, 100 mW/cm^2.

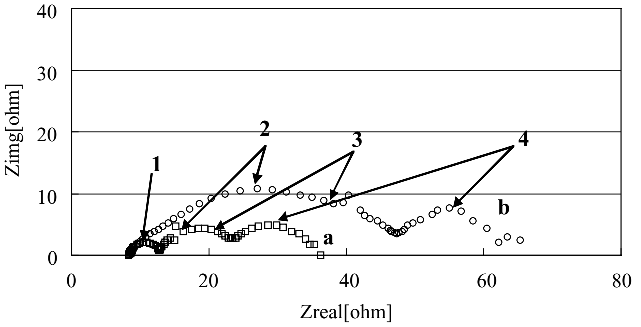


Fig. 5. Cole–cole plots for DSSC before and after acetic acid treatments electrolyte: Pr1, area 1 cm^2, photo-current was fixed at 3 mA/cm^2 (a) after acetic acid treatment; (b) before acetic acid treatment.

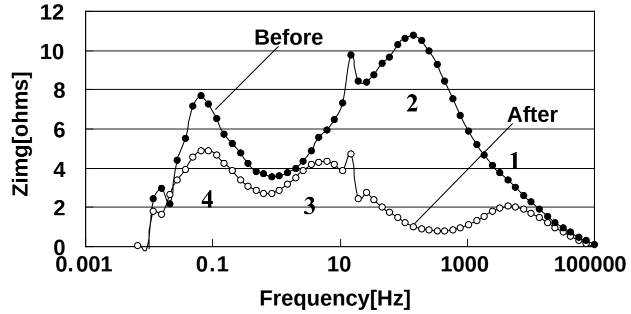


Fig. 6. Relation between frequency and Z'' (imaginary part) for DSSC before and after acetic acid treatments electrolyte: Pr1, area 1 cm^2; photo-current was fixed at 3 mA/cm^2.

treatment was different from that of *t*-butylpyridine. In our electrolytes, off-set of dark current did not changed after the acetic acid treatments.

In order to give a possible explanation to these phenomena, impedance for DSSCs before and after acetic acid treatment were measured. The measurement was carried out during exposure. During the measurement, the current density was controlled to be 3 mA/cm^2. Obtained cole–cole plots were fitted by using Power Suite, Zsimpwin software (Perkin-Elmer). At least four semi-circles were observed as shown in Fig. 5. The presence of four circles are well expected from Fig. 6. As (2) in Fig. 5 decreases, (1) and (3) become clearly observed. They were assigned to Pt/electrolyte interface (1) (3–5 kHz), TiO_2 layers (2) (300 Hz), TiO_2/electrolyte interface (3) (5–15 Hz) and bulk electrolytes (4) (60–70 MHz). (1) was assigned by using Pt/electrolyte/Pt symmetrical cells, where only a Pt/electrolyte interface is contained in the cell. Two circles were seen. A higher frequency circle (3–5 kHz) and a lower frequency circle (60–70 MHz) were coincident with those for (1) and (4) in the DSSC cell, respectively. When Pt surfaces were modified with B4Br, the high frequency semi-circles changed. Because of this, Pt/electrolyte interface was assigned to (1). (2) was assigned by changing the composition of TiO_2 particle. (2) and (3) changed when the exposed light strength was varied. It is considered that semi-circles associated with TiO_2 layers should be influenced most by the exposured light strength. Rutile type TiO_2 crystal (FTL 100, Ishihara Sangyo Kaisha Ltd.) and P25 was mixed in water and ethanol mixtures (TiO_2 0.5:water 1:ethanol 0.5). The mixture was stirred vigorously. The prepared paste was coated on SnO_2/F glass plates and the substrates were dried at 150. Dye sensitized solar cells were fabricated by using the TiO_2 electrodes in the same

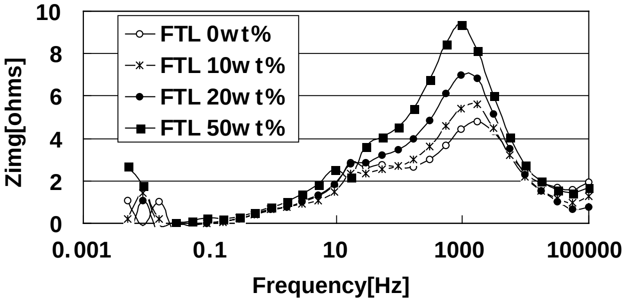


Fig. 7. Relation between frequency and Z'' (imaginary part) for DSSC FTL: FTL 100; rutile type TiO_2 crystal (Ishihara Sangyo). P25 and FTL 100 was mixed in water and ethyl alcohol. The mixture was dispersed by stirring.

Table 4
RC elements of cole–cole plots before and after treatment

	Before acetic acid treatment	After acetic acid treatment of TiO_2 electrode	Assignment
1			
R (Ω)	5.53	4.33	Electrolyte/Pt (3000–5000 Hz)
C (mF/cm^2)	7.52	7.3	
2			
R (Ω)	19.1	3.38	TiO_2/TiO_2 (300)
C (mF/cm^2)	0.0392	2.01	
3			
R (Ω)	13.8	7.59	TiO_2/electrode (5–15)
C (mF/cm^2)	0.738	5.19	
4			
R (Ω)	17.6	11.5	Electrolyte (0.06–0.07)
C (F/cm^2)	0.129	0.188	

procedure described in Section 3.1. Cole–cole plot for these cells was drawn. The relation between the imaginary part and frequency was plotted in Fig. 7. It is known that in Rutile type TiO_2, diffusion of electrons decreases [26]. As shown in Fig. 7, peaks seen at 1000 Hz increased with an increase in the amount of FTL 100. This implies that the peak observed at 1000 Hz is assigned to electron diffusions in TiO_2 layers. When iodine concentration in the Pr1 was increased from 300 to 600 mM, the peaks of (3) decreased. Therefore, this peak was assigned to TiO_2/electrolyte interfaces. In order to estimate each interfacial resistance, a equivalent circuit shown in Table 4 is employed. The fitting results are summarized in Table 4. Among them, the diameter of the semi-circle (2) assigned to TiO_2 layers drastically decreased from 19.1 to 3.38 Ω (1 cm^2 cell) after acetic acid treatments. Kang et al. have reported that when acetic acid was added directly into organic solvent type electrolytes, they observed decreases in interfacial resistances for TiO_2/TiO_2 interfaces. They concluded that acetic acid may reduce surface electron traps [22]. This mechanism may also explain our result well. Further investigations on the mechanism are under way.

4. Conclusions

TiO_2 electrodes were treated with carboxylic acid dilute solutions and dried. The DSSCs containing quasi-solid electrolytes containing ionic liquids were fabricated by using the treated TiO_2 electrodes. We observed large increase in J_{sc} and small increase in V_{oc}, which was more than that expected from the previous report, namely, addition of acetic acid directly in electrolytes. The effect was remarkable in ionic liquid electrolytes, compared with acetonitrile-based-electrolytes. Interfacial resistances relating to TiO_2 layers decreased after the treatments. This method is useful for fabricating high-performance DSSCs filled with non-volatile ionic liquids and gel electrolytes.

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