

# Latent gel electrolyte precursors for quasi-solid dye sensitized solar cells The comparison of nano-particle cross-linkers with polymer cross-linkers

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## Abstract

New latent gel electrolyte precursors (Precursor 1) consisting of ionic liquids and latent gelators are reported. The gelators are composed of poly(vinylpyridine) (PVP) and di-carboxylic acids. Gelation is caused by the reaction between PVP and di-carboxylic acid. Precursor 1 is liquid and is injected into cells and porous TiO<sub>2</sub> electrodes. Because of the latent properties, the viscosity of Precursor 1 does not increase at room temperature. After the Precursor 1 is injected into cells and into porous TiO<sub>2</sub> layers, the cell is heated at 90 °C. Solidification occurs swiftly. The latent mechanism is discussed. The trend of photo-voltaic performance for the cell filled with Precursor 1 before and after gelation was compared with that for the cell filled with previously reported latent gel electrolyte Precursor 2 composed of nano-particles and di-carboxylic acids. Photo-voltaic performance for the former decreased after quasi-solidification, but the latter did not. This is explained by insufficient phase-separations of gelator backbone from ionic liquid electrolytes after solidification.

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**Keywords:** Dye sensitized solar cells; Nano-particle; Electrolyte; Quasi-solid; Gel electrolytes; TiO<sub>2</sub>; Nano; Chemically cross-linked gel; Polyvinylpyridine; Silica; photo-conversion; Diffusion coefficient; Phase-separation; Phase-segregation

## 1. Introduction

Dye sensitized solar cells (DSC) have attracted interests because of high photo-energy conversion efficiencies and low cost cell fabrication processes [1]. One of the problems remaining is solidification of liquid electrolytes. All solid type DSCs with organic and inorganic conductive materials and polymer electrolytes have been reported [2–12]. We have focused on gel electrolytes using ionic liquid type electrolytes [13–17]. Because of the less volatility of these ionic liquids, vapor pressures for the solidified electrolytes are minimized. There are a lot of reports on DSCs containing ionic liquid type gel electrolytes [18–29]. Recently, gel electrolytes containing nano-particles have been paid attention because these soft gels do not decrease the photo-voltaic performances after solidification [12,26–30]. Graetzel and co-workers have reported ionic liquid type electrodes

containing silica nano-particles [26–28]. Yanagida and co-workers have also reported composite ionic gel electrolytes containing TiO<sub>2</sub> nano-particles [29]. These gel electrolytes are called physically cross-linked gels. Gelations are brought about by hydrophobic and hydrophilic interactions of gelators. They are originally solid at room temperature. Therefore, they are injected into cells at high temperatures, where the gel electrolytes become liquid. They are also injected into porous TiO<sub>2</sub> layers by diluting the gel electrolytes with volatile organic solvents, followed by heated in order to remove these solvents. We have reported chemically cross-linked gel electrolytes based on ionic liquid types for the first time [13]. Gelations were brought about by the chemical reaction between poly(vinylpyridene) (PVP) and tetrakis(bromomethyl)benzene. Gel electrolyte precursors were low viscosity-liquids, which enable the precursors to be injected into cells and nano-pores in TiO<sub>2</sub> layers even at room temperatures. Gelation was carried out in the cell directly at 80 °C. In addition, they exhibited high efficiencies associated with phase-separation of the gelator backbones

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from ionic liquid type electrolytes. This is one of the easiest solidification methods to fabricate quasi-solid dye sensitized solar cells. However, once the precursor is prepared, the viscosity of the precursor starts to increase even at room temperature. This makes it difficult to make large cells because the viscosity gradually increases during the insertion into the cells. In order to solve this problem, we have reported latent gel electrolyte precursors consisting of nano-particles and di-carboxylic acids as gelators [30]. Gelation occurs by the reaction between nano-particles and di-carboxylic acids. The photo-conversion efficiency for the quasi-solid dye sensitized solar cell reached 7% [30]. The precursor was low viscosity-liquid. The viscosity of the precursor did not increase during storage or impregnation into cells at room temperature. This made it possible to fill the large cell fully with the precursors. The electrolyte precursor was solidified at around 90 °C swiftly. The latent means that reaction activities are hidden at room temperature. But the reaction (solidification) occurs swiftly when temperature reaches a certain limit. In this manuscript, we report that the latent properties are also brought about by poly(vinylpyridine) instead of nano-particles. The difference in photo-voltaic performances between gel precursor containing polymers and gel precursor containing nano-particles is reported. In addition, essential items to keep high photo-conversion efficiency after solidification are discussed.

## 2. Experimental

Compositions for gel precursors are summarized in Table 1. Electrodes containing ionic liquids are abbreviated as ILE1 and ILE2. Poly(vinylpyridine), di-carboxylic acids, tetra(bromomethyl)benzene (B4Br) were purchased from Sigma–Aldrich Corporation. Silica nano-particle (300) was obtained from Japan Aerogel Corporation.

Methylpropylimidazolium iodide (MePrImI) was purchased from Shikoku Kasei Corporation. A gel precursor, ILE1-C16-PVP (Table 1), was prepared as follows. PVP was dissolved in ILE1 at 90 °C and the mixture was cooled to room temperature. C16 was separately added in ILE1. The mixture was heated at 90 °C and cooled to room temperature. The two solutions were mixed at room temperature mechanically. Gelation of the precursors was observed visually after the mixture was heated to 90 °C.

Viscosity change during storage at 25 °C was measured by Brook Field-Model viscometer. Phase-transition of gel electrolytes were monitored with differential scanning calorimeter (Simadzu-model DSC-60).

Ti-nanoxide D paste (Solaronix SA) was coated on SnO<sub>2</sub>/F layered glasses (30 Ω/sq, Nippon Sheet Glass Co. Ltd). The substrates were baked at 450 °C to fabricate 9 μm thickness of TiO<sub>2</sub> layers. The substrates were immersed in *cis*-Di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl-4,4'-di-carboxylato)ruthenium(II) (Kojima Kagaku) solution in ethanol (0.1%). Pt sputtered SnO<sub>2</sub>/F layered glass substrates were employed as counter electrodes. A plastic sheet (HIMILAN, Mitsui-Dupont Co. Ltd, 50 μm) was inserted between the TiO<sub>2</sub> electrode and the counter electrode as spacers. A gel precursor was injected in the cell at room temperature. Then the cell was heated at 90 °C for 1 min. The cell area was 0.25 cm<sup>2</sup>. Photo-electrochemical measurements were performed using a solar simulator (YSS-50A, Yamashita Denso Co. Ltd., AM 1.5, 100 mW/cm<sup>2</sup>). The light intensity was monitored with a polysilicon illuminometer.

The diffusion coefficient for I<sub>3</sub><sup>-</sup> species was measured by the method described in the previous literature [31,32]. The symmetrical cells, sandwiched with two sputtered or thermally deposited Pt electrodes fabricated on SnO<sub>2</sub>/F layered glass substrates, were used for the measurement. The cell gap was controlled to be 50 μm. Electrolytes were inserted in the cell and the cell was sealed. The electrode size was

Table 1  
Abbreviations and composition of gel electrolyte precursors

Abbreviation	Ionic liquid type electrolyte					Latent gelator			
	MePrImI (wt%) <sup>a</sup>	H <sub>2</sub> O (wt%)	I <sub>2</sub> (mM)	Lil (mM)	<i>t</i> -BuPy (mM) <sup>b</sup>	PVP (wt%) <sup>c</sup>	Si300 <sup>d</sup> (wt%)	Di-carboxylic acid (wt%)	Gelation
ILE1	100	5	300						–
ILE1-C6-PVP	100	5	300			2		C6 <sup>e</sup> 4	NG
ILE1-C9-PVP	100	5	300			2		C9 <sup>f</sup> 4	NG
ILE1-C12-PVP	100	5	300			2		C12 <sup>g</sup> 4	Gelled
ILE1-C16-PVP	100	5	300			2		C16 <sup>h</sup> 4	Gelled
ILE2	100	5	300	500	580				–
ILE2-C16-300	100	5	300	500	580		3	C16 <sup>h</sup> 3	Gelled

<sup>a</sup> Methylpropylimidazolium iodide.

<sup>b</sup> *t*-Butylpyridine.

<sup>c</sup> Poly(vinylpyridine).

<sup>d</sup> Silica nano-particle, (Nippon Aerogel) 7 nm diameter.

<sup>e</sup> HOCO(CH<sub>2</sub>)<sub>4</sub>COOH.

<sup>f</sup> HOCO(CH<sub>2</sub>)<sub>7</sub>COOH.

<sup>g</sup> HOCO(CH<sub>2</sub>)<sub>10</sub>COOH.

<sup>h</sup> HOCO(CH<sub>2</sub>)<sub>14</sub>COOH.

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