

**Solidification of ionic liquids for dye sensitized solar cells by use of carboxylic acids bearing long alkyl groups**

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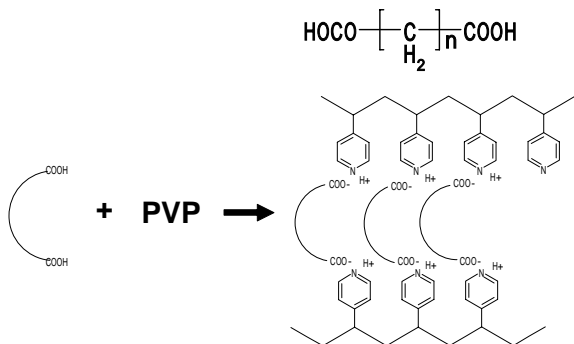
**Introduction:** Solidification of dye sensitized solar cells (DSC) is one of demands before DSCs are put into practical uses<sup>1-6</sup>. We have reported the chemically cross-linked gel electrolytes to solidify DSCs, where, polyvinylpyridine (PVP) and tetrabromomethylbenzen (B4Br) were employed as the gelator. We report here another type of cross-linkers replacing B4Br.

**Experimental :** Gel precursor compositions are summarized in Table 1. Gelation was carried out in the cell directly, the same way as B4Br/PVP gel electrolytes. Figure 1 shows the reaction scheme for the solidification. Ti-Nanoxide D paste (Solaronix SA) , SnO<sub>2</sub>/F layered glasses (30 ohm/square, Nippon Sheet Glass Co. Ltd), and N3( Solaronix SA) dye, and sputtered Pt counter

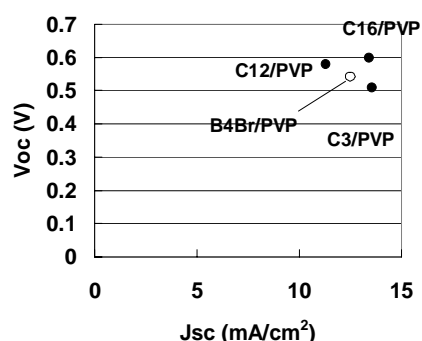
**Table 1 Gelator compositions and solidification by gelation**

Abbreviation	Cross-linker (wt%) compounds		PVP <sup>2</sup> (wt%)	Electrolyte (TS3) <sup>1</sup>	Gelation
	B4Br (4)	n <sup>3</sup>			
B4Br/PVP	B4Br (4)	-	2	100	OK
C1/PVP	Malonic acid(4)	1	2	100	OK
C4/PVP	Adipic acid (4)	4	2	100	NG
C7/PVP	Azelaic acid (4)	7	2	100	NG
C10/PVP	Dodecandioic acid (4)	10	2	100	OK
C14/PVP	Hexadecandioic acid (4)	14	2	100	OK

1)TS3: I<sub>2</sub> 300mM in Methylpropyl imidazolium iodide(5% water), 2) Poly(vinylpyridine), 3) The number of CH<sub>2</sub>



**Figure 1 PVP-Dicarboxylic acid gels**



**Figure 2 Relationship between Voc and Jsc**

Abbreviations: see Table 1; AM1.5, 1 sun, 0.25cm<sup>2</sup>

electrodes were employed for DSC fabrications.

**Results and discussion**

Solidification was observed for C1/PVP, C10/PVP and C14/PVP, however, not for C4/PVP and C7/PVP (Table 1). C1/PVP, C10/PVP and C14/PVP were turbid gels. Voc increased with an increase in the chain length (Figure 2). Jsc did not show clear relationships with the chain

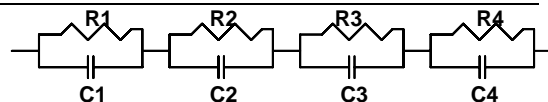
length. The best results were obtained in case of C16/PVP gel electrolyte.

In order to elucidate the reason why C16/PVP gel had better performance than C10/PVP gel, the electrical impedance spectroscopy (Cole-Cole plot) was measured. (Table 2) These assignments have been made in our previous report<sup>4,5</sup>. C14/PVP gel had lower interfacial charge transfer resistances. We have already reported that the interfacial charge transfer resistances decreased after electrolytes were solidified with B4Br/PVP gels<sup>2,6</sup>. The resistance of C16/PVP was almost the same as that of B4Br/PVP gel.

The interfacial resistances between TiO<sub>2</sub>/TiO<sub>2</sub> particles in nano-porous TiO<sub>2</sub> layers were lower for C14/PVP gels than for C10/PVP gels. We have already reported that the electron diffusion co-efficient increased when the

**Table 2 Interfacial charge transfer resistances**

	C12/PVP	C16/PVP
R1:electrolyte/Pt[ohms]	12.86	4.38
C1:electrolyte/Pt[μF/cm <sup>2</sup> ]	345	1.89
R2:TiO <sub>2</sub> /TiO <sub>2</sub> [ohms]	6.03	1.41
C2:TiO <sub>2</sub> /TiO <sub>2</sub> [mF/cm <sup>2</sup> ]	0.01	0.073
R3:TiO <sub>2</sub> /electrolyte[ohms]	6.79	11.01
C3:TiO <sub>2</sub> /electrolyte[mF/cm <sup>2</sup> ]	0.0017	0.31
R4:electrolyte[ohms]	18.06	10.44
C4:electrolyte[F/cm <sup>2</sup> ]	0.15	0.14



TiO<sub>2</sub> surfaces were modified with acetic acid<sup>4-5</sup>. In case of C14/PVP gels, TiO<sub>2</sub> layers would make better contacts with gel solids and the surface would be treated with C14 di-carboxylic acid.

C14/PVP had higher resistances between TiO<sub>2</sub> and gel electrolytes, suggesting that electron transfers from TiO<sub>2</sub> to electrolytes are retarded, probably because of the steric hindrances. This also supports the fact that C14 modified the TiO<sub>2</sub> surface better than that of C10 described in the previous section. Actually, we observed that the dark current for C14/PVP gel was lower than that for C10/PVP gel.

Impedances associated with ion diffusions were lower in case of C14/PVP gels than C10/PVP gels. The turbidity of C14/PVP gel was more remarkable than that of C10/PVP gel. The results can be described by our previous explanation that phase separated gels prevent retardations of ion diffusions<sup>1-4</sup>.

**Conclusion:** We found the new gel electrolytes for DSC solidification. Di-carboxylic acids bearing longer alkyl chains exhibited better results. It was proved again that phase separated gel shows better performances.

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