Dye-sensitized Solar Cells Consisting of CuI-containing Gels

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CuI-containing gels for dye-sensitized solar cells are reported. CuI-containing gels consist of CuI, methylpropylimidazolium iodide, iodine, and gelators consisting of polyvinylpyridine and tetra(iodomethyl)benzene. The efficiency increases with an increase in the amount of iodine molecules in the presence of methylpropylimidazolium iodide, which is different from the previous reports in the absence of methylpropylimidazolium iodide. Solidification of the sticky CuI layers is carried out by cross-linking reaction of gelators without decreasing the photovoltaic performances.

Solidification is one of the important research items for dye-sensitized solar cells (DSC).[1] All solid DSC comprising p-type conductors have been reported.[2–11] Among them, DSCs containing CuI is one of the most promising solid cells. One of the problems for the cells is that injection of CuI into nanopores of porous TiO_2 layers is difficult because CuI is solid and these crystals grow in the nanopores. In order to avoid these problems, the addition of ionic liquids to CuI has been reported.[2,3] The addition retards CuI-crystal-growth in TiO_2 nanopores and improves the contact between TiO_2 nanoparticles and CuI. However, sophisticated techniques associated with the injection of CuI into TiO_2 layers are still required to obtain high photovoltaic performances. We have focused on gel electrolytes, where, ionic liquid type electrolytes are hold in the three-dimensional gelator networks.[12–17] Gel electrolyte precursors were in liquid states and the precursors were injected into cells. After that, solidification was carried out directly in the cells. Because of this, good contacts between the TiO_2 nanoparticles and the solid electrolytes were expected.[12,17] We aimed at applying this to improve the contact between the TiO_2 nanoparticles and CuI layer. The idea is that high viscosity-CuI-gel precursors containing additives are solidified directly in the cell. The tacky precursors improve contacts between TiO_2 nanoparticles and CuI layers. There is no report on the gelation of CuI layers so far. We now report the new hole conductor gels consisting of CuI, a small amount of additives and gelators comprising polyvinylpyridine and tetra(iodomethyl)benzene.

Ti Nanoxide D paste (Solaronix SA) was coated on SnO_2/F layered glass substrates (30 Ω/square, Nippon Sheet Glass Co., Ltd). In advance, the surface was treated with ethanol solution of tetra(isopropoxy)titanium in order to avoid direct contact between CuI layer and SnO_2/F layer. The substrates were baked at 450 °C to fabricate 9 µm thickness of TiO_2 layers. The substrates were immersed in ethanol (0.1%) solution of *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (Kojima Kagaku). It was difficult to inject the high viscosity-CuI-containing gel electrolyte precursors into the cells. Therefore, acetonitrile solution of CuI and other additives was dropped on TiO_2 layers at 80 °C repeatedly over several minutes. When CuI-1, CuI-2, CuI-3, and CuI-4 which did not contain gelators were baked at 80 °C, these CuI layers were still sticky. However, in the case of CuI-5 and CuI-6 containing gelators, the stickiness disappeared. Pt-sputtered SnO_2/F-layered glass substrates were pressed on the CuI layers as counter electrodes. The cell area was 0.25 cm^2. Photoelectrochemical measurements were performed using a solar simulator (YSS-50A, Yamashita Denso Co., Ltd., AM 1.5, 100 mW/cm^2).

Table 1 shows these compositions and their abbreviations. When only CuI was injected into nanoporous TiO_2 layers, the photocurrent was very small. It has been reported that the addition of imidazolium salts such as ethylmethylimidazolium thiocyanate (EtMeImSCN) rendered the CuI crystal size small and the J_{SC} for DSCs increased.[18] In our experimental conditions, the addition of methylpropylimidazolium iodide (MePrImI) to the CuI layer did not increase the J_{SC} at all (CuI-4). When iodine was added in CuI-4, the J_{SC} increased drastically from 1.21 to 5.28 mA/cm^2 (CuI-3 in Table 2). The J_{SC} increased with an increase in the amount of iodine molecules (CuI-1, CuI-2, and CuI-3 in Table 2). It has been reported that the addition of iodine decreased the photovoltaic performance of CuI-based DSCs.[19,20] Tennakone and Perera have reported that stoichiometrically excess iodine molecules adsorbed at the CuI surfaces act as hole-trapping sites.[19] Tributsch and Sirimanne have reported that iodine is found to be competing with the oxidizing dye molecules in accepting electrons from CuI and decreases the efficiency of the cell.[20] They have reported that the addition of iodine to CuI increased conductivity of the CuI layers, but the iodine of the CuI layer became electron traps mediating recombination

Table 1. Compositions and abbreviations[a]

	CuI	MePrImI	EtMeImSCN	I_2	PVP	B4Br	B4I
		wt % (mol %) to CuI	wt % (mol %) to CuI	wt % (mol %) to CuI			
CuI-1	100	6.7(4.9)	—	0.07(0.05)	—	—	—
CuI-2	100	6.7(4.9)	—	0.33(0.25)	—	—	—
CuI-3	100	6.7(4.9)	—	0.66(0.5)	—	—	—
CuI-4	100	6.7(4.9)	—	—	—	—	—
CuI-5	100	6.7(4.9)	—	0.33(0.25)	0.13	0.26	—
CuI-6	100	6.7(4.9)	—	0.33(0.25)	0.13	—	0.26
CuI-SCN	100	—	6.7(4.9)	—	—	—	—

[a] Cell size: 0.25 cm^2, TiO_2 paste: Ti Nanoxide D paste (Solaronix SA), film prepared by doctor blade.

Table 2. Photovoltaic performances

	Efficiency/%	ff	V_{OC}/V	J_{SC}/mA·cm^{-2}
CuI-1	0.82	0.57	0.59	2.44
CuI-2	1.35	0.51	0.53	4.98
CuI-3	1.35	0.47	0.55	5.28
CuI-4	0.26	0.39	0.55	1.21

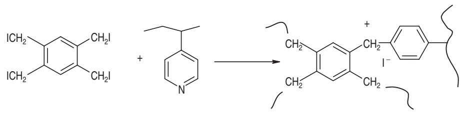
and V_{OC} decreased with an increase in the amount of added iodine.[19,20] In our results, V_{OC} did not decrease largely even when the amount of iodine increased as shown in Table 2. The difference between their works and our work is whether or not MePrImI was contained in the CuI composite. The addition of MePrImI to CuI seems to retard these V_{OC}-decreases when iodine was added. Considering the mechanism reported by Tennakone and his co-workers,[19] the added MePrImI may remove the I_2 (a recombination center decreasing V_{OC}) adsorbed on CuI crystal surfaces as I_3^- in the following reaction: $I_2 + \mathrm{MePrIm}^+I^- \rightarrow \mathrm{MePrIm}^+I_3^-$. This is the first report to show that the addition of iodine improved photovoltaic performances of CuI based DSCs. The X-ray diffraction patterns of the CuI layer did not change largely even when MePrImI and iodine was added to the CuI layers, suggesting that CuI crystals were present in the sticky CuI layer. Resistivity for CuI-4, CuI-1, CuI-2, and CuI-3 layers was 773.3, 71.6, 26.7, and 22.3 Ω, respectively, showing that conductivities increased with an increase in the amount of iodide. This is consistent with the results reported by Waggoner and Ayers.[21] They have reported that iodine acts as a dopant that induces p-type conductivity to CuI.[21] In addition, the stickiness increased with an increase in the amount of added I_2 molecules, suggesting that contact between the CuI layer and nano-TiO_2 particles is also expected to be improved.

Photocurrent decay curves when light was switched off were measured. In the case of a conventional CuI-based DSC containing CuI and 6.7 wt % of EtMeImSCN (CuI–SCN), the photocurrent decayed fast (100 msec). In the case of the DSC filled with a ionic liquid type electrolyte containing I_2 (300 mM), LiI (500 mM), and *t*-butylpyridine (580 mM), the photocurrent decay was very slow (300 msec). Photocurrent decay for the DSC containing CuI-2 was very close to that of the conventional CuI-based DSC containing CuI–SCN. In addition, when light was switched on, photocurrent rise of the DSC consisting of CuI–SCN was sharp, which was similar to that consisting of CuI-2. However, photocurrent for the DSC containing ionic liquid electrolyte rose slowly. These results suggest that the photovoltaic behavior of the cell containing CuI-2 is similar to that containing CuI–SCN.

CuI-1, CuI-2, and CuI-3 were sticky. A gelator consisting of polyvinylpyridine (PVP) and tetra(bromomethyl)benzene (B4Br) or tetra(iodomethy)benzene (B4I) was added to CuI-2 and the mixtures were baked at 80 °C. The surface stickiness disappeared and the CuI composite became solid (CuI-5 and CuI-6 in Table 3). The cross-linking reaction was caused by the addition reaction of bromomethyl or iodomethyl groups to pyridyl groups to form pyridinium salt structures[12] as shown in Scheme 1. Table 3 shows the photovoltaic performances before and after solidification. J_{SC} before solidification was 7.84 mA/cm^2 (Table 3, CuI-2). The J_{SC} value was different from that for CuI-2 in Table 2, because the preparation batch was different. Each experiment shown in each Table was carried out in the same conditions at the same time, which made it possible to compare these J_{SC} values within each table with about 5% accuracy. After solidification, J_{SC} was 7.94 and 7.73 mA/cm^2, respectively (Table 3, CuI-5 and CuI-6). It was found that CuI-gel precursors were solidified without decreasing the photovoltaic performances of the cell before gelations.

Table 3. Photovoltaic performance before and after gelation

	Efficiency/%	ff	V_{OC}/V	J_{SC}/mA·cm^{-2}
CuI-2	1.75	0.39	0.57	7.84
CuI-5	1.81	0.41	0.55	7.94
CuI-6	2.07	0.49	0.55	7.73



Scheme 1. Cross-linking reaction.

In conclusion, it was proved that the use of CuI-containing gels was one of methods to increase photovoltaic performances for CuI-based DSCs. Additives were added to CuI layers in order to soften the CuI layers. In addition, it was found that the additives consisting of iodine and MePrImI increased J_{SC} with maintaining V_{OC}, resulting in improving photovoltaic performance of the CuI-based cells. After cross-linking reactions, surface stickiness disappeared and CuI composites became solid without decreasing the photovoltaic performances of the parent cell.

This work is partially supported by Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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Published on the web (Advance View) March 25, 2006; DOI 10.1246/cl.2006.444