

Acetylacetone-Based Electrolyte in Dye Sensitized Solar Cell

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Abstract

Dye sensitized solar cells attract much attention for a clean energy generation device. Among several solvents for the electrolyte, we investigated here the cell characteristics with acetylacetone as a solvent. The electric conductivity of the electrolyte increases as the concentration of polyethylene glycol (PEG) decreases or that of ionic liquid increases. The addition of pyridine into the electrolyte improves both the open voltage and the short current density. On the other hand, the replacement of PEG with fluorinated oligomer in the gel electrolyte highly increases the short current density where the open voltage is not varied. As the concentration of ionic liquid increase, the open voltage and the short current density gradually increase. When more than 20 wt.% of the ionic liquid was mixed, the gelation was not obtained. As a result, acetylacetone is a practical solvent for a gel electrolyte with the fluorinated oligomer and ionic liquid.

Keywords

Ruthenium Ion Complex, Dye-Sensitized Solar Cell, Acetylacetone, Fluorinated Gel, Ionic Liquid

1. Introduction

Silicon solar cells are nowadays widely used in homes, factories and even electric power generating factories. The environment-friendly power generation will be more and more important in the future. A new type of solar cells that came into birth in 1990 is greatly worth paying attention to it. The study of dye-sensitized solar cells (DSCs) has been performed extensively so far [1] [2] [3] [4]. Even today, continuous efforts are being devoted to enlarge its conversion efficiency and durability [5].

The dye-sensitized solar cell can be divided into three parts: the cathode, the

anode and the electrolyte between the two electrodes. The cathode consists of a light-incoming nanostructured electrode carrying dyes where light is devoted to the electron excitation. Since the dye holds the centered role in generating electric power, it has been fully investigated so far [3] [6] [7]. The photoelectrode has been also studied with regard to its microstructure [8]. The counter electrode, the anode, is also important because of the role of electron injection [3].

We focus on the electrolyte here. The key issue is the redox reaction of I_2 in it, or sometimes LiI is also involved. The effects of other solvents have been studied before. Hara *et al.* reported the open voltage and the short current density with a variety of solvent in the electrolyte [9]: acetonitrile, propionitrile, methoxyacetonitrile, methoxypropionitrile, benzonitrile, phenylacetonitrile, nitromethane, propylene carbonate, dimethoxyethane, dimethylsulfoxide, tetrahydrofuran, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, six kinds of alcohol, and ethylene glycol. Their results showed acetonitrile gave the biggest short current density of 3.42 mA/cm². Acetonitrile is actually one of the solvent often used for the electrolyte. On the other hand, the biggest open voltage of 0.85 V was obtained from the cell with dimethylsulfoxide. Fukui *et al.* tried the mixing solvent in various combinations, and obtained the similar results that acetonitrile and dimethylsulfoxide gave the biggest short current density and open voltage [10]. We tried to use acetylacetone that has not attracted so much attention before. Acetylacetone is a simple molecular and can form various metal complexes at the same time. We expect it may expand the possibility of redox system in the electrolyte.

2. Experimental Details

We first describe the preparation of the cathode. The slurry containing titania particles whose dimension is between 50 and 75 nm was mixed for 15 minutes with polyethylene glycol (PEG) by 10 wt.% and titania powder of P-25 by 10 wt.%. In order to enhance the viscosity, Triton X (15 μ l) was added and the mixture was well mixed for 15 minutes further to make paste. The paste was spread over a piece of fluorinated tin oxide (FTO) (100 μ m) on a glass substrate, annealed at 450°C for 30 minutes, and then cooled down naturally to room temperature. The obtained cathode was then soaked in Ruthenium dye complex ($RuL_2(NCS)_2$, L = 4,4'-dicarboxy-2,2'-bipyridine) diluted in ethanol at 3×10^{-4} M for three hours at room temperature. The anode was prepared in such a way that Pt was deposited by a sputtering method on another FTO glass plate. The thickness of the Pt layer was around 10 nm.

The preparation of the electrolyte gel is described here. The mixture of acetylacetone and a kind of ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate) was used as a solvent. Into this solvent, LiI was added by 2 wt.% of the solvent and the mixture was well mixed for 10 minutes. Finally it was gelled by adding PEG and sonicated for 90 minutes.

In addition, we performed the extra experiments that the ionic liquid was replaced by another ionic liquid of a butyl-imidazolium system. Additionally we

tried that a fluorinated oligomer gel was used instead of PEG gel electrolyte.

The electric conductivity was determined on the basis of a Cole-Cole plot. The J - V characteristics were measured under the irradiation of white light (AM 1.5) with a filtered light from a xenon lamp (UXL500SX by USHIO) at 55 mW/cm². The load resistance was varied in the range between 0 and 100 k Ω .

3. Results and Discussion

Figure 1 shows the dependence of the electrical conductivity on PEG concentration. The concentration of ionic liquid to acetylacetone was fixed to be 15 wt.% here. As the PEG concentration increases, the electrical conductivity decreases monotonically. However, if the amount of PEG is not high enough, gelation cannot be achieved. There is rationally a trade-off between the gelation and conductivity because gelation means the enhancement of the viscosity which results in the difficulty in ionic movements. The gelation fundamentally conflicts with the high ionic conductivity in nature.

Figure 2 shows the relationship between the electric conductivity and the concentration of the ionic liquid. The concentration of PEG was fixed to 20 wt.%

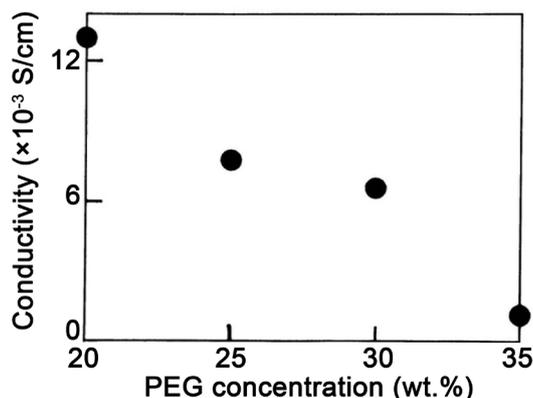


Figure 1. The dependence of the electrical conductivity on the PEG concentration. As the concentration decreases, the conductivity becomes larger. But if the PEG concentration is too low, the electrolyte is not be gelled.

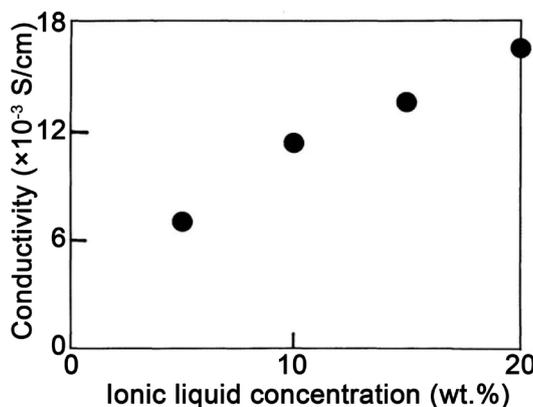


Figure 2. The dependence of the electrical conductivity on the concentration of ionic liquid. This figure shows positive correlation between them. However, the high ionic liquid concentration disrupts the gelation.

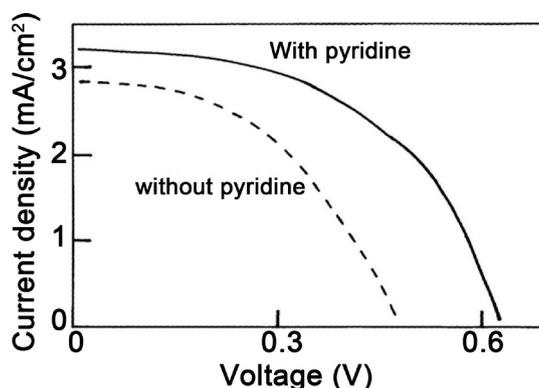


Figure 3. J - V characteristics of DSCs. Doping pyridine enhances the short current density as well as the open voltage.

in this case. The figure tells us that the conductivity increases along with the concentration of the ionic liquid. The ionic liquid raised the electric conduction regardless of the increase of its viscosity.

We next show the effect of pyridine. **Figure 3** shows J - V characteristics of the cells including pyridine (20 wt.%) and no pyridine for comparison. In this experiment, the concentrations of the ionic liquid and PEG were 20 wt.% and 30 wt.%, respectively. By introducing pyridine to the electrolyte, the open voltage increased from 0.48 to 0.63 V and the short current density increased from 2.77 to 3.10 mA/cm². We calculated the fill factor and conversion efficiency based on the data in **Figure 3**, and found that the fill factor increased from 0.48 to 0.53 and that the conversion efficiency increased from 1.17% to 1.91%. Several researchers have studied on the effect of pyridine [11] [12] [13]. In many cases, the effect of pyridine only appears in the increase in the open voltage. But in our experimental results, the short current density also increased. We next discuss this unfamiliar behavior.

Taura *et al.* showed that pyridine enhanced the open voltage but reduced the short current density on the other hand [14]. Their results suggested that the adsorption of pyridine on the surface of TiO₂ shifted the conduction band edge to a more negative potential, which led to the increase of the open voltage. This discussion can be applied to our result whereas acetonitrile was used as a solvent in their electrolyte. Our results also showed the increase in short current density by the addition of pyridine, which is contrary to their results. They owed the decrease to the weakening of light intensity into TiO₂. Our results give a kind of doubt to their discussion. These two opposite results apparently suggests some effects of pyridine on the electrolyte. The mechanism of the enhancement of the short current density is now the issue to be studied. It is possibly related to the kind of solvent in the electrolyte.

We describe here the additional experiment that the ionic liquid was replaced by the one of the butyl-imidazolium system. **Figure 4** shows J - V characteristic under light exposure where the concentration of the ionic liquid was between 5 wt.% and 20 wt.%. As the concentration increase, both the open voltage and the short current density increase gradually. Pyridine was also added in this experiment.

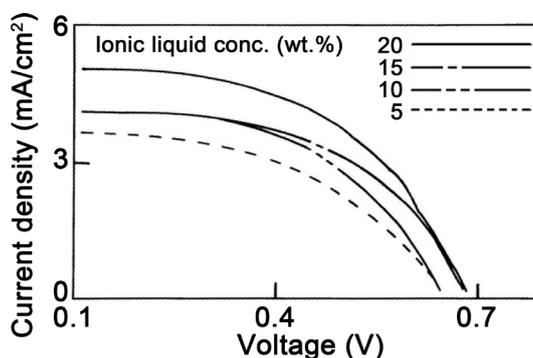


Figure 4. J - V characteristics of DSCs. As the concentration of ionic liquid (a kind of butyl-imidazolium system) is higher, both the open voltage and the short current density are gradually enlarged.

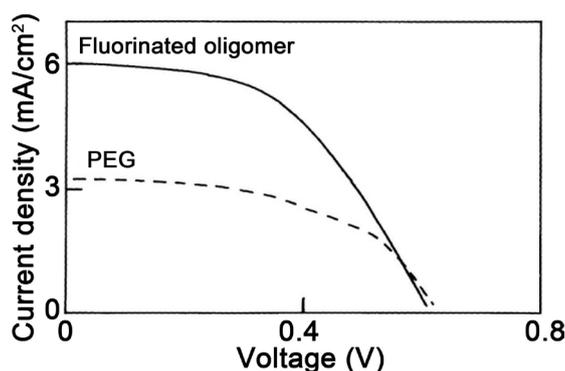


Figure 5. J - V characteristics of DSCs. Fluorinated oligomer provides noticeably large short current density; twice as large as PEG for gelation.

Compared with **Figure 3**, both the open voltage and the short current density are larger. The difference in molecular structure of the ionic liquid affected these values.

Finally, we show the interesting experimental results that the PEG-based gel was replaced by a fluorinated oligomer gel electrolyte. The fluorinated oligomer gel electrolyte has been investigated mainly by our group so far [15]. The detailed preparation method of the electrolyte and the performance of the cell with this kind of electrolyte should be referred to the literature. The ionic liquid used in this experiment was back to that of an ethyl-imidazolium system. The difference in the J - V characteristics between the two kinds of gel electrolytes are shown in **Figure 5**. It is surprising that the short current density enhances about twice by the replacement while the open voltage is not changed.

The fluorinated oligomer is linked with each other by both inter-molecular force between the bulky end groups and ionic attraction force between the side groups. As a result, it forms a bulky net structure including electrolyte or ionic liquid inside the net. The separation scheme into two micro phases is considered to enhance the ionic conduction in a gel state. In the case of PEG, long molecular chains attract each other to form a quasi-crystal state or a compact aggregated state so that there is little space for the electrolyte based on ionic liquid to move freely between the cathode and the anode. The fluorinated oligomer makes

a good framework for the confinement of the electrolyte with keeping its free conduction.

4. Conclusion

We investigated a DSC using acetylacetone-based electrolyte. In order to increase the electric conduction in the electrolyte, the concentration of PEG should be low and that of the ionic liquid is required to be high. But in the extreme end, the electrolyte cannot be gelled. The addition of pyridine enhances not only the open voltage but also the short current density at the same time. When the ionic liquid was replaced by one of the butylimidazolium system, both the open voltage and the current density gradually increased up to 0.68 V and 5.04 mA/cm², respectively, as the concentration increased to 20 wt.%. Finally, when the electrolyte was gelled with a fluorinated oligomer was used, the short current density leaped to 6.01 mA/cm². The fluorinated oligomer plays a prominent role to enhance the short current density. We expect the possibility of acetylacetone-based electrolyte gelled with the help of the fluorinated oligomer.

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