World Journal of Engineering and Technology, 2017, 5, 376-382
http://www.scirp.org/journal/wjet
ISSN Online: 2331-4249
ISSN Print: 2331-4222

Electric Conductivity of Fluorinated Oligomer Gel Electrolyte Including Ionic Liquid and Performance of Dye Sensitized Solar Cell

Masato Ohmukai[1], Jun Kyokane[2]

[1]Department of Electrical and Computer Engineering, Akashi College of Technology, Akashi, Japan
[2]Center for International Education, Toyohashi University of Technology, Toyohashi, Japan
Email: ohmukai@akashi.ac.jp

How to cite this paper: Ohmukai, M. and Kyokane, J. (2017) Electric Conductivity of Fluorinated Oligomer Gel Electrolyte Including Ionic Liquid and Performance of Dye Sensitized Solar Cell. *World Journal of Engineering and Technology*, **5**, 376-382.
https://doi.org/10.4236/wjet.2017.53031

Received: May 21, 2017
Accepted: July 9, 2017
Published: July 12, 2017

Abstract

Fluorinated oligomer gel is suitable to the electrolyte of dye sensitized solar cell. This article studied mainly in the scope of electric conductivity, including ionic liquid in the electrolyte. It was found that the ratio of mixing with dimetyl sulfoxide and the concentration of LiI affect the conductivity. The behavior is different depending on the type of ionic liquid. Although the mixing ionic liquid enhances the conductivity, the short circuit current density of assembled solar cell with it was suppressed so much.

Keywords

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

1. Introduction

The dye sensitized solar cell has been extensively studied these twenty years. It is a fascinating device not based on a conventional PN junction concept that is surely a key idea of silicon semiconductor technology. The dye sensitized solar cell has a practical advantage at the same time; it costs quite lower than the sophisticated silicon semiconductor technology that requires an extremely clean atmosphere. There are also some problems at present. The main problems are the low conversion efficiency and the low durability. Especially the low durability derives from the liquid electrolyte in the cell in an early stage because the liquid electrolyte may escape out the cell in the long-term use. In order to resolve the problem in its durability, solid-state electrolyte and gel electrolyte have been proposed. In addition, ionic liquid has been adopted widely nowadays because ionic liquid has a low vapor pressure and is hard to sublimate [1] [2] [3]. Recent development in solid-state dye-sensitized solar cells is summarized in the literature [4].

We are studying fluorinated oligomer gel electrolyte. Fluorinated oligomer gel includes a couple of positive and negative ions in a molecule that acts as an attractive force between two molecules as well as inter-molecular attractive force on alkyl groups. Two kinds of attractive force can realize firm aggregation to form a gel by itself by just mixing well. The great advantage of this material is no need to apply a cross-linking reaction for the aggregation often reported so far [5] [6]. The electrolyte has been applied to secondary battery at first [7].

The fluorinated oligomer gel has been applied to dye-sensitized solar cell. The conversion efficiency is not as high as other types of dye-sensitized solar cells at present, but the material is attractive to the production of the cells at lower cost. The experimental conditions such as the TiO_2 layer on the cathode [8], the amount of Pt sputtering deposition on the anode [9], and LiI concentration in the gel electrolyte [10]. The introduction of ionic liquid has been also considered [11]. The presence of ionic liquid or LiI can obstruct the aggregation of fluorinated oligomer to make a gel. In this article, two kinds of ionic liquid, imidazolium and pyrazolium systems have been studied in the scope of electric conductivity and cell performance.

2. Experimental

The fluorinated oligomer gel electrolyte was prepared as follows. LiI was mixed with the solvent of dimethyl sulfoxide (DMSO) and I_2 was not added because LiI plays more important role as reported before [10]. The amount of LiI was from 5 to 20 mmol/g. The mixture was sonicated for about 20 minitues for the well mixing. The fluorinated oligomer shown in **Figure 1** was added and then sonicated further for 200 minutes to form gel. The RF in **Figure 1** is a kind of fluoroalkyl group. The amount of the oligomer was about 200 g/l to the solvent that is a critical concentration for the gelation that had been experimentally found. When ionic liquid was mixed, it was mixed before the addition of fluorinated oligomer. The used ionic liquid was 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (Mi) or 3-methylpyrazolium tetrafluoroborate (Mp). The electric conductivity of the obtained gel electrolyte was determined from a Cole-Cole plot.

For assembling the solar cell, a cathode and an anode were prepared on FTO glass substrates. The slurry including TiO_2 with 50 to 70 nm in diameter (by Sumitomo titanium) was mixed for 15 minutes with P-25 and polyethylene glycol, each at the same weight, and triton X (15 μl) for raising its viscosity. The obtained

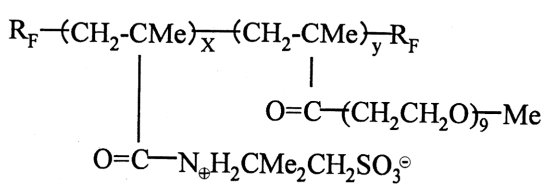

Figure 1. The molecular structure of the fluorinated oligomer.

paste was spread over an FTO glass substrate by a doctor knife method. This was dried and then sintered in a furnace at 450˚C for half an hour. It was then cooled down to room temperature naturally and soaked in a Ruthenium complex dye diluted with ethanol at 3×10^{4} mol/l at 50˚C for 24 hours. Onto another FTO glass substrate for an anode, Pt was slightly deposited by a sputtering method for 3 minutes as was reported before [9].

Finally the anode and the cathode were set together with the gel electrolyte between them and sealed with epoxy resin. The load characteristics were measured by varying attached resistive load between 0 and 20 kΩ during the exposure of white light (AM 1.5) from a filtered xenon lamp (UXL500SX by Ushio) at the intensity of 50 mW/cm^2.

3. Results and Discussion

Figure 2 shows how the electric conductivity depends on the mixing ratio of ionic liquid (Mi or Mp) and DMSO. The amount of LiI in this figure was 5 mmol/g in both cases. It is quite interesting that the tendency is oppositely different in the two kinds of ionic liquid. As for the electrolyte with Mp, the ratio of 7:3 gives the highest conductivity more than 15 mS/cm^2. But at the same ratio, the electrolyte with Mi showed the lowest conductivity. The electrolyte with Mp provided the highest conductivity at 9:1 instead.

The dependence of the conductivity on the concentration of LiI is shown in Figure 3. The effect of LiI concentration was discussed before [12]. So the same range was taken in this experiment as the Ref. 12. The mixing ratio of DMSO and ionic liquid was taken to be the one providing the highest conductivity in Figure 2: 7:3 for Mp and 9:1 for Mi, respectively. As a comparison, the electrolyte without any ionic liquid is also shown in the figure. Neither the electrolyte with DMSO only or with Mi shows meaningful dependence in the figure. For the electrolyte with Mp, LiI plays a role to suppress the conductivity down to the similar value of the other two cases.

The *J*-*V* characteristics of the three kinds are shown in Figure 4. The concentration of LiI was 10, 15 and 5 mmol/g for the electrolyte with only DMSO,

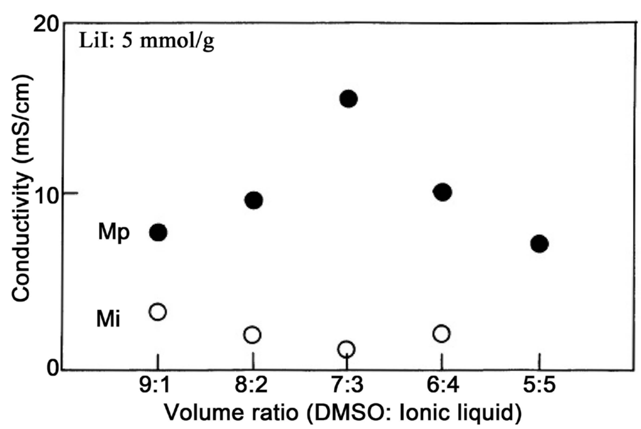

Figure 2. The conductivity of the gel as a function of volume ratio of ionic liquid to DMSO.

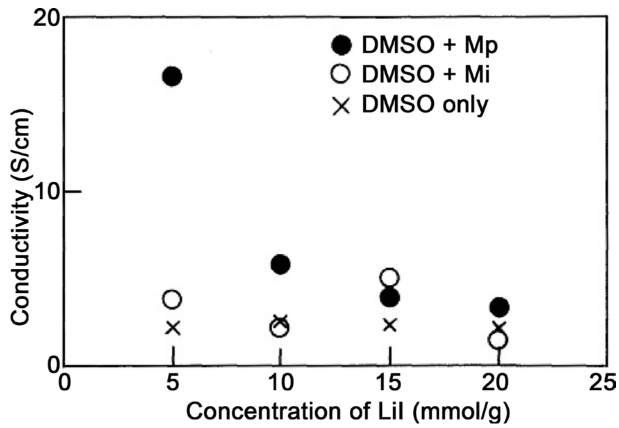

Figure 3. The conductivity of the gel as a function of LiI concentration.

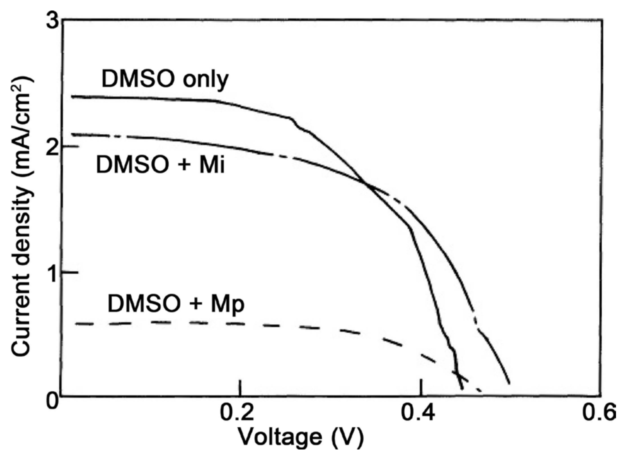

Figure 4. *J*-*V* characteristics of the cell containing three kinds of electrolytes. Ionic liquid suppresses the short current density.

DMSO including Mi, and DMSO including Mp, respectively. The open voltage did not so changed, but the short current density decreased to about 24% with the mixing of Mp. It seems that the higher conductivity results in the lower short current density. This tendency is noticeable in the electrolyte with Mp.

We discuss the conductivity with other published data. It was reported the results when 1-methyl-3-propylimidazolium iodide was mixed in 3-methoxy-propionitrile at different concentrations. The conductivity was down to 1 mS/cm in either material and increased with mixing together and saturated up to 10 mS/cm [13] [14]. Our experimental results showed the similar tendency in the case of Mp, but not in Mi. As for the short current density, Chengwu *et al.* reported that it increased by 2% as the concentration of ionic liquid was doubled. These results are quite different from ours that ionic liquid noticeably suppress the short current density. It may derive from the difference of the solution: propionitrile in theirs and DMSO in ours.

Shi *et al.* reported the effect of combination of two kinds of ionic liquid of an imidazolium system [15]. The conductivity increased 10 times by the mixing accompanied by the decrease to no less than a half. Our results also showed that the introduction of Mi did not suppress the short current density so much although

Mp suppressed it noticeably. Ishimaru *et al.* performed the comparison of Mi and Mp in the scope of *J-V* characteristics and reported that the short current density is higher by 10% in Mp electrolyte [3]. Unfortunately they did not report the electric conductivity of the two materials. The combination of pyrazolium and DMSO may not be recommended.

Koh *et al.* reported interesting results on the crosslinking of electrolytes in which polyethylene glycol with terminal azide groups was used [5]. They used 1-methyl-3-propylimidazolium iodide as ionic liquid and compared the cell performance with that included LiI as a salt. The electrolyte with ionic liquid has higher electric conductivity and higher short current density at the same time. It is not similar to our results that the short current density is suppressed as the electric conductivity becomes higher. Some other researcher also reported a positive correlation between the short current density and electric conductivity [16] [17].

The published results described above suggest the contrary relationship between the electric conductivity and the short current density in our experiments seems to show an abnormal behavior. The co-existence of ionic couple in the fluorinated oligomer and ionic liquid obstruct the electric conduction in the electrolyte in a way. The electric conduction seems to be based on the ionic conduction. It is possible that the other mechanism for electric conduction in the electrolyte of fluorinated oligomer gel: hopping conduction on the molecule for example.

4. Conclusion

We studied the dye-sensitized solar cell with a fluorinated oligomer gel electrolyte with mixing two kinds of ionic liquid (imidazolium and pyrazolium systems) in the scope of electric conductivity and the cell performance. It was found that the two kinds of ionic liquid showed a different behavior in electric conductivity. As the ionic liquid is added, the electric conductivity increases in the case of pyrazolium ionic liquid, but contrarily decreases in the case of imidazolium ionic liquid. LiI has the effect of suppressing the electric conductivity for pyrazolium ionic liquid, but there is no dependence in the case of imidazolium ionic liquid and DMSO without any ionic liquid. The solar cell performance exhibited that the DMSO without any ionic liquid provided the largest short current density. Ionic liquid worsens the cell performance because ion couple on the fluorinated oligomer plays an undesirable role for the electric conduction. It should be investigated how the ion couple on the fluorinated oligomer affects the ion conduction in the electrolyte.

Acknowledgements

The authors wish to thank Prof. Hideo Sawada for the preparation of fluorinated oligomer of AMPS used in our experiments.

References

[1] Kato, N., Higuchi, K., Tanaka, H., Nakajima, J., Sano, T. and Toyoda, T. (2011) Im-

provement in Long-Term Stability of Dye-Sensitized Solar Cell for Outdoor Use. *Solar Energy Materials and Solar Cells*, **95**, 301-305.
https://doi.org/10.1016/j.solmat.2010.04.019

[2] Berginc, M., Krašovec, U.O., Jankovec, M. and Topič, M. (2007) The Effect of Temperature on the Performance of Dye-Sensitized Solar Cells Based on a Propyl-Methyl-Imidazolium Iodide Electrolyte. *Solar Energy Materials and Solar Cells*, **91**, 821-828. https://doi.org/10.1016/j.solmat.2007.02.001

[3] Ishimaru, N., Kubo, W., Kitamura, T., Yanagida, S., Tsukahara, Y., Maitani, M.M. and Wada, Y. (2011) Quasi-Gel-State Ionic Liquid Electrolyte with Alkyl-Pyrazolium Iodide for Dye-Sensitized Solar Cells. *Materials Science and Engineering*: *B*, **176**, 996-1001. https://doi.org/10.1016/j.mseb.2011.05.033

[4] Li, B., Wang, L., Kang, B., Wang, P. and Qiu, Y. (2006) Review of Recent Progress in Solid-State Dye-Sensitized Solar Cells. *Solar Energy Materials and Solar Cells*, **90**, 549-573. https://doi.org/10.1016/j.solmat.2005.04.039

[5] Koh, J.H., Koh, J.K., Park, N.-G. and Kim, J.H. (2010) Azide-Induced Cross Linking of Electrolytes and Its Application in Solid-State Dye-Sensitized Solar Cells. *Solar Energy Materials and Solar Cells*, **94**, 436-441.
https://doi.org/10.1016/j.solmat.2009.10.024

[6] Wei, T.C., Wan, C.C. and Wang, Y.Y. (2007) Preparation and Characterization of a Micro-Porous Polymer Electrolyte with Cross-Linking Network Structure for Dye-Sensitized Solar Cell. *Solar Energy Materials and Solar Cells*, **91**, 1892-1897.
https://doi.org/10.1016/j.solmat.2007.07.005

[7] Kyokane, J., Shima, K., Sawada, H., Ueda, H. and Satio, K. (2003) Electrical Properties of Fluorinated Gel Electrolytes Using High Ionic Conducting Solution and Its Application to Secondary Battery. *Thin Solid Films*, **438-439**, 257-261.
https://doi.org/10.1016/S0040-6090(03)00794-6

[8] Kyokane, J. and Ohmukai, M. (2013) Dye-Sensitized Solar Cell with Fluorinated Gel Electrolyte: Effect of TiO_2 Particle Size on Performance. *Advances in Nanoparticles*, **2**, 318-322. https://doi.org/10.4236/anp.2013.24043

[9] Ohmukai, M. and Kyokane, J. (2013) Pt Deposition on Anode Enhances the Performance of Dye-Sensitized Solar Cell with Non-Cross-Linked Gel Electrolyte. *Journal of Materials Science and Chemical Engineering*, **1**, 16-19.

[10] Ohmukai, M. and Kyokane, J. (2013) LiI Enhances the Performance of Dye-Sensitized Solar Cell with Fluorinated Oligomer gel Electrolyte. *Journal of Nano Energy and Power Research*, **2**, 135-138. https://doi.org/10.1166/jnepr.2013.1018

[11] Ohmukai, M. and Kyokane, J. (2014) The Effect of Ionic Liquid to Dye-Sensitized Solar Cell with Fluorinated Oligomer Electrolyte. *Materials Focus*, **3**, 75-77.
https://doi.org/10.1166/mat.2014.1151

[12] Ohmukai, M. and Kyoknae, J. (2014) Electric Conductivity of Fluorinated Oligomer Gel Electrolyte: The Effect of LiI Concentration. *Advanced Science Focus*, **2**, 83-85.
https://doi.org/10.1166/asfo.2014.1074

[13] Chengwu, S., Songyuan, D., Kongjia, W., Xu, P., Li, G., Longyue, Z., Linhua, H. and Fantai, K. (2005) Influence of 1-Methyl-3-Propylimidazolium Iodide on I_3^-/I^- Redox Behavior and Photovoltaic Performance of Dye-Sensitized Solar Cells. *Solar Energy Materials and Solar Cells*, **86**,527-535. https://doi.org/10.1016/j.solmat.2004.09.004

[14] Shi, C., Ge, Q., Han, S., Cai, M., Dai, S., Fang, X. and Pan, X. (2008) An Improved Preparation of 1-Methyl-3-Propylimidazolium Iodide and Its Application in Dye-Sensitized Solar Cells. *Solar Energy*, **82**, 385-388.
https://doi.org/10.1016/j.solener.2007.10.013

[15] Shi, C., Ge, Q., Zhou, F., Cai, M. Wang, X., Fang, X. and Pan, X. (2009) An Improved Preparation of 3-Ethyl-1-Methylimidazolium Trifluoroacetate and Its Application in Dye Sensitized Solar Cells. *Solar Energy*, **83**, 108-112. https://doi.org/10.1016/j.solener.2008.07.002

[16] Paulsson, H., Berggrund, M., Svantesson, E., Hagfeldt, A. and Kloo, L. (2004) Molten and Solid Metal-Iodide-Doped Trialkylsulphonium Iodides and Polyiodides as Electrolytes in Dye-Sensitized Nanocrystalline Solar Cells. *Solar Energy Materials and Solar Cells*, **82**, 345-360. https://doi.org/10.1016/j.solmat.2003.12.005

[17] Wang, Y., Sun, Y., Song, B. and Xi, J. (2008) Ionic Liquid Electrolytes Based on 1-Vinyl-3-Alkylimidazolium Iodides for Dye-Sensitized Solar Cells. *Solar Energy Materials and Solar Cells*, **92**, 660-666. https://doi.org/10.1016/j.solmat.2008.01.017