

Homeotropic Aligned Liquid Crystal Molecules in Dye-sensitized Solar Cells for High Efficiency

Hyeon-Kyung KIM, Seung-Yeol HUR, Wan-Seok KANG and Gi-Dong LEE*

Department of Electronic Engineering, Dong-A University, Busan 604-714

Sung-Ho JIN[†]

Department of Chemistry Education & Interdisciplinary Program of Advanced Information and Display Materials, Pusan National University, Busan 609-735

(Received 21 January 2010, in final form 7 April 2010)

We optimized the alignment of the embedded liquid crystal (LC) molecular in quasi-solid state dye-sensitized solar cells (DSSC) to enhance the photovoltaic performance. The aligned LC molecular increases the ordering strength in the electrolyte so that it can provide a better pathway to transfer generated charges inside the polymer electrolyte. We performed experiments with three types of electrolytes, a typical polymer electrolyte, a polymer electrolyte with LC, and a polymer electrolyte with an aligned LC. The electro-optical characteristics obtained from these experiments were compared with each other for validation. We found that the aligned LCs in a polymer electrolyte can provide higher photovoltaic performance than conventional electrolytes.

PACS numbers: 84.60.Jt, 77.84.Nh, 61.30.Gd

Keywords: Dye-sensitized solar cell, Liquid crystal, Homeotropic alignment, Polymer electrolyte

DOI: 10.3938/jkps.56.1519

I. INTRODUCTION

The dye-sensitized solar cell was presented by the O'Regan and Gratzel [1] group and has been in the spotlight among the several nominated device modes for solar cells because of its high energy-conversion efficiency [2], low cost for manufacturing [3], and environmental friendliness.

Dye-sensitized solar cells (DSSC) have a sandwich structure that consists of TiO₂ nano-particles coated with dye and a counter electrode. The inside of the electrodes is filled with electrolytes with an iodide/tri-iodide redox mediator [4].

In general, a liquid-type electrolyte shows a merit in that it can provide a high power-conversion efficiency (PCE). On the contrary, it also has a problem of electrolyte leakage so that long-term instability may be a serious demerit for its use in solar devices. Therefore, many researchers have been studying polymer electrolytes, solid electrolytes, and so instead of liquid electrolytes. Among them, polymer electrolytes show a quasi-solid phase so that they have high stability, which can overcome the leakage of the electrolyte in DSSC. For enhancing performance in DSSC, we studied the ef-

fect of a polymer electrolyte with the liquid crystal (LC) molecules [5].

In this paper, we report the effect of the LC alignment inside a polymer electrolyte on the PCE of DSSC. In this research, we aligned the LC molecules in the electrolyte homeotropically by applying a voltage. We compared the performances of photovoltaic cells employing three different electrolytes: a typical polymer electrolyte without LCs, a polymer electrolyte containing LCs, and a polymer electrolyte with the LCs aligned homeotropically to each other. From this, we could confirm that the alignment of the LC molecules and the LC alignment in the polymer electrolyte helped to increase the photovoltaic performance in DSSC.

The concentration of the LCs in the electrolyte was varied to find the optimal value in the LC in our previous research [6]. We optimized the LC concentration at about 10 wt% in the polymer electrolyte used for the experiment reported in this paper.

II. EXPERIMENTS AND DISCUSSION

The process for preparing the DSSC devices can be described as follows: First of all, a TiO₂ paste (Ti-Nanoxide HT/SP, Solaronix SA) was coated by using a doctor blade on FTO conducting glass. It was dried in

*E-mail: gdlee@dau.ac.kr; Fax: +82-51-200-7712

[†]E-mail: shjin@pusan.ac.kr

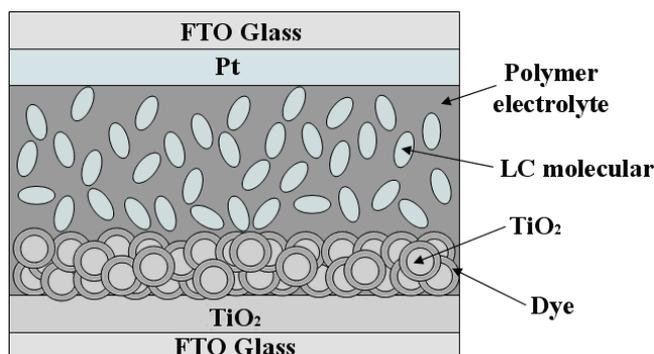


Fig. 1. Schematic diagram of a dye-sensitized solar cell using a homogeneous mixture of LC molecules.

the atmosphere for 5 minutes and sintered at 450 °C for 30 min. For absorbing the dye layer into the TiO₂, the annealed nc-TiO₂ electrodes were immersed in absolute ethanol containing 0.3 mM of N 719 dye (not purified) for 24 h at ambient temperature. Pt counter electrodes were formed by coating platinum paste (Pt-Catalyst T/SP, Solaronix SA) on the glass at 400 °C for 20 minutes. The polymer electrolytes consist of ethylene carbonate, propylene carbonate, acetonitrile, tetrabutylammonium iodide, iodine, 1-propyl-3-methylimidazolium iodide, and polycrylonitrile (Mw = 86,200, Aldrich Co). The used LCs (E7, Merck Co) were mixed at 10 wt%, the optimized LC concentration, in the polymer electrolyte. For an appropriate mixture of the electrolyte and the LCs, we applied 65 °C for 24 hours by using a magnetic stirrer [5]. Secondly, the prepared dye-coated TiO₂ electrode and the Pt counter electrode were fabricated using 60- μ m-thick surlyn (SX1170-60, DuPont). Finally, a voltage of AC 10V was applied to the fabricated cell for 1 hour by using function generator (Tektronix Inc., model AFG 3022) for homeotropic LC alignment. During the applied voltage, the solvent in the polymer electrolyte was evaporated, and the LC molecules were fixed in the DSSC.

Photocurrent-voltage curves were measured using a Keithly model 2400 source measure unit. A class-A solar simulator (Yamashita Denso, model YSS-200A) was equipped with a 1600-W Xenon lamp as a light source, where the light intensity was adjusted using a Fraunhofer ISE-calibrated mono Si solar cell with KG-3 filter to approximate AM 1.5G 1 sun illumination.

Figure 1 shows a schematic of the quasi-solid state DSSC using a homogeneous mixture of the embedded LC molecules in a polymer electrolyte. In general, the photovoltaic efficiency of the DSSC mainly depends on the diffusion rate of the redox species, which is strongly related to the transfer probability of generated charges. Besides, the transfer rate of the particles can be increased by adding LC molecules to the polymer electrolyte because the embedded LC molecules make the “hopping effect” between the molecules higher. Generally, the scalar order parameter of the liquid crystals was mea-

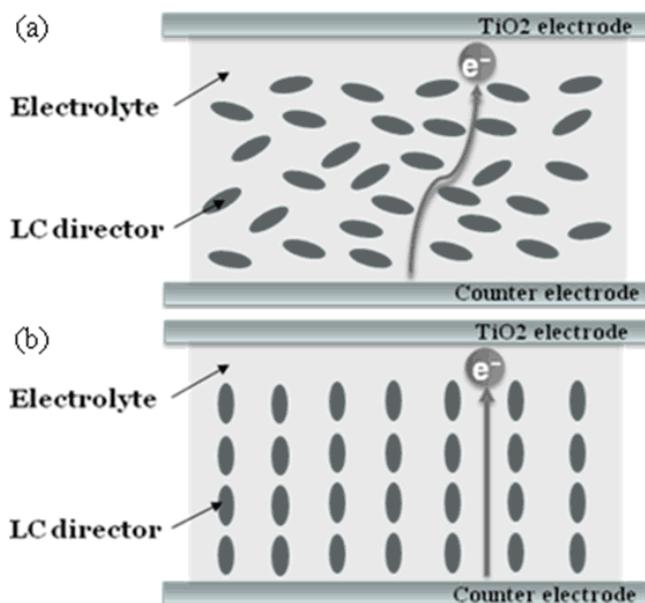


Fig. 2. Compared diagrams of DSSC with embedded LC molecules and vertically aligned LC molecules: (a) the LC alignment in the electrolyte before the voltages applied and (b) homeotropic alignment of the LC molecules in the electrolyte with the voltage applied.

sured in the range 0.5 - 0.7 at room temperature. This implies that the neighboring liquid-crystal molecules will be aligned in almost the same direction to each other so that the total effective order parameter of the electrolyte will be increased by the embedded LC molecules. Therefore, the high order parameter of a polymer electrolyte with LC molecules embedded induces a transport pathway for a high transfer probability of the redox species, which leads to an increase in the photocurrent density and an improved photovoltaic performance [5].

For the experiment, we prepared a mixture of PAN, EC, PC, AN, TBAI, I2, and PMII for the electrolyte and the desired concentration of liquid crystals at room temperature. We used E7 as a compounded LC mixture in the electrolyte. E7 has CN₋ as the terminal group due to the fact that PAN as a polymer matrix for liquid crystal embedded in polymer electrolyte induces molecular similarity between the E7 and the PAN.

From the experimental result [5,6], we optimized the concentration of the LC (E7) for a high PCE of the DSSC. As a result, we found that the highest PCE could be achieved at a LC concentration of 10 wt% by confirming a 4.52% increase of the PCE of a DSSC compared to a conventional DSSC.

From a previous experiment, we could confirm that the embedded LC molecules obviously helped increase the PCE of the DSSC because the high order parameter of the LC molecules could provide a better pathway between the molecules of the electrolyte. Therefore, control of the LC alignment, which is directly related to the ordering strength of the LC molecular, can also increase the

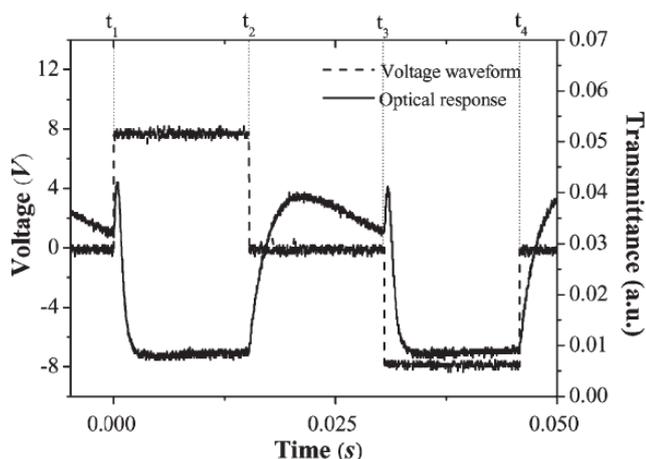


Fig. 3. Measured electro-optical response of the quasi-solid state DSSCs with liquid crystals embedded in a polymeric electrolyte between cross-Nicol polarizers [5].

PCE of the DSSC. The alignment of the LC molecules can be controlled by applying a voltage at the electrode of the cell containing the electrolyte layer. The LC E7, which is a positive dielectric anisotropic material, moves in the direction of the electric field [7]. Therefore, if we apply a high voltage across the DSSC, most of the LC molecules in the electrolyte will be oriented in the direction of the electric field. Finally, we can expect a high ordering strength of the LC molecules so that the effective total scalar ordering strength of the electrolyte will also increase.

Figure 2 shows the LC alignment in the electrolyte of the DSSC. Figure 2(a) indicates the LC alignment in the electrolyte before we apply the voltage. In this case, the LC molecules are distributed homogeneously with 0.5 - 0.7 of the scalar order parameter at room temperature. However, we can expect a high order parameter when a high voltage is applied, as shown in Fig. 2(b). Figure 2(b) shows the LC alignment in the electrolyte when we apply a high voltage. As mentioned before, the positive LC molecules follow their orientation in the direction of the applied electric field. Therefore, all the LC molecules in the polymer electrolyte will align along the applied electric field. This will result in a scalar order parameter higher than for other electrolytes so that high hopping is provided for a high PCE of the DSSC cell.

In a previous paper, we confirmed that the LC molecules in quasi-solid state DSSCs were aligned along the applied voltage as shown in Fig. 3 [5], which shows the measured electro-optical response of the LC molecules in DSSCs under cross-Nicol polarizers. The times between t_1 and t_2 , t_3 , and t_4 in the Fig. 3 represent the application times of the voltage to the DSSC cell. In this time, we can observe that the optical transmittance becomes lower, which means the LC molecules are vertically aligned in the DSSC cell. We can simply calculate the reaction of the LC molecules in the DSSC

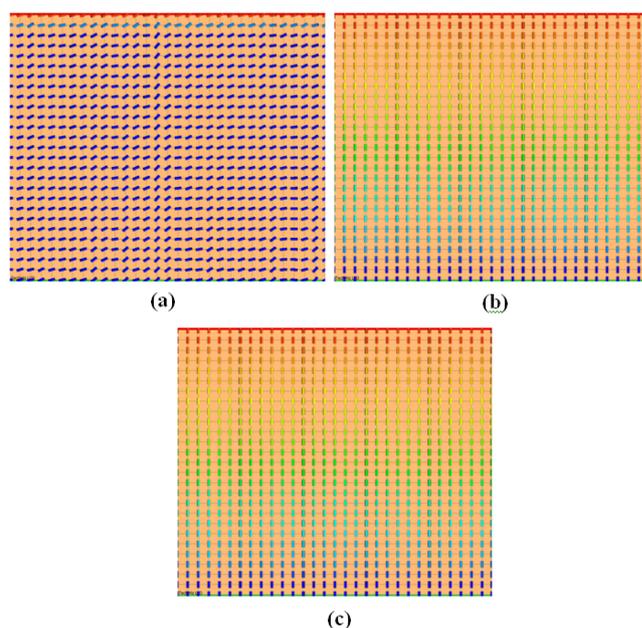


Fig. 4. Simulated configuration of the LC director: (a) at 0 V (initial state), (b) at 8 V, and (c) at 10 V.

cell by using the Oseen-Frank equation [8]. For the calculation of the LC configurations, we use the commercial LC software TechWiz LCD provided by the SANAYI System Co in Korea. Figure 4 shows the calculated LC configurations in the DSSC cell. The cell gap for calculation was set to $60 \mu\text{m}$, and the LC used was E7 (elastic constant $k_{11} = 12$ (pN), $k_{22} = 9$ (pN), $k_{33} = 19.5$ (pN), dielectric anisotropy $\Delta\epsilon = 14.5$). Figure 4(a) shows the initial state of the embedded LC directors in the DSSC cell, which is random because no alignment layer is applied in the cell. After applying a voltage to the DSSC cell, however, the LC molecules in the DSSC cell become vertically aligned because of the applied voltage. Figures 4(b) and (c) show the LC alignments in the cell at 8 V and 10 V, respectively. In Fig. 4, we can observe that the random LC distribution in the initial state becomes vertically aligned by applying a high voltage in the DSSC cell. This implies that the scalar order parameter of the LC molecules can be increased by applying a voltage in the DSSC cell. Therefore, solidification of the DSSC cell during the application of a voltage can fix the LC molecules, vertical alignment in a quasi-solid electrolyte so that we may expect a higher scalar order parameter.

In order to verify the effect of the LC alignment on the PCE of the DSSC, we compared the performance of photovoltaic cells employing three different electrolytes: a polymer electrolyte without LCs, a polymer electrolyte containing 10 wt% LCs, and a polymer electrolyte with aligned LCs. We made the three DSSCs using three different electrolytes and measured the photocurrent-voltage curves, the fill factor, and the PCE (η) for each polymer electrolyte.

Figure 5 shows the measured photocurrent density-

Table 1. Photovoltaic performances of the typical polymer electrolyte, the polymer electrolyte with LCs, and the polymer electrolyte with homeotropically aligned LCs under A.M 1.5G 1 sun illumination (100 mW/cm^2).

1 sun (100 mW/cm^2)	J_{SC}	V_{OC} (V)	Fill Factor	η (%)
Typical polymer electrolyte	4.53	0.54	0.57	1.38
Polymer electrolyte with LCs	5.40	0.56	0.64	1.94
Polymer electrolyte aligned LCs	6.05	0.65	0.65	2.55

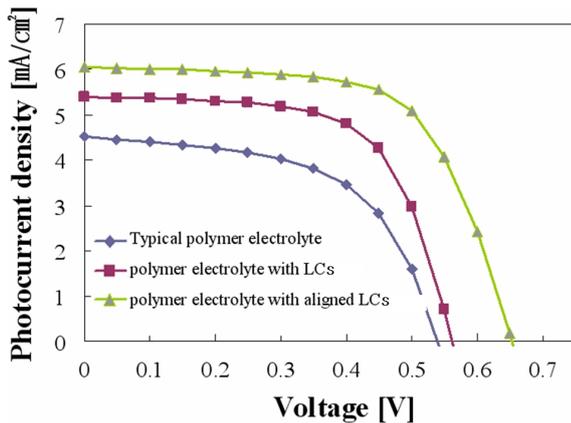


Fig. 5. Measured J - V curve under A.M 1.5G 1 sun illumination (100 mW/cm^2).

voltage (J - V) curves for each cell. In the figure, the electrolyte with aligned LCs has both a high photocurrent density and a high open circuit voltage. Therefore, we can recognize that the embedded aligned LCs permit a large fill factor compared to the other cases so that we can expect a larger PCE.

Table 1 presents the photovoltaic performances, the photocurrent density (J_{SC}), the open circuit voltage (V_{OC}), the power conversion efficiency (η), and the fill factor, for each cell. The experimental results reported in this paper do not show an excellent and maximum PCE from the proposed DSSC. Nevertheless, we can obviously confirm that the polymer electrolyte provides better performance when the embedded LCs are aligned in the polymer electrolyte. As for the PCE, η , of the DSSC, about 80% and 25% improvements are shown in Table 1 by using the aligned LC molecules compared to the typical DSSC and the DSSC with embedded LC molecules, respectively. Thus, we believed that η can be increased by applying a voltage, which causes a high order of LC alignment in the electrolyte.

III. CONCLUSION

In conclusion, we observed the effect of the alignment of the embedded liquid crystal (LC) molecular on the PCE of a quasi-solid-state dye-sensitized solar cell (DSSC). In order to increase the PCE of the cell, we increase the ordering strength of the embedded LC molecules by applying the voltage, which can lead to the homeotropic LC alignment. Verification of the effect of the LC alignment was done by comparing the PCE of the cell using the polymer electrolyte with the aligned LC to that of the conventional DSSC experimentally. As a result, we could increase the PCE by about 25% compared to the non-aligned LC and by about 80% compared to the conventional DSSC.

ACKNOWLEDGMENTS

This work was support by the Dong-A University Research Fund.

REFERENCES

- [1] B. O'Regan and M. Gratzel, *Nature* **353**, 737 (1991).
- [2] A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.* **33**, 269 (2000).
- [3] A. Goetzberger, J. Luther and G. Willeke, *Sol. Energy Mater. Sol. Cells* **74**, 316 (2002).
- [4] M. Grätzel, *Prog. Photovoltaics Res. Appl.* **8**, 171 (2000).
- [5] S. C. Kim, M. K. Song, T. I. Ryu, M. J. Lee, S.-H. Jin, Y. S. Gal, H. K. Kim, G.-D. Lee and Y. S. Kang, *Macromol. Chem. Phys.* **210**, 1844 (2009).
- [6] H. K. Kim, M. J. Lee, S.-H. Jin and G.-D. Lee, *Mol. Cryst. Liq. Cryst.* **510**, 323 (2009).
- [7] P. Yeh and C. Gu, *Optics of Liquid Crystal Displays* (John Wiley & Sons Inc, New York, 1999).
- [8] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).