

Development of Dye-Sensitized Solar Cells Composed of Liquid Crystal Embedded, Electrospun Poly(vinylidene fluoride-co-hexafluoropropylene) Nanofibers as Polymer Gel Electrolytes

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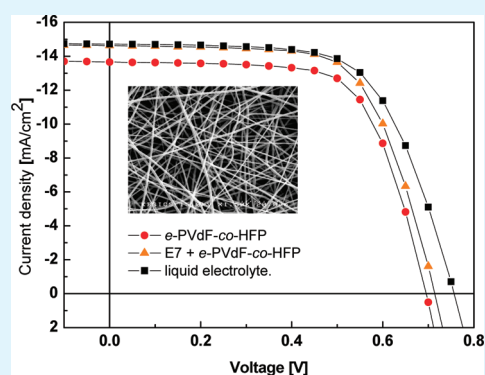
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ABSTRACT: In order to overcome the problems associated with the use of liquid electrolytes in dye-sensitized solar cells (DSSCs), a new system composed of liquid crystal embedded, polymer electrolytes has been developed. For this purpose, three types of DSSCs have been fabricated. The cells contain electrospun poly(vinylidene fluoride-co-hexafluoropropylene) (*e*-PVdF-co-HFP) polymer gel electrolyte, with and without doping with the liquid crystal E7 and with a liquid electrolyte. The morphologies of the newly prepared DSSCs were explored using field emission scanning electron microscopy (FE-SEM). Analysis of the FE-SEM images indicate that the DSSC composed of E7 embedded on *e*-PVdF-co-HFP polymer gel electrolyte has a greatly regular morphology with an average diameter. The ionic conductivity of E7 embedded on *e*-PVdF-co-HFP polymer gel electrolyte was found to be 2.9×10^{-3} S/cm at room temperature, a value that is 37% higher than that of *e*-PVdF-co-HFP polymer gel electrolyte. The DSSC containing the E7 embedded, *e*-PVdF-co-HFP polymer gel electrolyte was observed to possess a much higher power conversion efficiency (PCE = 6.82%) than that of an *e*-PVdF-co-HFP nanofiber (6.35%). In addition, DSSCs parameters of the E7 embedded, *e*-PVdF-co-HFP polymer gel electrolyte ($V_{oc} = 0.72$ V, $J_{sc} = 14.62$ mA/cm², FF = 64.8%, and PCE = 6.82% at 1 sun intensity) are comparable to those of a liquid electrolyte ($V_{oc} = 0.75$ V, $J_{sc} = 14.71$ mA/cm², FF = 64.9%, and PCE = 7.17%, both at a 1 sun intensity).

KEYWORDS: dye-sensitized solar cells, liquid crystals, polymer gel electrolyte, electrospinning, PVdF-co-HFP



INTRODUCTION

The need for a substantial expansion of power generation is high owing to environmental problems associated with existing methods including nuclear, thermal, and hydroelectric. Solar cells directly convert solar energy into electrical energy and can produce electricity without special maintenance and environmental concerns. Silicon-based inorganic solar cells have been utilized for this purpose in the last few decades, but drawbacks exist with this type of solar cell, such as manufacturing costs and an unwieldy fabrication process. As a result, a great effort is underway to develop solar cells that consist of more easily processed and low-cost materials.

Since the first report by Grätzel,¹ dye-sensitized solar cells (DSSCs) have gained much attention. The Grätzel group demonstrated that a power conversion efficiency (PCE) of 12% could be obtained using a liquid electrolyte-based DSSC. Importantly, this efficiency is very close to those of amorphous silicon-based inorganic solar cells.^{2,3} Unfortunately, losses of liquid electrolytes by leakage and/or volatilization is a major drawback that restrict the long-term stabilities of DSSCs. To

overcome this problem, alternatives, such as inorganic or organic hole conductors,^{4,5} ionic liquids,^{6,7} and polymer gel electrolytes,^{8–11} have been sought as replacements for liquid electrolytes in DSSCs.

Recently, growing attention has been given to quasi-solid-state DSSCs that employ polymer gel electrolytes, owing to their nonflammable nature, negligible vapor pressure, good permeability into the mesoporous TiO₂, and high ionic conductivity.^{10,12} Polymer gel electrolytes such as poly(acrylonitrile),^{13,14} poly(ethylene glycol),^{15,16} poly(methyl methacrylate),^{17,18} and poly(oligoethylene glycol methacrylate),¹⁹ with different plasticizers have been employed in quasi-solid-state DSSCs. Although DSSCs composed of polymer gel electrolytes do not suffer from electrolyte loss problems, they have low PCEs because of the lower electron injection efficiencies of the electrolyte material. It has been

Received: January 12, 2012

Accepted: March 15, 2012

Published: March 15, 2012

demonstrated that, among the polymer gel electrolytes, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) has a relatively high ionic conductivity at room temperature and that quasi-solid-state DSSCs based on a PVdF-co-HFP matrix exhibit a 6% PCE.¹⁰

Liquid crystals have been used often to template inorganic and organic materials, especially polyacetylene and polythiophene derivatives, thereby increasing carrier mobility and electrical conductivity.^{20–22} Room temperature liquid crystals are attractive candidates for replacement of volatile liquid electrolytes in DSSCs because they form a mesophase with high ionic conductivity. Recently, a few reports have appeared describing applications of liquid crystals in quasi-solid-state DSSCs.^{23–26}

Electrospinning is a novel technology that utilizes an electrostatic force to produce nanofibers, which have applications in a number of areas, including medicine and filtration technologies, as well as for the fabrication of DSSCs. The main advantage of the electrospinning process is associated with the high degree of control that is available over morphology, porosity, and composition using simple equipment.

Below, we describe the results of a study that has led to the development of a liquid crystal embedded polymer gel electrolytes that is constructed using the electrospinning technique. The photochemically stable, fluorine polymer, PVdF-co-HFP, was used as the electrolyte components of quasi-solid-state DSSCs, whose performance was evaluated. The utilization of electrospun polymer gel electrolytes embedded on liquid crystal has not been reported, to the best of our knowledge in DSSCs.

EXPERIMENTAL SECTION

Preparation of Electrospun PVdF-co-HFP Nanofiber. The electrospun PVdF-co-HFP nanofiber (hereafter referred to as *e*-PVdF-co-HFP) was prepared from 15 wt % solution of PVdF-co-HFP in a mixture of acetone/*N,N*-dimethylacetamide (7:3 wt %) at 80 °C with constant stirring to form a transparent homogeneous polymer solution.²⁷ The solution was cooled to room temperature. The polymer solution was connected to a stainless steel needle (21G) using a syringe pump (KD Scientific, model CPS-40K03VIT), and a high voltage of 13 kV was applied to the end of the needle. The *e*-PVdF-co-HFP nanofiber was deposited onto a wall, where the tip-ground distance was fixed at 15 cm. The thickness of *e*-PVdF-co-HFP nanofiber was controlled to 60 μm, and the resulting nanofibers were vacuum-dried at 80 °C for 24 h to remove solvent molecules.

Fabrication of DSSCs. The screen-printable technique was used for fabrication of DSSCs. The nanocrystalline TiO₂ (nc-TiO₂) pastes were prepared using ethyl cellulose (Aldrich), lauric acid (Fluka), and terpineol (Fluka) as described elsewhere.²⁴ The prepared nc-TiO₂ paste was coated on a FTO conducting glass (TEC8, Pilkington, 8 Ωcm⁻¹, glass thickness of 2.3 mm), dried in air at an ambient temperature for 5 min, and sintered at 500 °C for 30 min. The thicknesses of the annealed films were determined to be 20 ± 1 μm using Alpha-step IQ surface profiler (KLA Tencor). The annealed nc-TiO₂ electrodes were immersed in absolute ethanol containing 0.5 mM of N719 dye (Ru[LL'(NCS)₂], L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, L' = 2,2'-bipyridyl-4,4'-ditetrabutylammonium carboxylate) for 24 h at an ambient temperature for the dye adsorption process. Pt counter electrodes were prepared using thermal reduction of thin films formed from 7 mM of H₂PtCl₆ in 2-propanol solution at 400 °C for 20 min, employing the doctor blade method. The dye-adsorbed nc-TiO₂ electrode and Pt counter electrode were assembled using 60 μm thick Surlun (Dupont 1702). The quasi-solid-state DSSCs were fabricated using the *e*-PVdF-co-HFP polymer gel electrolyte by sandwiching a slice of the *e*-PVdF-co-HFP nanofibers

between a dye-sensitized TiO₂ electrode and Pt counter electrode. The liquid crystal embedded on *e*-PVdF-co-HFP polymer gel electrolyte components were composed of iodine (I₂), tetrabutylammonium iodide (TBAI), 1-propyl-3-methylimidazolium iodide (PMII) as an ionic liquid, ethylene carbonate (EC)/propylene carbonate (PC) (3/1 as weight ratio), a liquid crystal (E7) (Merck Co) as a plasticizer, and acetonitrile. E7, composed of four CN-biphenyl derivatives, is widely used in polymer dispersed liquid crystalline displays.²⁸ The polymer gel electrolyte components were filled between two electrodes using a vacuum pump in hot plate. A uniform film of E7 embedded on *e*-PVdF-co-HFP polymer gel electrolyte layer was formed in the DSSC after cooling to room ambient temperature.

For comparison studies, control DSSCs were fabricated using *e*-PVdF-co-HFP polymer gel electrolyte without E7 and liquid electrolyte. The liquid electrolyte was composed of I₂, TBAI, PMII, EC/PC (3/1 as weight ratio), and acetonitrile. The active areas of the dye-coated TiO₂ films were determined using an image analysis program equipped with a digital microscope camera (Moticam 1000). The performance of DSSCs was determined using a calibrated AM 1.5G solar simulator (Orel 300 W simulator, models 81150) with a light intensity of 100 mW cm⁻² adjusted using a standard PV reference cell (2 cm × 2 cm monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA) and a computer-controlled Keithley 236 measure unit.

The PCE (η) of a solar cell given by

$$\eta = P_{\text{out}}/P_{\text{in}} = (J_{\text{sc}} \times V_{\text{oc}}) \times \text{FF}/P_{\text{in}}$$

with $\text{FF} = P_{\text{max}}/(J_{\text{sc}} \times V_{\text{oc}}) = (J_{\text{max}} \times V_{\text{max}})/(J_{\text{sc}} \times V_{\text{oc}})$, where P_{out} is the output electrical power of the device under illumination and P_{in} is the intensity of incident light (e.g., in Wm⁻² or mWcm⁻²). V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, and fill factor (FF) is calculated from the values of V_{oc} , J_{sc} , and the maximum power point, P_{max} . All fabrication steps and characterization measurements were carried out in an ambient environment without a protective atmosphere. While measuring the current density–voltage (J – V) curves for DSSCs, a black mask was used and only the effective area of the cell was exposed to light irradiation. Data for the DSSCs were accumulated over more than 5 measurements carried out under the same conditions.

Measurements. The ionic conductivity (σ) was calculated using $\sigma = L/(R_b A)$, where L and A are the thickness and area of the *e*-PVdF-co-HFP nanofiber, respectively. R_b is the bulk resistance, and it was calculated by AC impedance investigation. The thickness (L) of the *e*-PVdF-co-HFP nanofiber (60 μm) was determined using a digimatic micrometer. The area (A) of the *e*-PVdF-co-HFP nanofiber was ca. 0.9–1.0 cm². The morphologies of *e*-PVdF-co-HFP nanofiber were analyzed using field emission scanning electron microscopy (FE-SEM). The resistance for ionic conductivity was measured using the alternating current (AC) impedance test and an electrochemical impedance analyzer (Reference Dummy cell, WEISS00 instruments). The blocking cell of platinum/*e*-PVdF-co-HFP/platinum was used in the 1–10⁶ Hz frequency range at room temperature. The applied bias voltage and AC amplitude were set to the open-circuit voltage of the cells and 100 mV, respectively. The electrochemical impedance spectroscopy (EIS) data was also accumulated using an impedance analyzer under the same conditions employed for the FTO/TiO₂/electrolyte/Pt/FTO cells and fitted by Z-MAN software (WONA-TECH) and Echem analyst (WEISS00).

RESULTS AND DISCUSSION

In the preparation of the *e*-PVdF-co-HFP nanofiber, several parameters, such as applied voltage, tip-to-contact-distance (TCD), and concentration of PVdF-co-HFP solution were controlled. The nanofiber, generated using a 15 wt % PVdF-co-HFP solution, 13 kV applied voltage, and 15 cm TCD with a 10 mL/h flow rate, displayed a highly regular morphology with an average diameter.²⁷ An image, recorded using FE-SEM (Figure 1), shows that *e*-PVdF-co-HFP nanofiber is composed of a

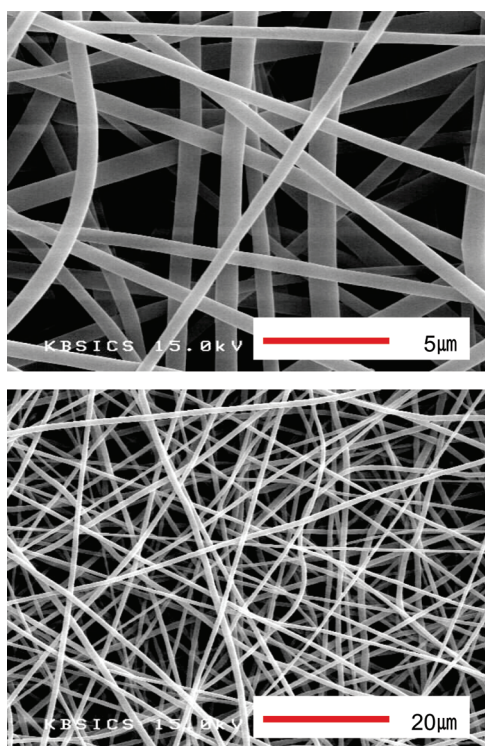


Figure 1. SEM images of the *e*-PVdF-*co*-HFP nanofiber.

three-dimensional network that is fully interconnected. Owing to these properties, the *e*-PVdF-*co*-HFP nanofiber should be able to incorporate electrolytes.

The high photovoltaic performance observed earlier for DSSCs when liquid crystals are incorporated as components of polymer gel electrolyte is a consequence of an increase in molecular ordering and ionic conductivity as well the formation of diffusion pathways for the redox species. In the current study, we selected the liquid crystal E7 as an additive to the polymer gel electrolyte of a DSSC because we felt that its cyanobiphenyl groups would participate in ideal dipole–dipole interactions with groups in the *e*-PVdF-*co*-HFP nanofiber.^{23–26}

In general, the power conversion efficiencies (PCE) of DSSCs are dependent on the ionic conductivity of the polymeric matrix. An example of this phenomenon is found in the increased ionic conductivity of the polymer gel electrolytes caused by incorporation of suitable plasticizers or additives.^{12,29,30} Typically, the ionic conductivities of PAN/LiCF₃SO₃ and PEG/LiBF₄ complex are ca. 10^{−3} and 10^{−6}–10^{−7} S/cm, respectively.^{31,32} Results of ionic conductivity studies with the *e*-PVdF-*co*-HFP polymer gel electrolyte in the presence and absence of E7 are summarized in Table 1. The observations show that the ionic conductivity of E7 embedded on *e*-PVdF-*co*-HFP polymer gel electrolyte is 2.9 × 10^{−3} S/cm

Table 1. Impedances and Ionic Conductivities of the *e*-PVdF-*co*-HFP Nanofiber-Based Polymer Gel Electrolytes with and without E7 and Liquid Electrolyte

| electrolyte | impedance | ionic conductivity |
|------------------------------------|-----------|------------------------|
| <i>e</i> -PVdF- <i>co</i> -HFP | 32.01 | 2.1 × 10 ^{−3} |
| E7+ <i>e</i> -PVdF- <i>co</i> -HFP | 22.50 | 2.9 × 10 ^{−3} |
| liquid electrolyte | 21.03 | 3.2 × 10 ^{−3} |

at room temperature, which corresponds to a 37% increase over that of *e*-PVdF-*co*-HFP polymer gel electrolyte without E7. The parameters J_{sc} and FF are greatly influenced by the ionic conductivity of the polymer gel electrolyte. In the case of *e*-PVdF-*co*-HFP polymer gel electrolyte incorporating E7, the high ionic conductivity is a likely consequence of the induced ease of transport of the redox species.

In Figure 2 are shown photocurrent density–voltage (J – V) curves at 1 sun conditions of the SnO₂:F/TiO₂/N719 Dye/

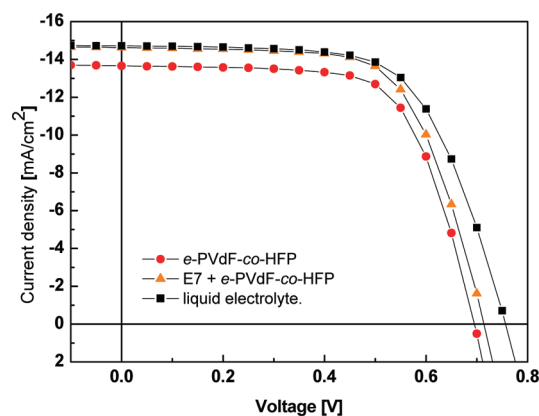


Figure 2. Photocurrent–voltage curves for DSSCs with *e*-PVdF-*co*-HFP-based polymer gel electrolyte with and without E7 and the liquid electrolyte.

polymer gel and liquid electrolytes/Pt devices constructed using *e*-PVdF-*co*-HFP nanofiber, with E7 embedded on *e*-PVdF-*co*-HFP nanofiber as the polymer gel electrolyte. For comparison purposes, measurements were also made on a system employing a liquid electrolyte. The results indicate that the DSSC containing a combination of E7 and *e*-PVdF-*co*-HFP nanofiber has an improved photovoltaic performance in comparison with that made using the *e*-PVdF-*co*-HFP polymer gel electrolyte alone. Specifically, the photovoltaic performance of the DSSC composed of E7 embedded on the *e*-PVdF-*co*-HFP polymer gel electrolyte is reflected by $V_{oc} = 0.72$ V, $J_{sc} = 14.62$ mA/cm², FF = 64.8%, and PCE = 6.82% at 1 sun intensity. In contrast, the J – V curve of the DSSC containing only the *e*-PVdF-*co*-HFP polymer gel electrolyte has a performance associated with a V_{oc} of 0.70 V, J_{sc} of 13.65 mA/cm², FF of 66.5%, and PCE of 6.35%, while one composed of a liquid electrolyte has $V_{oc} = 0.75$ V, $J_{sc} = 14.71$ mA/cm², FF = 64.9%, and PCE = 7.17%, both at a 1 sun intensity (Table 2).

Table 2. Photovoltaic Parameter of the DSSCs with *e*-PVdF-*co*-HFP Nanofiber-Based Polymer Gel Electrolytes with and without E7 and Liquid Electrolyte

| 1 sun (100 mW/cm ²) | J_{sc} (mA/cm ²) | V_{oc} (V) | FF (%) | η (%) |
|------------------------------------|--------------------------------|--------------|--------|------------|
| <i>e</i> -PVdF- <i>co</i> -HFP | 13.65 | 0.70 | 66.5 | 6.35 |
| E7+ <i>e</i> -PVdF- <i>co</i> -HFP | 14.62 | 0.72 | 64.8 | 6.82 |
| liquid electrolyte | 14.71 | 0.75 | 64.9 | 7.17 |

It is clear from viewing these results that the photovoltaic performance of DSSC, prepared using E7 embedded on *e*-PVdF-*co*-HFP polymer gel electrolyte, displays a much higher performance than that of *e*-PVdF-*co*-HFP polymer gel electrolyte. Moreover, the photovoltaic performance of the E7 embedded on *e*-PVdF-*co*-HFP polymer gel electrolyte derived

DSSC has J_{sc} and FF values that resemble those of DSSC composed of a liquid electrolyte.

In addition, we have analyzed the FTO/TiO₂/electrolyte/Pt/FTO cells using electrochemical and photoelectrochemical methods that are typically employed to determine variations in impedances associated with different interfaces.^{33,34} The interfacial charge transfer resistances of the DSSCs were determined using EIS measurements. Nyquist plots of charge transfer resistances and the equivalent circuit model of the DSSCs are shown in Figure 3. The R_s , R_{1CT} , R_{2CT} , Q_1 , and Q_2

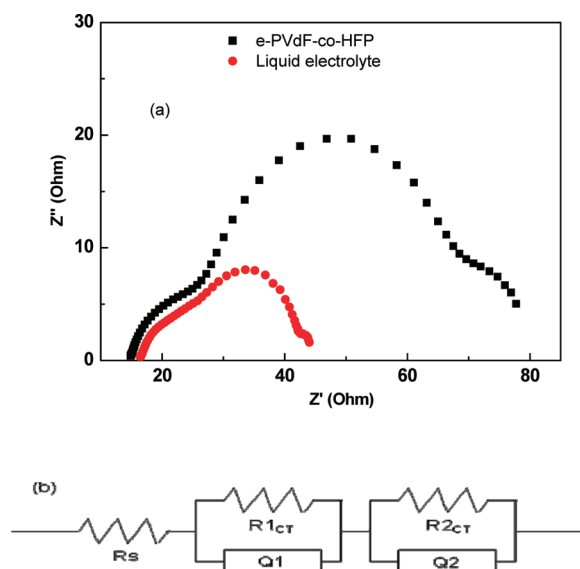


Figure 3. Nyquist plots of the FTO/TiO₂/electrolyte/Pt/FTO device using *e*-PVdF-*co*-HFP-based polymer gel electrolyte and liquid electrolyte (a) and the equivalent circuit model used for the DSSCs in this study.

values correspond to the respective series resistance, charge transfer resistance of Pt/dye/electrolyte interface, and charge transfer resistance of the TiO₂/electrolyte interface, and constant phase element. These values of the DSSC made using the liquid electrolyte are superior to those associated with the DSSC containing the *e*-PVdF-*co*-HFP polymer gel electrolyte and no E7 (Table 3). Significantly, the DSSC containing

Table 3. Series Resistances (R_s), Charge Transfer Resistances of the Pt/Electrolyte (R_{1CT}), and TiO₂/Electrolyte (R_{2CT}) in DSSC Devices under AM 1.5 by EIS Measurements

| | R_s | R_{1CT} | Q_1 | R_{2CT} | Q_2 |
|--------------------------------|--------|-----------|--------|-----------|----------|
| <i>e</i> -PVdF- <i>co</i> -HFP | 15.096 | 11.13 | 4.799u | 44.516 | 77.146u |
| liquid electrolyte | 16.724 | 7.669 | 6.753u | 18.006 | 105.407u |

the *e*-PVdF-*co*-HFP polymer gel electrolyte has both a higher resistance than the one derived using the liquid electrolyte and a poorer Γ/I_3^- activity between Pt and electrolyte, a phenomenon that should affect the J_{sc} .

CONCLUSION

In the effort described above, a new approach has been taken for the fabrication of quasi-solid-state DSSCs that involves the use of the liquid crystal, E7 embedded in the *e*-PVdF-*co*-HFP polymer gel electrolyte. Owing to the high ionic conductivity

(2.9×10^{-3}) of the E7 embedded on *e*-PVdF-*co*-HFP polymer gel electrolyte, higher values of J_{sc} (14.62 mA/cm²) and PCE (6.82%) of the quasi-solid-state DSSCs are achieved. The quasi-solid-state DSSC of *e*-PVdF-*co*-HFP polymer gel electrolyte was found to have a 6.35% PCE. In addition to that, overall PCE of the newly prepared DSSCs is 6.82%, which was nearly equivalent to that of a DSSC made using liquid electrolyte. It is believed that DSSCs, containing E7 embedded on *e*-PVdF-*co*-HFP polymer gel electrolyte, will find commercial utility.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by grant funds from the National Research Foundation of Korea (NRF) of the Ministry of Education, Science and Technology (MEST) of Korea (No. 2011-0028320), the New & Renewable Energy program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) (No. 20103020010050) of the Ministry of Knowledge Economy, and the Converging Research Center Program through the Ministry of Education, Science and Technology (2010K000973), Republic of Korea.

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