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ORIGINAL PAPER

An efficient and nonflammable organic phosphate electrolyte for dye-sensitized solar cells

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Abstract A new fire-retardant, diethyl ethyl phosphate (DEEP), was tested as a nonflammable electrolyte solvent for dye-sensitized solar cells (DSSCs). Electrochemical measurements demonstrated that the DEEP electrolyte has a wide potential window (>5 V), sufficient ionic conductivity (3.5×10^{-3} S cm^{-1} at 25 °C), and electrochemical activity for the I^-/I_3^- redox couple. The DEEP-based DSSCs exhibited an open circuit voltage of 0.72 V, short circuit photocurrent of 10.45 mA cm^{-2}, and a light-to-electricity conversion efficiency of 4.53%, which are almost the same as those observed from the DSSCs using currently optimized organic carbonate electrolytes. Meanwhile, the long-term stability of the DSSCs was greatly improved with the use of the DEEP electrolyte, showing a potential application of this new electrolyte for the construction of efficient, stable, and nonflammable DSSCs.

Keywords Diethyl ethyl phosphate · Nonflammable electrolyte · Electrochemical stability · Dye-sensitized solar cells

1 Introduction

Dye-sensitized solar cells (DSSCs) have attracted growing attentions as a future generation of cost-effective photovoltaic cells since the first report of about 11% overall light-to-electric energy conversion efficiency by Grätzel et al. in 1991 [1]. The original DSSC used an organic liquid electrolyte, which helped to establish a record conversion efficiency [2, 3], but also brought about a problem of long-term instability due to the leakage and volatilization of the electrolyte. To solve this problem, many attempts have been made to replace the liquid electrolyte by polymer electrolyte [4], hole-transporting materials [5–7], or other solid state ionic conductors [8, 9]. However, the conversion efficiencies of these DSSCs using the solid electrolytes were considerably smaller, obviously due to lower ionic conductivity of the solid electrolytes and imperfect contact at the electrolytes/electrodes interface [10]. To obtain a compromise between the flexible processability and high photoconversion efficiency, a number of studies were devoted to develop gel polymer electrolytes for DSSCs [11], in which organic liquid electrolyte was embedded to help ionic transport. To our understanding, it is possible to construct a stable DSSC with a liquid electrolyte if the liquid electrolyte was thermally and photochemically stable.

Following this understanding, we found organic phosphates to be a good choice. Organic phosphates are a large family of polar liquid compounds, extensively used as flame-retardants in many aspects of fire prevention [12, 13]. Some liquid phosphates have very similar physical and chemical properties to organic ketones, esters, and carbonates, such as liquidus temperature range, solvating ability, and electrochemical stability, promising a suitable electrolyte solvent for DSSCs. To evaluate the feasibility of organic phosphates for DSSCs, we found that use of diethyl ethyl phosphate (DEEP, $(CH_3CH_2O)_2POCH_2CH_3$) as an electrolyte solvent can effectively improve the operation stability of the DSSCs. In this article, we report the electrochemical properties of nonflammable DEEP electrolyte and the performance characteristics of the DSSCs using this electrolyte.

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2 Experimental

2.1 Fabrication of DSSC cells

TiO_2 photoelectrodes were prepared by coating a TiO_2 paste (0.3 g TiO_2 powder (P25, Degussa), 0.06 g ethyl cellulose, 6 mL ethanol and 1 ml terpineol) on a F-doped tin oxide glass (FTO, 15 Ω cm^{-2}, Nippon Sheet Glass) using the “doctor blading” technique, followed by sintering at 500 °C for 30 min to form a mesoporous TiO_2 film of ~15 μm thickness. The TiO_2 film electrode was immersed overnight in a 5×10^{-4} mol L^{-1} ethanol solution of Ru(dcbpy)$_2$ (NCS)$_2$ (535-bis TBA or N719, Solaronix) and then rinsed with anhydrous ethanol and dried again. The counter electrode was prepared by electrodeposition of platinum onto a FTO glass. For comparison, the two types of electrolytes used for DSSC measurements were 0.5 mol L^{-1} LiI, 0.05 mol L^{-1} iodine, 0.5 mol L^{-1} 4-tertbutylpyridine (TBP), and 0.5 mol L^{-1} 1-propyl-3-methyl- imidazolium iodide (PMII) dissolved in DEEP solvent (DEEP electrolyte) and in propylene carbonate (PC electrolyte).

2.2 Characterization and instruments

Cyclic voltammogramms (CV) of the electrolytes were carried out in a two electrode cell using a Pt microdisk electrode ($\phi = 100$ μm) as the working electrode and a large lithium or Pt foil as a reference electrode. The data acquisition and analysis in CV measurements were carried out on a CHI 660A electrochemical workstation (Shanghai, China). The photocurrent–photovoltage curves were recorded on an electrochemical station (Lanlike chemical electronic high-tech Co., Ltd, Tianjin, China, LK3200). A solar light simulator (Oriel, 91160) was used as the white light source to give AM 1.5 illumination on the surface of the solar cells. The power of the incident white light from the Xenon lamp was 100 mW cm^{-2}. The intensity of incident light was measured with a radiant power/energy meter (Oriel, 70260) before each experiment.

3 Results and discussion

3.1 Electrochemical window

DEEP is a new member of flame-retardant liquid phosphates. It has a high dielectric constant, low vapor pressure, low toxicity, and high chemical stability, which are well qualified to be used as an electrolyte solvent. To ensure the feasible application of DEEP for DSSCs, we examined the available potential window of DEEP by cyclic voltammetry. Figure 1 shows the cyclic voltammograms of a microdisk Pt electrode in 0.5 mol L^{-1} $LiClO_4$ DEEP and PC solutions. As it is shown in Fig. 1, there was not any distinguishable CV peaks but only a small background current observed on the CV curve from the DEEP electrolyte at the potential scan from +5.0 V to 0 V, whereas some oxidation peaks and reduction current emerged from the PC electrolyte at the potential of >4.5 V and <0.5 V, respectively. These CV features suggest that DEEP electrolyte is electrochemically more stable than PC electrolyte in the potential range for DSSC operation [14].

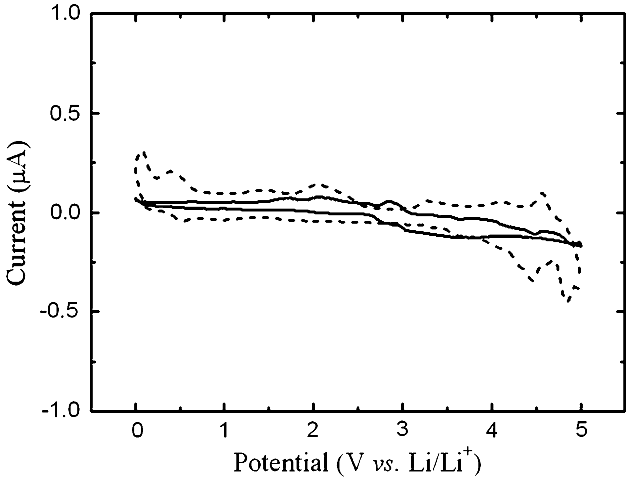

Fig. 1 Cyclic voltammograms of a Pt electrode in DEEP (*solid line*) and PC (*dash line*) solutions containing 0.5 mol L^{-1} $LiClO_4$

3.2 Ionic conductivity measurements

To evaluate the ionic conductivity of the DEEP electrolyte, we measured the conductivities of the DEEP and PC electrolytes containing 0.5 mol L^{-1} $LiClO_4$. It was found that the ionic conductivity of the DEEP electrolyte varied from 2.5×10^{-3} S cm^{-1} at 0 °C to 1×10^{-2} S cm^{-1} at 50 °C, slightly lower than that of PC electrolyte (5×10^{-3} S cm^{-1} at 0 °C and 1.8×10^{-2} S cm^{-1} at 50 °C). Though the DEEP electrolyte has an ionic conductivity not as high as PC electrolyte, it is sufficient enough for supporting the current flow in DSSCs.

3.3 Diffusion coefficient of iodine and triiodide

In DSSCs, the dye regeneration and hole transport are carried out by the I^-/I_3^- redox couple in the electrolyte. Therefore, the electrochemical activity of the I^-/I_3^- couple in the electrolyte is a determining factor for the photoconversion efficiency of a DSSC. Figure 2 compares the CVs of the I^-/I_3^- couple in the DEEP and PC electrolytes, respectively, at a scan rate of 100 mV s^{-1}. In both cases, two pairs of reversible redox peaks were well defined at the same or similar potentials as reported in literature [15, 16], which characterizes the oxidation/reduction of iodide and triiodide,

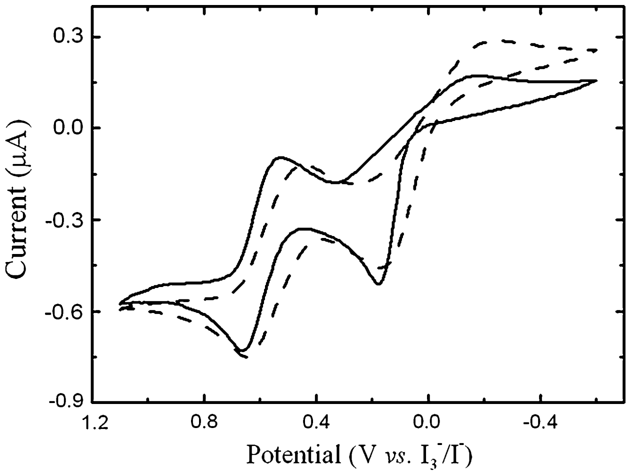

Fig. 2 Cyclic voltammograms of a Pt microelectrode ($\phi = 100$ μm) in the DEEP (*solid line*) and PC electrolyte (*dash line*) containing 0.1 mol L^{-1} LiI, 0.01 mol L^{-1} I_2, 0.01 mol L^{-1} MPII and 0.5 mol L^{-1} $LiClO_4$. Scan rate: 100 mV s^{-1}

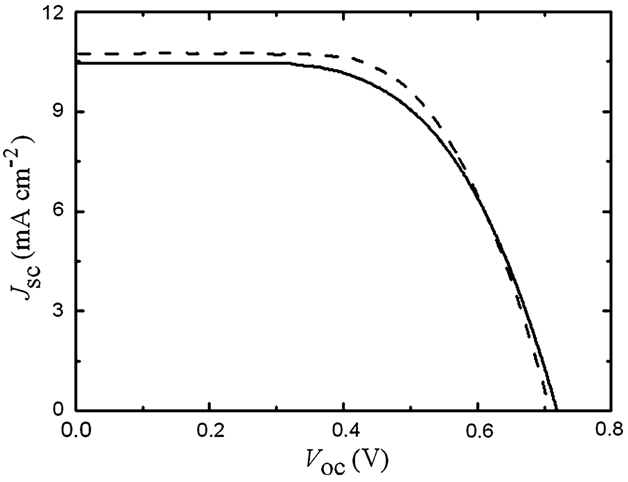

Fig. 3 *I–V* curves of DSSCs using the DEEP (*solid line*) and PC (*dash line*) electrolyte

respectively. In comparison, the two CV peaks of the I^-/I_3^- couple in the DEEP or PC electrolyte appeared very similarly in the shape and the potential position, showing an electrochemical feasibility of the DEEP electrolyte for the redox reactions of I^-/I_3^- couple. To determine the transporting rates of iodide and triiodide ions in the DEEP electrolyte, we measured the steady-state polarization curves using a Pt microelectrode ($\phi = 100$ μm) at a slow scan of 10 mV s^{-1} and calculated the diffusion coefficient (D_i) of I^- and I_3^- according to the formula for the limiting current on a microelectrode [17]: $I_d = 4nFDCr^0$. The diffusion coefficients of I^- and I_3^- were calculated to be 3.45 × 10^{-6} cm^2 s^{-1} and 1.52 × 10^{-6} cm^2 s^{-1} in DEEP electrolyte, which are comparable to those of I^- (6.53 × 10^{-6} cm^2 s^{-1}) and I_3^- (1.63 × 10^{-6} cm^2 s^{-1}) in the PC electrolyte.

3.4 Photovoltaic performance

Figure 3 compares the photocurrent–photovoltage curves of the DSSCs assembled with the DEEP and PC electrolytes. The open circuit voltage (V_{oc}), short circuit photocurrent (I_{sc}), and conversion efficiency (η) of the DSSCs using the DEEP electrolyte are 0.72 V, 10.45 mA cm^{-2}, and 4.53%, respectively, which are very similar to those of the DSSCs using PC electrolyte ($V_{oc} = 0.70$ V, $I_{sc} = 10.74$ mA cm^{-2} and $\eta = 4.81\%$). This similarity further confirms that DEEP has, as a new electrolyte solvent, the same electrochemical performances as currently used PC solvent.

3.5 Durability of DSSCs employing DEEP electrolytes

Since the long-term stability is a major concern for the DSSCs using liquid electrolytes, we paid particular attention to the changes in the photovoltaic behaviors of the DSSCs at a longer duration. Figure 4 displays the changes of the conversion efficiency η with time for the DSSCs using DEEP and PC electrolyte. It can be seen that the DSSC with the PC electrolyte remained at only 42% of its initial photoconversion efficiency after about 500 h, similar as reported in the literature [18]. Meanwhile, the DSSC using the DEEP electrolyte still exhibited a light-to-electricity conversion efficiency of ~4%, which is more than 80% of its initial efficiency. This is almost impossible to achieve for the DSSCs using organic carbonate electrolytes or volatile organic nitrile electrolytes. Since, DEEP and PC have very similar physical properties such as vapor pressure, decomposition temperature, and flash point, a possible reason for the instability of PC electrolyte may come from the fact that PC is electrochemically unstable with a

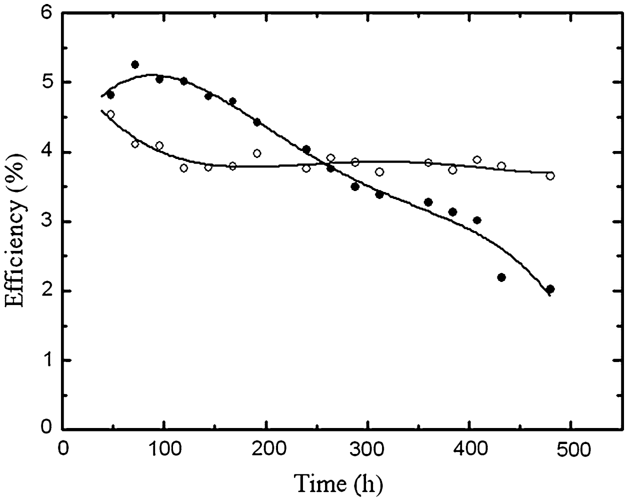

Fig. 4 Comparison of the changes in the conversion efficiency η with time for the DSSCs using DEEP (*solid line*) and PC (*dash line*) electrolytes

greater tendency to be reduced at negative potentials or to be oxidized at more positive potentials as pointed out by a number of researchers in the optimization of electrolyte systems for Li-ion batteries [14, 19].

In addition, DEEP has an important advantage of strong flame-retardancy as an electrolyte solvent. This may avoid possible firing of the DSSCs even overheated under light radiation.

4 Conclusions

In summary, we have investigated nonflammable organic phosphates as stable electrolyte solvent for DSSC applications and found that DEEP has the required physical properties and electrochemical stability, promising a good alternative for the organic carbonate electrolytes currently used in DSSCs. The DSSCs using the DEEP electrolyte exhibited an open circuit voltage of 0.72 V, short circuit photocurrent of 10.45 mA cm^{-2}, and a light-to-electric conversion efficiency of 4.53%, almost the same as those observed from the DSSCs using organic carbonate electrolytes. In addition, the DSSCs displayed considerable working stability with less than 20% reduction in the light-to-electric conversion efficiency after 480 h, which is almost impossible for the DSSCs using conventional organic nitriles- or carbonates- based electrolytes. The chemical and electrochemical stability of the organic phosphate enables the construction of efficient DSSCs with improved long-term operation stability.

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