

An improved preparation of 1-methyl-3-propylimidazolium iodide and its application in dye-sensitized solar cells

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Abstract

In this paper, we reported an improved preparation of 1-methyl-3-propylimidazolium iodide (MPII), which was the alkylation reaction of *n*-propyl iodide and 1-methylimidazole under solvent-free conditions by Teflon-lined, stainless autoclaves. It was shown that the resulting MPII was high pure, the conversion rate of 1-methylimidazole was close to 100% and the procedure was simple and eco-friendly. Moreover, the apparent diffusion coefficients of triiodide and iodide in the mixture with different ratios of MPII and 3-methoxypropionitrile were demonstrated by cyclic voltammetry using a Pt ultramicroelectrode. The dye-sensitized solar cells with the electrolyte, which was composed of 0.13 M I₂, 0.10 M LiI, 0.50 M 4-*tert*-butylpyridine in the mixture of 3-methoxypropionitrile and MPII (weight ratio 0.65:1), gave short circuit photocurrent density of 14.82 mA/cm², open-circuit voltage of 0.69 V, and fill factor of 0.66, corresponding to the photoelectric conversion efficiency of 6.73% at the illumination (AM 1.5, 100 mW/cm²).

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1. Introduction

During the past decades, dye-sensitized solar cells (DSCs) have attracted much attention as low-cost alternatives to conventional p–n junction photovoltaic devices (O'Regan and Grätzel, 1991; Hagfeldt and Grätzel, 1995; Kambe et al., 2002; Dai et al., 2004; Dai et al., 2005; Shi et al., 2005a,b). Electrolytes are one of the critical components in DSCs. Alkylimidazolium iodides are widely employed as the electrolyte because they can enhance the conductivity of electrolytes containing the redox couple of I[−]/I₃[−] and increase the electron diffusion coefficient in TiO₂ films (Kambe et al., 2002; Kubo et al., 2003).

Alkylimidazolium halides can be prepared by the alkylation reaction of the appropriate haloalkane and alkylimidazole derivatives *via* a conventional heating method in refluxing solvents or a microwave-assisted approach. The conventional heating method uses an excess of reactants (Varma and Namboodiri, 2001; Namboodiri and Varma, 2002; Deetlefs and Seddon, 2003) and takes several hours. The microwave-assisted approach requires also an excess of reactants and only a few minutes. However, the microwave-assisted approach has serious disadvantages, overheating, decomposition of the reaction mixture and the possibility of reaction runaway. Because the resulting alkylimidazolium halides are more polar and likely to strongly absorb microwave but there is no effective heat dissipation by solvents (Law et al., 2002). Although subcritical solvothermal synthesis of condensed inorganic materials has been developed early, the preparation of alkylimidazolium

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halides under solvent-free conditions by Teflon-lined, stainless steel autoclaves (Walton, 2002) has not been reported.

In this paper, Teflon-lined, stainless autoclaves were employed for the synthesis of 1-methyl-3-propylimidazolium iodide under solvent-free conditions. The I^-/I_3^- redox behavior in 1-methyl-3-propylimidazolium iodide containing low concentrations of 3-methoxypropionitrile was investigated by cyclic voltammetry using a Pt ultramicroelectrode. The photovoltaic performances of DSCs with a small amount of 3-methoxypropionitrile were measured.

2. Experimental section

2.1. Materials

Anhydrous lithium iodide, 4-*tert*-butylpyridine (TBP) and 3-methoxypropionitrile (MePN) were purchased from Fluka and used as received. 1-Methylimidazole (SUZHOU MEIHUA DAILY USE PERFUME CO., LTD) and *n*-propyl iodide (Fluka) were distilled under vacuum before use.

2.2. DSCs assembly

The preparation of DSCs was similar to the previous reports (Dai et al., 2004, 2005). The TiO_2 film was 10 μm thick and a 4- μm -thick light scattering layer was used. The total active electrode areas of DSCs was 0.25 cm^2 .

2.3. Synthesis and characterization

The mixture of 1-methylimidazole (50.0 mmol) and *n*-propyl iodide (52.5 mmol) was placed in a 58 mL Teflon-lined, stainless steel autoclave (its structure is similar to the literature (Walton, 2002)), and then was heated in an oven at 100 °C, 120 °C, 140 °C for 3 h, respectively. The resulting alkylimidazolium iodide was decanted and dried under vacuum at 70 °C for 6 h to remove residual *n*-propyl iodide. 1H NMR spectra of 1-methyl-3-propylimidazolium iodide (MPII) were measured on a Bruker DMX 500 spectrometer, using acetone- d_6 as solvents. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Advantage Max, electrospray source, ion trap instrument on a sample diluted in methanol.

2.4. Measurement

Conductivity of the mixture of MPII and MePN were measured by lab conductivity meter (DDS-307) with two platinum black electrodes conductance cell (DJS-1, REX, the area of each platinum black electrode is about 0.25 cm^2 , the distance between two platinum black electrodes is about 0.50 cm, the cell constant is 0.974, determined by aqueous KCl standard solution). Cyclic voltammetry was achieved by using an electrochemical workstation (CHI660B). The working electrode was a 5.0 μm radius Pt disk ultramicroelectrode (CHI107), the

auxiliary electrode and the reference electrode were a 1.0 mm radius Pt disk electrode (CHI102). A slow scan rate at 5 mV/s was used to obtain steady-state current voltage curves. The apparent diffusion coefficient (D_{app}) of triiodide and iodide in the mixture of MPII and MePN can be calculated from the steady-state current (I_{ss}) according to the following equation, $I_{ss} = 4ncaFD_{app}$ (Wang et al., 2003, 2004). The photovoltaic performances of DSCs were measured with a Keithley 2420 source meter controlled by Testpoint software under solar simulator (Xenon lamp, AM 1.5, 100 mW/cm^2 , Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Science, calibrated with standard crystalline silicon solar cell).

3. Results and discussion

3.1. Influence of reaction temperature on the synthesis of MPII

Fig. 1 shows the 1H NMR of MPII prepared at three different reaction temperatures. There was no obvious difference in sample A, B, C, and the starting materials, 1-methylimidazole and *n*-propyl iodide, were not detected. This indicated that the resulting MPII was high pure. Because it was difficult to remove 1-methylimidazole from MPII due to its high boiling point (198 °C) (Law et al., 2002) and the mass loss of the crude MPII during the drying procedure equaled to the excess of *n*-propyl iodide, it can be concluded that the conversion rates of 1-methylimidazole at the three reaction temperatures were close to 100%. Moreover, with the increase of the reaction temperature, the colour of MPII became darker, but the amount of impurity causing this phenomena was generally extremely small, being undetectable by 1H NMR. Thus, the reaction temperature, 100 °C, is appropriate for synthesis of MPII under solvent-free conditions by Teflon-lined, stainless steel autoclaves. This is not consistent with the previous result that the temperature of the quaternization reaction should be kept as low as possible (not more than

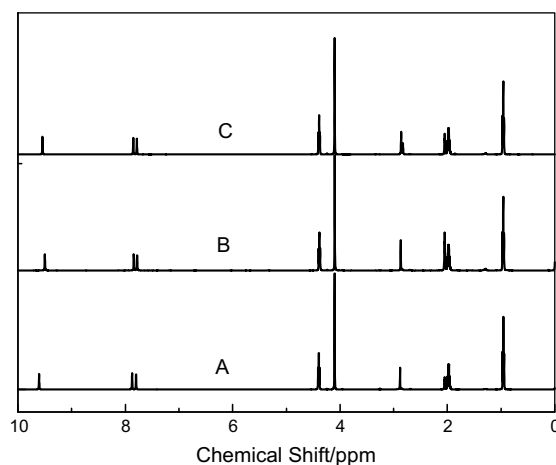


Fig. 1. 1H NMR chemical shifts of MPII in acetone- d_6 . Reaction temperature: (A) 100 °C, (B) 120 °C, (C) 140 °C.

ca. 80 °C for Cl^- salts, and lower for Br^- and I^- salts) (Wasserscheid and Welton, 2002).

MS identification of MPII prepared at 100 °C showed that there were only 1-methyl-3-propylimidazolium cation (MPI^+), iodide anion (I^-) and their stackings, $(\text{MPI}^+)_2 \text{I}^-$, $\text{MPI}^+(\text{I}^-)_2$, $(\text{MPI}^+)_2(\text{I}^-)_3$, $(\text{MPI}^+)_3(\text{I}^-)_4$. This was consistent with the result of ^1H NMR. MS of MPII at 140 °C was similar to that of 100 °C. Because 1,3-dipropylimidazolium cation or 1,3-dimethyl-imidazolium cation was not detected, the reversal of the quaternization reaction and partial decomposition of MPII did not occur at high temperature in the autoclave. This result is not in accordance with that of microwave-assisted approach (Law et al., 2002). Moreover, 3-hexyl-1-methylimidazolium iodide and 1-methyl-3-ethylimidazolium trifluoroacetate were prepared by the same procedure in our lab. These results agreed with the result of MPII. It was deduced that alkylimidazolium halides can be prepared by this procedure.

3.2. Influence of mixture component on the redox behavior of triiodide and iodide

Fig. 2 illustrated the relationship between the conductivity of mixture and the content of MePN in MPII at 20 °C. With the increase of the weight ratio of MePN and MPII, the mixture conductivity increased until the ratio was 0.65, and then increased slowly. It is suggested that the optimum ratio is 0.65 for the electrolyte of DSCs.

From Fig. 3, the apparent diffusion coefficients of triiodide and iodide increased with the increase of MePN content in mixtures A–E. This result is consistent with the relationship between the conductivity of mixture and the content of MePN in MPII.

3.3. Photovoltaic performances of DSCs

Table 1 listed the photovoltaic performances of DSCs with electrolytes A–E, and Fig. 4 shows the photocur-

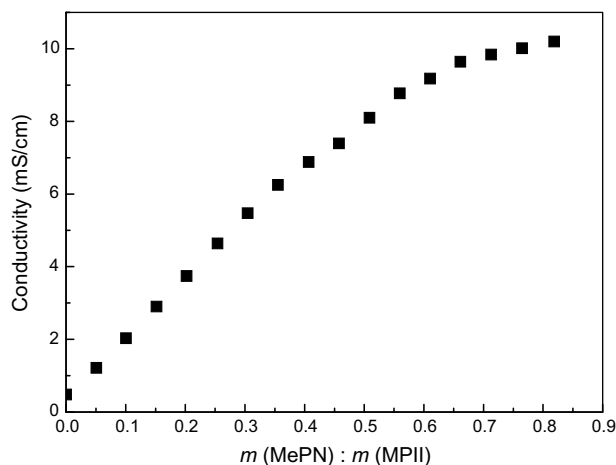


Fig. 2. The relationship between the conductivity and the content of MePN in MPII at 20 °C.

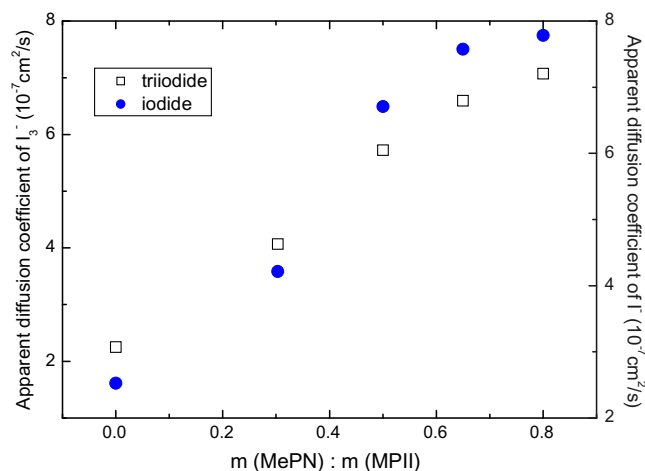


Fig. 3. Apparent diffusion coefficient of triiodide and iodide in mixtures A–E at 20 °C. $m(\text{MePN}) : m(\text{MPII})$: (A) 0.00, (B) 0.30, (C) 0.50, (D) 0.65, (E) 0.80 and I_2 : 0.13 M.

Table 1
Photovoltaic performances of DSCs with electrolytes A–E

Electrolyte*	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
A. $m(\text{MePN}) : m(\text{MPII}) = 0.00$	12.70	0.66	0.49	4.11
B. $m(\text{MePN}) : m(\text{MPII}) = 0.30$	13.72	0.68	0.61	5.66
C. $m(\text{MePN}) : m(\text{MPII}) = 0.50$	14.36	0.69	0.67	6.55
D. $m(\text{MePN}) : m(\text{MPII}) = 0.65$	14.82	0.69	0.67	6.73
E. $m(\text{MePN}) : m(\text{MPII}) = 0.80$	14.96	0.69	0.62	6.40

Illumination: AM 1.5, 100 mW/cm^2 . Cell active area of DSCs: 0.25 cm^2 .

* The other components of electrolytes are same 0.13 M I_2 , 0.10 M LiI, 0.50 M TBP.

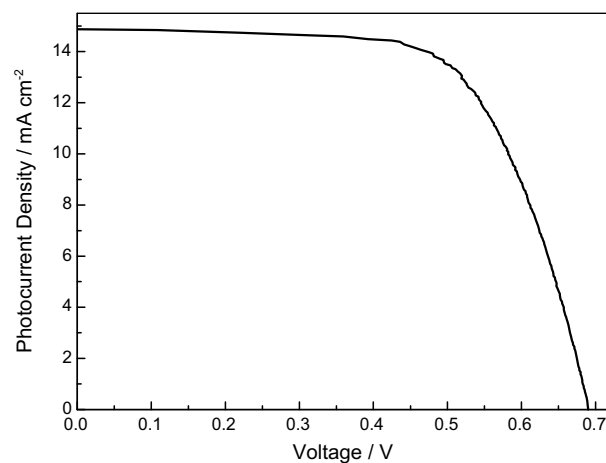


Fig. 4. Photocurrent–voltage characteristics of DSCs with electrolyte D.

rent–voltage curve of DSCs with electrolyte E, $m(\text{MePN}) : m(\text{MPII}) = 0.65$. The open-circuit voltage (V_{oc}) increased from electrolytes A–C. This was consistent with the literature (Ryuji and Masayoshi, 2003). That is, the equilibrium potentials of I^-/I_3^- and open-circuit voltages of DSCs increased with the decrease of total concentrations ($[\text{I}^-] + [\text{I}_3^-]$) in the ionic liquid mixtures. Moreover, the

short circuit photocurrent density and fill factor increased from electrolytes A–D, which was due to the increase of the apparent diffusion coefficients of triiodide and iodide. Therefore, DSCs with the electrolyte, which was composed of 0.13 M I₂, 0.10 M LiI, 0.50 M 4-*tert*-butylpyridine in the mixture of MePN and MPII (weight ratio 0.65:1), gave the photoelectric conversion efficiency of 6.73% at the illumination (AM 1.5, 100 mW/cm²).

4. Conclusion

In this paper, the improved preparation of MPII under solvent-free conditions by Teflon-lined, stainless autoclaves has been described. It is shown that the resulting MPII was high pure, the conversion rate of 1-methylimidazole was close to 100% and the procedure was simple and eco-friendly. This result means the feasibility of using only stoichiometric amounts of reagents. The DSCs with the electrolyte of MePN in MPII (weight ratio 0.65:1), 0.13 M I₂, 0.10 M (LiI, 0.50 M TBP) give short circuit photocurrent density (J_{sc}) of 14.82 mA/cm², open circuit voltage (V_{oc}) of 0.69 V, and fill factor (FF) of 0.66, corresponding to the photoelectric conversion efficiency (η) of 6.73%.

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Appendix A. Supplementary material

Data of ¹H NMR and MS, the picture of Teflon-lined, stainless autoclaves, and steady-state voltammograms can be found. Supplementary data associated with this article can be found, in the online version at [doi:10.1016/j.solener.2007.10.013](https://doi.org/10.1016/j.solener.2007.10.013).

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