Research Article

Nanosize Copper Dispersed Ionic Liquids As an Electrolyte of New Dye-Sensitized Solar Cells

Fu-Lin Chen,¹ I.-Wen Sun,^{1,2} H. Paul Wang,^{2,3} and C.-H. Huang³

¹ Department of Chemistry, National Cheng Kung University, Tainan City 701, Taiwan

² Sustainable Environment Research Center, National Cheng Kung University, Tainan City 701, Taiwan

³ Department of Environmental Engineering, National Cheng Kung University, Tainan City 701, Taiwan

Correspondence should be addressed to H. Paul Wang, wanghp@mail.ncku.edu.tw

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To enhance the electrical conductivity of the electrolyte for a newly developed dye-sensitized solar cell (DSSC), metallic copper (Cu) encapsulated within the carbon shell (Cu@C) nanoparticles dispersed in a room temperature ionic liquid (RTIL) (e.g., [bmim⁺][PF₆⁻]) has been studied in the present work. By the pulsed-field gradient spin-echo NMR method, the self-diffusion coefficients of cations and anions of the RTIL have been determined. The self-diffusion coefficient of the [bmim⁺] cations in the RTIL dispersed with 0.08% of Cu@C nanoparticles is increased by 35%. The electrical conductivity of the Cu@C dispersed RTIL is also increased by 65% (1.0 → 2.3 ms/cm). It is very clear the nanosize Cu@C dispersed RTIL with a relatively greater diffusion coefficient and electrical conductivity can be a very effective electrolyte especially utilized in DSSCs.

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1. Introduction

Crystalline silicon solar cells have relatively high efficiencies, nevertheless, limited by the high manufacturing cost and long payback period [1, 2]. On the contrary, organic solar cells have arisen more attentions simply due to the high possibility of creating extremely lightweight, easily integration, low-cost, and flexible solar cells [3]. One of the drawbacks on the performance of dye-sensitized solar cells (DSSCs) is the mediocre stability of the liquid electrolyte in the cells.

Room temperature ionic liquids (RTILs) are of increasing interest and importance in clean industrial processes such as liquid solvents for chemical reactions and extractions and in electrochemical applications as electrolytes for DSSCs, fuel cells and lithium batteries [4, 5]. Room temperature ionic liquids can also be utilized in gas sensors and biosensors [6]. To increase photovoltaic properties and stability of a DSSC, a composite ionic liquid electrolyte of mixing silica nanoparticles in the 1-methyl-3-propylimidazolium iodide (MPII) has been used to replace the conventional electrolyte [7–9]. An ionic liquid electrolyte containing dispersed carbon nanoparticles, carbon nanotubes, or titanium

oxide nanoparticles in the 1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide had a better photocurrent density and voltage [10].

In the separate experiments, size-controllable Cu@C nanoparticles were synthesized by carbonization of Cu²⁺-starch or -cyclodextrins complexes at 673–873 K [11]. In the present work, a very small amount of Cu@C nanoparticles with particle sizes as small as 7–20 nm were dispersed in the RTIL. Their self-diffusion coefficients were determined by pulsed-field gradient spin-echo NMR.

2. Experimental

The RTILs were synthesized by the modified procedures reported by Cammarata et al. [12], Tokuda et al. [13, 14] and Yeon et al. [15]. The nanosize Cu (7, 14, and 20 nm in diameter) encapsulated in the carbon shell (Cu@C) was obtained by carbonization of the Cu²⁺-starch complexes at 673 K for two hours. The ¹H NMR chemical shifts and self-diffusion coefficients were measured using a double-layer tube in which deuterium oxide-d₂ (Aldrich) and the sample were filled in the inner tube (closed system) and outer tube,

TABLE 1: The self-diffusion coefficient and electrical conductivity of the Cu@C dispersed RTIL ([bmim⁺] [PF₆⁻]) measured at 300 K.

Cu size (nm)	Cu@C (wt%)	Self-diffusion coefficients (10 ⁻¹² m ² s ⁻¹)		Electrical conductivity (ms/cm)	Viscosity (cp)
		[bmim ⁺]	[PF ₆ ⁻]		
	0	5.1	5.3	2.0	178
7	0.08	6.4	5.5	3.1	168
14	0.08	6.7	5.5	3.4	165
20	0.08	6.9	5.6	3.3	164

FIGURE 1: The TEM image of the Cu@C (Cu size = 14 nm) dispersed in the RTIL ([bmim⁺] [PF₆⁻]).

respectively [16]. Electrolyte conductivities of the Cu@C dispersed RTIL were measured on the Suntex sc-170 at 300 K. Images of the Cu@C dispersed RTIL were also determined by high resolution transmission electron microscopy (TEM) (Philips CM-200).

The K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra of copper in the Cu@C (0.08%) dispersed RTIL were collected on the Wiggler beam line at the Taiwan National Synchrotron Radiation Research Center. The electron storage was operated at 1.5 GeV (current of 300 mA). The beam energy was calibrated by the adsorption edge of a copper foil at energy of 8979 eV. The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 8.0 simulation programs [17, 18]. The background of the X-ray absorption spectra was justified by the AUTOBK program [17]. The isolated EXAFS data were normalized to the edge jump and converted to the wavenumber scale. The Fourier transform of the spectra was performed on the k^3 -weighted EXAFS oscillations in the range of 3.5 to 11.5 Å⁻¹. Empirical fits of model compounds have an error of ±0.01 Å in radius and ±10% in coordination number (CN) for the first shell atoms.

3. Results and Discussion

Table 1 shows the self-diffusion coefficients of the [bmim⁺] cations and [PF₆⁻] anions in the Cu@C dispersed RTIL determined by ¹H and ¹⁹F nuclei NMR spectroscopy at

300. The diffusion coefficient of the [bmim⁺] cations in the RTIL dispersed with 0.08% of Cu@C nanoparticles is increased by 25–35% if compared with the plain RTIL. Dispersion and insertion of the Cu@C nanoparticles (Cu sizes = 7–20 nm) in the matrix of the RTIL may cause a reduction of the ionic bonding energy between its cations ([bmim⁺]) and anions ([PF₆⁻]), leading to an increase of the self-diffusion coefficient of the [bmim⁺] cations from 5.1 to 6.9 × 10⁻¹² m²s⁻¹ and a decrease of the RTIL's viscosity from 178 to 164 centipoise (cp). It seems that the Cu@C nanoparticles interact more preferably with the [bmim⁺] cations of the RTIL as the self-diffusion coefficient of the [PF₆⁻] anions influenced by the dispersed Cu@C nanoparticles is relatively insignificant.

In Table 1, in addition to the increase of the self-diffusion coefficients of the [bmim⁺] cations in the RTIL dispersed with the Cu@C nanoparticles, an increase (up to 70%) of the RTIL's electrical conductivity is also found. It is worth noting that the uniform-size Cu@C nanoparticles are well dispersed in the RTIL (see Figure 1). The metallic copper (Cu) having sizes of 7–20 nm is encapsulated in the carbon shell which is consisted of diamond and graphite carbons with a sp³/sp² of 0.5–0.7 (determined by Raman spectroscopy [11]). The greater electrical conductivity of the ionic liquid electrolyte for the new DSSC may be attributed to the electron-rich carbon shell surfaces of the Cu@C nanoparticles that interact with the [bmim⁺] cations in the RTIL.

Molecular-scale data of Cu coated with the carbon shell dispersed in the RTIL in terms of the bond distance and coordination number (CN) of near neighbor atoms can be determined by EXAFS spectroscopy. An over 99% reliability of the EXAFS data fitting for copper species in the RTIL is shown in Table 2. Their Debye-Waller factors are less than 0.01. In the RTIL, Cu (7–20 nm) in the Cu@C nanoparticles has Cu–Cu bond distances of 2.530–2.535 Å, and its CNs increase from 6.2 to 8.7 as the Cu sizes increase.

Figure 2 shows the XANES spectra of copper in the Cu@C nanoparticles dispersed RTIL. Their preedge XANES spectra exhibit a very weak 1s-to-3d transition (8975–8980 eV) which is forbidden by the selection rule in the case of perfect octahedral symmetry. A shoulder at (8984–8988 eV) and an intense band at (8995–9002 eV) is due to the 1s to 4p transition that indicates the existence of the Cu(II) species. The XANES spectrum of copper in the Cu@C is very similar to that in the Cu@C dispersed in the RTIL. Nevertheless, about 11% of Cu originally in the core of the core-shell Cu@C nanoparticles (dispersed in the RTIL) is

TABLE 2: Structure parameters of copper in the Cu@C (0.08%) dispersed RTIL ([bmim]⁺ [PF₆]⁻).

Size (nm)	Shell	Bond distance (Å)	Coordination number	Dybe-Weller factor (σ^2)
7	Cu–Cu	2.533	6.2	0.0079
14	Cu–Cu	2.535	6.3	0.0081
20	Cu–Cu	2.530	8.7	0.0075

FIGURE 2: The least-square fitted XANES spectra of copper in (a) nanosize Cu and Cu@C (0.08%) having Cu sizes of (b) 7, (c) 14, and (d) 20 nm dispersed in the RTIL ([bmim]⁺ [PF₆]⁻).

oxidized to CuO. Note that the fraction of surface Cu atoms to the total atoms for the Cu nanoparticle having a size of 7 nm is 11%. It is very likely that in the RTIL the encapsulated Cu may involve in oxidation with residual oxygen in the RTIL on the surfaces of the Cu nanoparticles. The CuO layer on the surfaces of the core Cu in the Cu@C may also facilitate the electron transport limited to the surfaces of the carbon shell for a better efficiency.

4. Conclusion

Dispersion of a very small amount (0.08%) of Cu@C nanoparticles in the RTIL can increase the diffusion coefficient of the cations in the RTIL by 35%. The diffusion coefficient of the anions in the Cu@C dispersed RTIL is relatively less influenced. An increase (up to 70%) of the Cu@C dispersed RTIL's electrical conductivity is also found. The greater electrical conductivity of the ionic liquid electrolyte for the new DSSC may be attributed to the electron-rich carbon shell surfaces of the Cu@C nanoparticles that interact with the [bmim]⁺ cations in the RTIL. The CuO layer on the surfaces of the core Cu in the Cu@C may also facilitate the electron transport limited to the surfaces of the carbon shell for a better efficiency.

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