Journal of Molecular Liquids 267 (2018) 81–88

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Investigation of the conduction properties of ionic liquid crystal electrolyte used in dye sensitized solar cells

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ARTICLE INFO

Article history:
Received 5 November 2017
Accepted 2 January 2018
Available online 5 January 2018

JEL classification:
68.43.Mn
66.10.C-
47.57.J-
47.57.E-
5.40.Fb

ABSTRACT

To investigate the conduction properties of ionic liquid crystal electrolytes and to correlate them to their molecular structure, two electrolytes based on imidazolium iodides have been chosen for a comparative study: one ionic liquid crystal (1-dodecyl-3-methylimidazolium iodide) (C12) and one ionic liquid (1-hexyl-3-methylimidazolium iodide) (C6). For the electrical characterization of the samples the electrochemical impedance spectroscopy technique (EIS) has been used in the frequency range 1 MHz ÷ 10 mHz. For both electrolytes three frequency domains have been singled out. At large frequencies a hopping mechanism ensures the relative high conductivity of ionic liquids. A good fit of the conductivity data with respect to temperature with a Vogel-Tamman-Fulcher (VTF) equation has been done. The interesting result is that although C12 has a higher viscosity than C6 and thus a smaller conductivity was expected the observed conductivity is actually larger, this fact being attributed to the smectic A liquid crystal order of C12. At medium frequencies and especially at low frequencies the buildup of double layers by the electrodes is well observed. Assuming that in this region (10 Hz ÷ 10 mHz) the cell is equivalent to an electric circuit formed by the parallel of a resistance, R_0, and a capacitance, C_0, the simple Debye relaxation model, characterized by one relaxation time, has been modified taking into account the adsorption phenomenon in the Langmuir approximation. A theoretical interpretation of the experimental results based on the double layer model is presented.

1. Introduction

The potential of many ionic liquids (ILs) to act as electrolytes has contributed to a large range of electrochemical applications such as batteries, fuel cells or dye-sensitized solar cells (DSSCs). The efficiency of dye sensitized solar cells is strongly conditioned by the charge transfer processes within the electrolyte containing the redox couple, usually the I^-/I_3^- system. Devices based on ionic liquids electrolytes have been intensively studied and developed, being an extremely active area of electrochemical research [1,2].

In order to improve the durability of the DSSC, ILs, exhibiting high thermal and chemical stability, good ionic conductivity and low volatility are an alternative as constituent of the electrolyte [3]. However, in comparison with conventional liquid based electrolytes, the high viscosity of ILs limits the mass transport thus slowing the charge carrier diffusion.

Using an ionic smectic A liquid crystal (ILCs) electrolyte, when the stratified assembling of the molecules forms anisotropic long distance conduction channels, a significant increase of charge carrier diffusion is induced [4], the exchange reactions in the hole transport layer are promoted and the short-circuit current in the DSSCs increases [5]. To investigate the conduction properties of ionic liquid crystal electrolytes and to correlate these properties to their molecular structure, two compounds have been chosen for a comparative study: one ionic liquid crystal (1-dodecyl-3-methylimidazolium iodide) [6], and one ionic liquid (1-hexyl-3-methylimidazolium iodide) [7].

The aim of this paper is to allow for a description of the electrical conduction of I^-/I_3^- in a series of imidazolium-based ionic liquids analyzing the ionic diffusion between two parallel charged surfaces in response to an applied voltage.

In Section 2, materials synthesis and characterization methods are presented. The next section - Section 3 - presents the electrochemical impedance spectroscopy (EIS) characterization and explains the specific electric characteristics for three frequency domains. An adsorption mechanism assumed to better explain the

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https://doi.org/10.1016/j.molliq.2018.01.010

temperature dependence of both real and imaginary parts of the impedance is largely presented in Section 4. Section 5 summarize the main experimental and theoretical results.

2. Experimental

2.1. Materials

1-Methylimidazole, 1-iodododecane and 1-iodohexane were purchased from Merck and used as received. HPLC grade toluene, heptane, ethyl acetate and acetonitrile were obtained from Aldrich. Iodine (sublimated, for analysis) was purchased from Fluka. Imidazolium iodides were synthesized starting from the corresponding alkyl iodides and 1-methylimidazole using toluene as solvent, following the procedure of Lucas et al. [8].

2.1.1. Preparation of 1-dodecyl-3-methylimidazolium iodide (C12)

For the synthesis of 1-dodecyl-3-methylimidazolium iodide, 4 mL (50.2 mmol) 1-methylimidazole and 12.5 mL (50.7 mmol) 1-iodododecane were dissolved in 50 mL toluene and refluxed under argon for 24 h. The resulting imidazolium iodide was decanted, washed several times with heptane and then dried at room temperature under vacuum (5 mmHg) for 24 h. 1-Dodecyl-3-methylimidazolium iodide was further purified through low-temperature (−20 °C) recrystallization from ethyl acetate. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer.

^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 0.88 (t, 3H, CH_3-CH_2-); 1.25–1.35 (m, 18H, $-CH_2-$); 1.94 (m, 2H,$-CH_2-$ CH_2-N-); 4.14 (s, 3H, CH_3-N-); 4.34 (t, 2H, $-CH_2-N-$); 7.58 and 7.71 (t, 1H, $-N-CH=CH-N-$); 9.94 (s, 1H, $-N-CH=N-$)

^{13}C-NMR (400 MHz, $CDCl_3$, ppm) δ: 14.11, 22.65, 26.24, 28.99, 29.3, 29.38, 29.5, 29.57, 30.3, 31.87, 37.16, 50.24, 122.38, 124.0, 136.5

2.1.2. Preparation of 1-hexyl-3-methylimidazolium iodide (C6)

The compound was obtained from 4 mL (50.2 mmol) 1-methylimidazole and 7.5 mL (50.8 mmol) 1-iodohexane using the same procedure described above.

^{1}H-RMN (400 MHz, $CDCl_3$, ppm) δ: 0.88 (t, 3H, CH_3-CH_2-); 1.30–1.36 (m, 6H, $-CH_2-$); 1.95 (m, 2H,$-CH_2-CH_2-N-$); 4.14 (s, 3H, CH_3-N-); 4.35 (t, 2H, $-CH_2-N-$); 7.59 and 7.70 (t, 1H, $-N-CH=CH-N-$); 9.95 (s, 1H, $-N-CH=N-$)

^{13}C-RMN (400 MHz, $CDCl_3$, ppm) δ: 13.55, 21.95, 25.42, 29.81, 30.63, 36.74, 49.8, 122.01, 123.55, 136.11

The electrolytes were obtained as follows: a small quantity of acetonitrile was added to the weighed amount of imidazolium iodide and elemental iodine, the resulting mixture was briefly heated and stirred until it became homogenous and then acetonitrile was evaporated by heating in a vacuum (60 °C, 5 mmHg) for 24 h. Electrolytes containing iodine will be called in the following analysis C12 and C6, respectively.

2.2. Methods

The thermal phase behavior of 1-dodecyl-3-methylimidazolium iodide with added iodine was studied using a Netzsch DSC 204 F1 differential scanning calorimeter. The samples (10 mg) were weighed in aluminum pans sealed with a lid containing a pinhole, and thermal scans were performed in a nitrogen atmosphere using the following temperature program: samples were cooled to −40 °C, held for 20 min, heated to 100 °C, cooled from 100 to −40 °C and finally heated to 100 °C. Heating and cooling rates were 5 °C/min and data were collected during the second cooling and heating steps (Fig. 1).

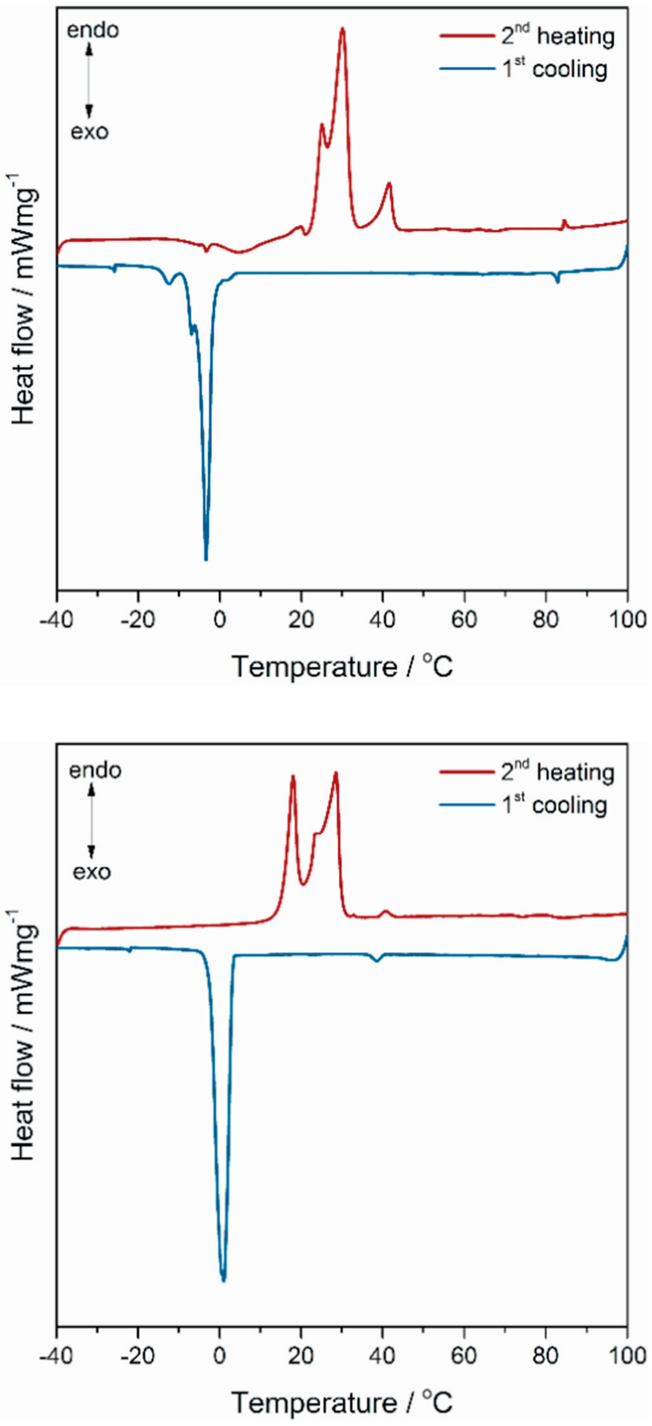

Fig. 1. DSC thermograms of (up) 1-dodecyl-3-methylimidazolium iodide and (down)1-dodecyl-3-methylimidazolium iodide containing 20 mol.% elemental I_2.

Raman spectra reported in Fig. 2 were recorded in the range 200–50 cm^{-1} using a Thermo Fisher Scientific DXR dispersive Raman microscope employing a 780 nm laser with a power of 14 mW.

The electrochemical impedance spectroscopy technique (EIS) has been used for the electrical characterization of the samples. The measurements were performed with a Potentiostat/galvanostat (Methrom, model 128N) fitted with a frequency response analyzer module, in the frequency range of 1 MHz–10 mHz and amplitude of the applied signal 10 mV. The cells having the shape of a slab delimited by transparent FTO (Flourine-doped Tin Oxide) electrodes,