Electrochimica Acta 55 (2010) 2275–2279

Contents lists available at ScienceDirect

Electrochimica Acta

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

Effect of gelator structures on electrochemical properties of ionic-liquid supramolecular gel electrolytes

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ARTICLE INFO

Article history:
Received 15 July 2009
Received in revised form
12 November 2009
Accepted 14 November 2009
Available online 24 November 2009

Keywords:
Chemical structure
Gelator
Ionic liquid
Supramolecular gel
Electrolytes

ABSTRACT

Bis(4-acylaminophenyl)methane (G1) and bis(4-acylaminophenyl)ether (G2) with varied acyl chains were found to be efficient gelators for the gelation of imidazole-based ionic liquids. The supramolecular gel electrolytes were formed via the self-assembly of these gelators in ionic liquids. The minimum gelator concentrations (MGCs) for the gelation of ionic liquids depend on the chemical structures of the gelators. The longer the acyl chains, the lower the MGCs. Polarized optical microscopy images of the ionic-liquid gels reveal the formation of spherical crystallites resulting from the fibrillar aggregates of the gelators. In addition, the phase transition temperatures of the ionic-liquid gels increase with an increase of the acyl chain length of the gelators. The impedance spectra of the ionic-liquid gels indicate that the temperature dependence of the conductivity follows the classical Arrhenius equation. The conductivities of ionic-liquid gels also decrease with an increase of the acyl chain length, but the differences in conductivities between the gels and corresponding ionic liquids are in one order of magnitude. The ionic-liquid gels possess a stable electrochemical window.

1. Introduction

Supramolecular gels are semi-solid materials formed by the self-assembly of the low-molecular weight gelators in organic or aqueous liquids [1–4]. Ionic liquids are molten salts at room temperature, which have recently received increasing attention because of their unique properties, such as nonvolatility, wide range of liquid phase temperature, nonflammability, high ionic conductivity, and a wide electrochemical window [5–7]. Ionic liquids can also be gelatinized in the presence of gelators to form ionic-liquid supramolecular gels, which reduce their fluidity and overcome leakage in certain applications such as gel electrolytes [8].

In recent years, Kimizuka and Nakashima [9] reported physical gelation of ionic liquids formed by the addition of amide-group enriched glycolipids and L-glutamic acid derivatives as gelators, providing self-assembling gels. However, these carbohydrates seem to be good gelators only for selected ionic liquids containing hydrophilic bromide as anions, not for those containing hexafluorophosphate (PF_6^-). Shinkai and co-workers prepared ionic-liquid gels in the presence of gelators synthesized from cholesteryl chloroformate and 4-nitrophenyl-α-D-glucopyranoside, but the gelation requires acetone as co-solvent because of the limited solubility of the gelator [10]. Mohmeyer et al. [11] found that amphiphilic cyclohexanecarboxylic acid-[4-(3-tetradecylureido)phenyl] amide was an efficient gelator for binary mixtures of ionic liquids. The resultant ionic-liquid gels make it possible to prepare stable quasi-solid-state dye-sensitized solar cells. Yanagida and co-workers reported a dye-sensitized solar cell fabricated using ionic-liquid gel electrolytes formed by *N*-benzyloxycarbonyl-L-isoleucyl aminooctadecane as gelator, which showed a 5% light-to-electricity conversion efficiency and high temperature stability [12,13]. Hanabusa et al. [8] synthesized two types of gelators which allowed gel formation of a wide variety of ionic liquids including imidazolium, pyridinium, pyrazolidinium, piperidinium, morpholinium and ammonium salts. Most recently, Tu et al. [14] used carbene complexes as efficient gelators to prepare different types of ionic-liquid gels at concentrations as low as 0.5 mg mL^{-1}. To the best of our knowledge, little further attention has been paid to the effects of chemical structures of gelators on the gelation of ionic liquids and properties of the corresponding ionic-liquids gels, particularly on the electrochemical properties of the ionic-liquid gels.

In this work, two types of gelators with different acyl groups were used for the gelation of imidazole-based ionic liquids. The influence of the chemical structure of the gelators on the gelation of the ionic liquids and on the properties of the resultant ionic-liquids

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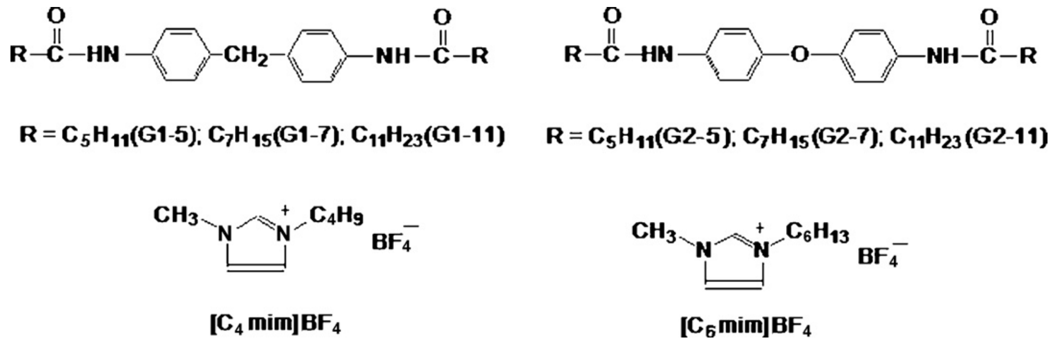
doi:10.1016/j.electacta.2009.11.042



Scheme 1. Chemical structures of two series of gelators (G1 and G2) and two types of ionic liquids.

gels has been investigated via minimum gelator concentrations, sol–gel phase transition temperature and electrochemical properties. The investigations not only increase our understanding of the relationship between the structure of the gelator and the electrochemical properties of ionic-liquid gels, but also are significant for the properties of potentially useful electrolyte materials, modulated by variation of the structures of the gelators.

2. Experimental

2.1. Materials

The ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim]BF_4) and 1-hexyl-3-methylimidazolium tetrafluoroborate ([C_6mim]BF_4) were purchased from Shanghai Chenjie Chemical Co. Ltd. The purity of ionic liquids is 99.9%. Traces of water in the ionic liquids were removed by applying a vacuum for 12 h at 80 °C [15]. Two series of gelators, bis(4-acylaminophenyl)methane (G1) and bis(4-acylaminophenyl)ether (G2) were synthesized according to the methods described previously [16,17]. The chemical structures of the G1 and G2 gelators and the ionic liquids are shown in Scheme 1.

2.2. Preparation and characterization of the ionic-liquid gels

Calculated amounts of gelators and ionic liquids were put into glass vials and heated until the solid completely dissolved. The solution was allowed to cool at room temperature and exhibited no gravitational flow upon inversion of the vials. The required minimum gelator concentrations (MGCs) [17] were measured at an increment of 0.1 mg mL^{-1} of the gelator.

Measurements of gel–sol phase transition temperatures (T_{GS}) were conducted according to the method of ball falling described elsewhere [18]. A small steel ball (250 mg, Φ 4 mm) was placed on the top of the ionic-liquid gel in a glass vial. Then the sample was slowly heated (5 °C/h) in a thermostatted oil bath. When the ball fell to the bottom of the vial, the temperature was defined as the gel–sol transition temperature (T_{GS}).

Hot solution mixtures of gelator and ionic liquid were dropped on a pre-heated glass plate and then allowed to cool at room temperature. After the gel sample was kept in a dark place for 4 h, the gel sample was imaged by optical polarized microscope (POM, BH-2, Olympus).

2.3. Electrochemical measurements

The ionic-liquid gels were prepared in a three-electrode cell, containing a glass carbon as the work electrode, Pt wire and Pt plate as the reference and counter electrode, respectively [15]. Linear sweep of the ionic-liquid gels was measured using a Zhanner IM6e electrochemical working station under a N_2 atmosphere at a scanning rate of 5 mV s^{-1}. The experiments were conducted at 25 ± 1 °C. Similarly, the ionic-liquid gels were prepared in a glass vessel equipped with a Teflon stopper. Two mirror polished stainless steel electrodes (10 mm × 10 mm) were stably fixed into the Teflon stopper. Ionic conductivity was measured by the impedance technique over a frequency range from 50 MHz to 1 MHz at an oscillation level of 100 mV. The software for data treatment was Zview.

3. Results and discussion

3.1. Gelation of ionic liquids

In general, the gelation of liquid media is a process of self-assembly of gelator molecules via noncovalent interactions such as hydrogen bonding resulting in a three-dimensional network of supramolecular structures [2]. The molecules of the liquid medium are immobilized in this three-dimensional network by capillary forces. In our experiments, the G1 and G2 gelators were found to be efficient gelation agents for the imidazole-based ionic liquids without any co-solvent. The gelation ability of the gelators can be characterized by minimum gelator concentrations (MGCs), which are summarized in Table 1.

For a certain ionic liquid, the MGCs of the G2 gelators were lower than those of the G1 gelators, indicating that the gelation ability of G2 gelators is superior to that of G1. Theoretically, this can be most likely ascribed to the ether oxygen group in the G2 gelators. Herein, the presence of two lone pairs of electrons on the oxygen atoms redounds to the formation of intermolecular hydrogen bonding of G2 gelators. In addition, the data in Table 1 also reveal that the longer the length of the acyl chains in the gelator, the lower the MGCs of the gelators. This may be explained in terms of more solvophilic characteristic of the gelators with higher flexible long acyl chains or more likely that the long acyl chains modify the solvent compatibility of the gelator, resulting in less gelator molecules required for the immobilization of ionic-liquid molecules.

Usually gelators self-assemble into fibrillar aggregates in organic media [2,11]. This process, in nature, is a kind of crystallization of the gelators in solvents. In the present work, the morphology of fibrillar aggregates could not be imaged by SEM micrographs because of the nonvolatility of ionic liquids, which hardly convert ionic-liquid gels to xerogels. Thus, the morphology of the gelator aggregates has to be indirectly characterized

Table 1
Minimum gelator concentrations (mg mL^{-1}) of ionic liquids using G1 and G2 gelators.

	G1-5	G1-7	G1-11	G2-5	G2-7	G2-11
C_4mimBF_4	30.8	21.5	17.8	7.0	6.0	5.2
C_6mimBF_4	38.5	15.0	6.0	6.0	5.2	4.4