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Role of reduced precursor and solvolytic reagent molar ratio on preparation and properties of ionogel

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ABSTRACT

In the present study, ionogels have been synthesized by immobilizing IL (1-ethyl-3-methylimidazolium tetrafluoroborate) in silica gel matrices using non-aqueous route. In this process, tetraethyl orho-silane (TEOS) as a precursor to silicon dioxide and formic acid as a solvolytic gelating reagent in reduced molar ratio 1:4 were used. We find that reduced molar concentration of formic acid results the formation of ionogels having less number of closed pores (totally isolated from their neighbours), larger density and stable monolithic form. TEM and SEM measurements are used to visualize the morphology of sample and closed pores present in the sample. N_2-sorption measurement is used to measure the pore parameters of the silica matrices which shows the mesoporous structure. DSC and TGA results show the change in phase transition temperature and thermal stability of IL upon confinement in silica matrices. Moreover, ionic conductivity of bulk and confined IL is measured using impedance spectroscopy and it has been found that it increases with increasing the temperature as well as concentration of IL in ionogels. Apart from these characterization techniques, ionogels have been characterized using FTIR and fluorescence spectroscopy which exhibit the change in vibrational frequencies and fluorescence behaviour of confined IL.

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1. Introduction

The availability of the materials like ionic liquids (ILs) owing to its interesting properties like high ionic conductivity, non-flammability and high ionic density (only ions; cations and anions) intrinsically offers much opportunity to synthesize a material according to the need of the current electrochemical devices [1–12]. Earlier, liquid electrolytes were useful for conventional cells which were suffering from disadvantages like low temperature range of operation, portability and leakage etc. In the last few decades, interest of the material scientists has grown to develop solid electrolytes useful for solid energy devices which overcome the limitations associated with the conventional solid electrolytes such as need of availability of suitable solvent and narrow temperature range of operation [13]. Recently, ILs have been used in many applications due to its many attracting properties such as low vapor pressure, high thermal stability, wide electrochemical window and wide liquid temperature range etc. But, ILs suffer from limitations such as leakage problem, portability, corrosion and handling problems etc. but immobilization of the IL into suitable porous matrices and polymeric membranes provides them mechanical stability and solid network for their movement and at the same time results in high liquid like conductivity and makes the devices more safer [13].

Ionogels (IGs) are solid hybrid materials obtained by immobilizing IL into suitable porous matrices such as porous silica, carbon nanotube; polymeric membranes which combine the properties of the IL and results in new materials of interest [13–15]. In recent studies, the properties of ILs are found to get affected upon confinement due to interaction of IL molecules with the pore wall surface of silica. It has been also reported that properties of ILs in confined systems depend on confining matrices, size and steric hindrance offered due to availability of low dimension for the movement of ions of IL [14–17] Immobilizing the ILs in the matrix has many advantages such as overcoming the leakage problem associated with IL and improving the stability and performance in the solid state devices. The advantage of IGs over ILs increases the interest to develop desired materials for catalysis and electrolyte materials for solid devices.

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ILs immobilized solid materials (Ionogels) have been fabricated using various structural and solid supports such as polymers, organic gelators, inorganic materials (TiO_2, SiO_2, SnO_2 etc.), CNT etc. For the synthesis of ionogels (IGs), efforts have been made using different techniques [11,15]. However, for immobilization of IL in inorganic materials (TiO_2, SiO_2, SnO_2 etc.) hydrolytic and non-hydrolytic sol-gel process have been used. In the hydrolytic sol-gel process ionogels have been prepared by the conventional hydrolysis-condensation reaction of precursor in a water-methanol/ethanol solution e.g. precursors to silicon oxides [Tetramethyl orthosilicate (TMOS), Tetraethyl orthosilicate (TEOS) etc.]. Moreover in the non-hydrolytic sol-gel process, precursors (TMOS/TEOS as precursor to silicon oxide) and formic acid as catalytic reagent are used to immobilize ILs at ambient temperature. Nowadays, non-hydrolytic sol-gel process has been used to immobilize IL in different matrices [15,18–26]. But, immobilization of IL into silica matrix is widely reported [21–27]. Since, the work of Dai et al. [23], in most of the studies molar concentration of formic acid to precursor were taken between 6 and 8 i.e. molar ratio of FA: precursor is 6-8. Horowitz et al. [28] have reported compliant (IL rich) and brittle ionogels with molar ratio of TMOS: FA: IL as 1:6:6 and 1:7.8:1 respectively. They have synthesized high IL (~94%) containing mechanically compliant silica ionogels. High amount of IL containing ionogels have also been prepared by taking molar ratio of TMOS and FA as 1: 8 [29]. In a recent study, more than 20 formulations have been investigated for the synthesis of ionogels at different molar concentration of FA, TMOS and IL [21]. It has been reported that when the FA/TMOS molar ratio and IL volume percentage are low, brittle ionogels are formed. However, with high IL content and high FA/TMOS molar ratio, compliant ionogels are produced and slow gelling formulation with high IL fraction and at low FA: TMOS molar ratio have been reported. Gelation times are found to increase with increasing IL volume percentage or decreasing FA/TMOS molar ratio. But, in recent studies [25,26,30,31], Martinelli et al. have reported the synthesis of ionogels in which molar concentration of TMOS:FA was chosen as 1:4. They monitored the chemical reaction during gelation (in non-hydrolytic sol-gel process) by in situ time resolved Raman and ^{1}H NMR spectroscopy [25]. They found that the IL shows catalytic effect and also accelerates the consumption of formic acid, precursor (TMOS) and intermediate product (methyl formate). They also showed that the chemical reaction was completed at tetramethyl orthosilicate (TMOS) and formic acid (FA) in molar ratio of 1:4 [25]. In another study [30], silica ionogels have been synthesized using FA and TMOS molar ratio of 4:1 and following the reaction pathway from the start of reaction to well beyond gelation by use of in situ time resolved Raman spectroscopy. They have been able to pick out different silica species and found that hydrolysis of TMOS was very fast in both the cases i.e. with and without protic IL and linear silica species are the most abundant. They also observed that protic IL does not change the reaction pathway but accelerates the cyclization process [30].

Earlier, we had immobilized IL ([EMIM][BF_4]) in mesoporous silica matrix using TEOS, formic acid and IL at molar ratio 1/8/x, where x=0.25, 0.35 by non-hydrolytic sol-gel process at the ambient temperature [14]. The synthesized IGs were brittle with low density and gelation of ionogels was found very fast ~50–55 s. The fast gelation of the matrix at the ambient temperature resulted in the creation of large number of unintentional closed pores in the silica matrix in the presence of IL which caused reduced stability and very less density of the IGs. The fast gelation of the matrix may be due to two reasons firstly; due to the large amount of the formic acid which acts as gelating reagent in the reaction and secondly, the temperature of the chemical reaction [14] Therefore, an attempt was made by us for slowing down the gelation rate by controlling the temperature of synthesis of IGs. Different IGs were synthesized at the lower temperature (such as; 0 and −10 °C) by us [24] The IGs synthesized at the lower temperatures (0 and −10 °C) took larger time for gelation to complete and were less stable though showed higher density. The higher densities of the IGs synthesized at the low temperatures were due to the entrapment of one of the sol-gel reaction products; ethyl formate inside the matrix due to slow evaporation of the reaction product at this temperature which increased the density. The entrapment of ethyl formate affects the properties of ionogel and makes them unsuitable for application.

It may be remarked here that in our previous studies, we had taken molar ratio of TMOS:FA as 1:8 as well as reduced the synthesis temperature. But, we found that IGs were less stable and they contained ethyl formate. Therefore, in the present investigation, an attempt has been made to synthesize IGs which are expected to be stable and free from above drawbacks (i.e. presence of closed pores and retention of ethyl formate) by controlling the amount of gelating agent (formic acid) and temperature of synthesis. Therefore, for the synthesis of IGs with varying amount of IL, we have reduced the molar ratio of TMOS: FA as 1:4. It has been found that IGs synthesized with higher mol% of IL and controlled amount of formic acid have less number of closed pores, larger density with stable structure as compared to the IGs synthesized at molar ratios of TEOS:HCOOH:IL ([EMIM][BF_4])::1:8:x (where x=0.25, 0.35 mol%) at ambient temperature.

2. Experimental section

2.1. Materials

The IL (with a stated purity greater than 98.9%) and TEOS were purchased from Sigma-Aldrich. Formic acid of GR grade was purchased from Merck, Germany. IL and synthesized IGs were dried under vacuum (~10^{-6} Torr) along with heating at 100 °C for 24 h and then stored in glove box to prevent the materials from the moisture. Water content in pure IL was 200 ppm as measured using Mettler Toledo C20 Karl Fischer Coulometric Titrator.

2.2. Preparation of IL confined silica gel material

The samples with different amounts of IL in porous silica matrices were obtained by sol-gel process as described by us earlier [14,17,24]. For the preparation of IGs, initially, tetraethylortho-silicate (TEOS) and formic acid (HCOOH) were mixed in molar ratio 1:4 at room temperature in a argon filled glove box (M Braun Lapstar, O_2 and H_2O content < 0.5 ppm) containing inert atmosphere and then reaction was allowed to occur in the presence of IL, 1-ethyl 3-methyl imidazolium tetra fluoro-borate [EMIM][BF_4] with different mole percentage of IL (x=0.25, 0.35, 045, 0.65, 0.75 and 0.85). The complete reaction can be described as [23,32]:

$$2HCOOH+(C_2H_5O)_4Si \rightarrow SiO_2+2C_2H_5OH+2HCOOC_2H_5 \quad (1)$$

Following IGs and gel have been studied and their names are abbreviated as follows:

#SIL2: 0.25 mol% IL loading
#SIL3: 0.35 mol% IL loading
#SIL4: 0.45 mol% IL loading
#SIL5: 0.65 mol% IL loading
#SIL6: 0.75 mol% IL loading
#SIL7: 0.85 mol% IL loading

2.3. Characterization techniques

Density of the synthesized IGs was calculated using mass and volume of the disk shaped IGs.

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