Available online at ScienceDirect

ScienceDirect

J. Mater. Sci. Technol., 2014, 30(11), 1096−1102

JMST

www.JMST.org

Ionic Conductivity in Gelatin-Based Hybrid Solid Electrolytes: The Non-trivial Role of Nanoclay

Ali Ghadami[a)], *Nader Taheri Qazvini*[a,b)], *Nasser Nikfarjam*[a)*]

a) Polymer Division, School of Chemistry, College of Science, University of Tehran, Tehran, Iran

b) Biomaterials Research Center (BRC), University of Tehran, Tehran, Iran

[Manuscript received August 24, 2013, in revised form October 23, 2013, Available online 24 June 2014]

In this study, the ionic conductivity behavior in hybrid gelatin-based transparent electrolytes including various types of nanoclays with different size, shape and surface properties was characterized. The effects of nanoclay type and nanoclay concentration as well as different experimental conditions, e.g., pH, temperature and crosslinking were also investigated. In general, the impedance spectroscopy results suggested a non-trivial role for nanoclay. Regardless of the nanoclay type, the ionic conductivity slightly increased first and then decreased by increasing the nanoclay concentration. Furthermore, among sodium montmorillonite (Na^+MMT), lithium montmorillonite (Li^+MMT), laponite and hydrotalcite, the hybrid electrolytes prepared by Li^+MMT showed higher ionic conductivity. The results also showed that the chemical crosslinking along with sample preparation at optimum pH, where the gelatin chains might be efficiently adsorbed on exfoliated, negatively charged clay nanosheets, plays an important role. In comparison with the ionic conductivity of the neat sample at room temperature ($\sim 10^{-7}$ S cm^{-1}), a ten-fold increase was observed for the crosslinked sample containing 2 wt% of Li^+MMT prepared at optimum pH 3.5. The conductivity behavior as a function of temperature revealed the obedience with the Vogel−Fulcher−Tammann (VFT) model for all samples, suggesting the important role of segmental motions in the ionic conductivity. Finally, a qualitative explanation was presented for the mechanism of the ionic conduction in gelatin-nanoclay hybrid electrolytes.

KEY WORDS: Gelatin; Solid-state electrolytes; Ionic conductivity; Montmorillonite; Laponite; Impedance spectroscopy

1. Introduction

Due to the particular physical and chemical properties, polymers have been an unsurpassed option for producing new generations of solid electrolytes called solid polymer electrolytes (SPEs)[1,2]. It is commonly accepted that the ionic conductivity in SPEs relies on the interactions between lithium ions and oxygen atoms; ionic mobility is assisted by the segmental motions of the host polymer[1,2]. Apart from poly(ethylene oxide) which by far is the best polymer for such applications, natural polymers like chitosan, starch and cellulose derivatives, are particularly interesting due to their richness in nature, very low cost, renewability and principally biodegradability and biocompatibility properties[3−5]. In some particular applications, e.g. in electrochromic devices, where the transparency of the electrolyte is indispensable, gelatin can be considered as an appropriate candidate[6−14]. Recently, gelatin-based SPEs have been prepared and the effect of particular salts like $LiBF_4$[6], LiI/I_2[7], $LiClO_4$[8−11] and/or particular acids like acetic acid[12,13] and hydrochloric acid[14] on the ionic conductivity have been investigated. Depending on formulation, the ionic conductivity behavior of gelatin-based solid electrolytes has been shown to obey the Arrhenius[8−14] or Vogel−Fulcher−Tammann (VFT) equations[7].

Furthermore, several groups have investigated hybrid solid electrolytes based on inorganic nanoparticles in which the mutual interactions of nanoparticle-polymer, ion-polymer, as well as ion-particle are important in ionic conductivity[15−22]. The results suggest that the layered silicates (nanoclay), in an optimum amount, can enhance the ionic conductivity. Actually, when exfoliated, each individual layer of nanoclay possesses numerous negative charges and therefore is able to dissociate the lithium salts. This increases the number of charge carriers (i.e. lithium ions). Moreover, nanoclay can interfere with polymer crystallization and therefore increase the amorphous parts in the sample, which is favorite for ionic transport because the chains in amorphous regions has flexibility creating more free volume, which leads to polymer segmental mobility[18,21,22].

* Corresponding author. Tel.: +98 9125778718; Fax: +98 21 66495291; E-mail address: Nikfarjam@ut.ac.ir (N. Nikfarjam).

http://dx.doi.org/10.1016/j.jmst.2014.06.008

The addition of nanoclay into gelatin films has shown to enhance mechanical properties without adverse effect on optical properties, i.e. transparency[23−25]. Nevertheless, the effect of nanoclay on the ionic conductivity of gelatin-based electrolytes is unknown and, to the best of our knowledge, no work has been done in this area.

The present work focuses on the preparation of gelatin-based SPEs containing different types of nanoclays with different sizes, shapes and surface properties as well as investigation of the effect of gelatin/nanoclay/salt interactions on ionic conductivity behavior. The hybrid solid electrolyte systems were prepared under various physicochemical conditions and were crosslinked with formaldehyde and plasticized with glycerol. The ionic conductivity behavior of the hybrid SPE films were characterized by alternate current (AC) impedance spectroscopy in a broad range of temperatures.

2. Experimental

2.1. Materials

All chemicals were of reagent grade and used without further purification. Gelatin type B (Bloom 80−120), glycerol, formaldehyde (37% aqueous solution), HCl and NaOH were obtained from Merck. Lithium perchlorate ($LiClO_4$, battery grade), sodium montmorillonite (Na^+MMT) and hydrotalacite (HT) were provided by Aldrich. Laponite® RD was purchased from Southern Clay Products (USA). The pH value of the double distilled water is ~5, which was used for all the experiments.

Lithium montmorillonite (Li^+MMT) was prepared in the following procedure. 12 g of Na^+MMT nanoclay was dispersed in 200 mL of 1 mol/L $LiClO_4$ solution and was stirred under 300 r/min at 80 °C for 24 h to promote the complete ion exchange reaction. After that, the suspension was centrifuged at 9000 r/min for 20 min to separate Li^+MMT. The obtained nanoclay was dispersed in deionized water and then centrifuged. This procedure was repeated for several times till complete elimination of chloride anions, as checked by the silver nitrate test. Finally, the Li^+MMT was dried under vacuum at 50 °C for 48 h and then ground[24].

For each nanoclay (Li^+MMT, Na^+MMT, Laponite and HT), a 1% (w/v) aqueous dispersion was prepared by stirring at 300 r/min for 24 h and then sonication treated in 3 cycles of 10 min/cycle.

2.2. Preparation of solid polymer electrolyte

Gelatin of 0.5 g was dispersed in 10 mL distilled water and heated under the magnetic stirring up to 50 °C for complete dissolution. Then, the solution cooled to 30 °C and glycerol as plasticizer (0.125 g; 25 wt% based on gelatin) and $LiClO_4$ (0.005 g; 1 wt% based on gelatin) were added to the solution. Next, different quantities of the prepared nanoclay dispersions were added to the solution and stirred for 4 h. Finally, formaldehyde as crosslinking agent (0.005 g; 1 wt% based on gelatin) was added to the solution and stirred for 1 min. The solution was poured on petri plate and stayed in 30 °C for 2 weeks in incubator. To prepare the samples with different pH, all the procedures were the same as mentioned above, but before adding formaldehyde, the solution pH was adjusted by HCl and NaOH solutions (0.1 mol/L) to the considered pH value. Table 1 lists the composition of the samples investigated.

Table 1 Composition of gelatin-based electrolytes crosslinked by formaldehyde in the presence of different types of nanoclay in various amounts and different pH values

Sample	Nanoclay type	Nanoclay content (wt%)[a]	Crosslinker content (wt%)[a]	pH
GF 1	Li^+MMT	0	1	5
GF 2	Li^+MMT	2	1	5
GF 3	Li^+MMT	4.5	1	5
GF 4	Li^+MMT	6	1	5
GF 5	Li^+MMT	8	1	5
GF 6	Li^+MMT	10.5	1	5
C1	Li^+MMT	2	1	2.5
C2	Li^+MMT	2	1	3.5
C3	Li^+MMT	2	1	5
C4	Li^+MMT	2	1	7
A1	Na^+MMT	2	1	5
A2	Laponite®	2	1	5
A3	Hydrotalacite	2	1	5
A4	−	0	1	5
A5	Li^+MMT	2	0	5
A6	−	0	0	5

[a] Based on gelatin content.

2.3. Characterization

A customized potentiostat was used for ionic conductivity measurements. The ionic conductivity was determined by measuring the complex impedances of sandwiched cells of an electrolyte sample of 100 μm in thickness and 10 mm in diameter, between gold-coated copper electrodes. All measurements were carried out in the frequency range of 100 Hz to 1 MHz in a temperature-controlled chamber (±0.5 °C). For thermal equilibration, the samples were kept for 15 min at each temperature prior to the measurement.

Differential scanning calorimetry (DSC) was performed with TA Instruments DSC-Q100 V 9.0 in the temperature range of −90 °C to 400 °C at 20 °C/min under 50 mL/min argon flow. Electrophoretic mobility of the samples was investigated using Zetasizer Nano ZS (Malvern Co, UK).

3. Results and Discussion

3.1. Effect of nanoclay amount

The ionic conductivity (σ) of samples was obtained by the complex impedance spectrum (Z'' vs. Z') so-called Nyquist plot. Fig. 1 shows the typical impedance plot for gelatin-based electrolytes containing different concentrations of Li^+MMT at 50 °C. The ionic conductivity was calculated using the relation $\sigma = t/R_bA$, where t is the thickness of the electrolyte sample, A is the contact area between the electrode and the electrolyte and R_b is the measured resistance. This resistance value was determined by the intercept of the semicircle with real axis of complex impedance plot (Z' axis). With the addition of Li^+MMT to the electrolyte up to certain amount (2 wt%), the real part of the impedance decreases, meaning that the electrolyte resistance (R_b) decreases as well (Fig. 1). Moreover, with the increase in Li^+MMT, the real part of impedance, and therefore the electrolyte resistance increases. The ionic conductivity at ambient temperature as a function of Li^+MMT concentration is shown in Fig. 2. Apart from a slight increase at 2 wt%, the ionic conductivity decreases with the increase in the Li^+MMT concentration. Either