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Poly-acrylonitrile-based gel-polymer electrolytes for sodium-ion batteries

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Abstract Research and development activities on sodium-ion batteries are becoming prominent in the past few years. Compared to lithium-based batteries, the sodium-based batteries will be cheaper because of the abundancy of sodium raw materials in the earth's crust and also in seawater. In the current study, we synthesized and characterized poly-acrylonitrile (PAN)-based gel-polymer electrolytes formed with $NaClO_4$ and dissolved in ethylene carbonate (EC) and propylene carbonate (PC). By systematically varying the weight ratios of polymer, salt, and the solvents, we obtained an optimum room temperature ionic conductivity of 4.5 mS cm^{-1} for the composition 11PAN-12$NaClO_4$-40EC-37PC (wt.%), which is reasonably good for practical applications. This value of conductivity is comparable to a few other Na^+ ion conducting gel-polymer electrolyte systems studied in the recent past. Variation of ionic conductivity with inverse temperature showed Arrhenius behavior. Activation energies estimated for all the samples showed only a slight variation suggesting that a single activation process which depends on the EC/PC co-solvent governs the ionic mobility in these gel-polymer electrolytes. Thermo-gravimetric analysis (TGA) revealed that there is no noticeable weight loss of these electrolytes up to 100 °C and hence the electrolytes are thermally stable for operating temperatures up to 100 °C.

Keywords Gel-polymer electrolytes · Sodium-ion batteries · Ionic conductivity · Impedance analysis

Introduction

Research efforts on sodium-ion batteries (SIBs) have been growing fast after the commercialization of an aqueous electrolyte-based SIB in 2014 by a company "Aquion Energy" in Pittsburgh, USA, and the announcement of successful production of a prototype 18650 sodium-ion cell in 2015 by the researchers of RS2E electrochemical network in France [1, 2]. The SIBs are becoming popular, particularly in the R&D level, because of the limited availability and ever increasing prices of lithium raw materials. The prices of lithium raw materials have now almost doubled since the first commercial lithium-ion battery (LIB) was commercialized in 1991 [3]. Sodium is highly abundant in the earth's crust and also in the ocean, and hence, the sodium raw materials would be less expensive than its lithium counterparts. As secondary batteries are in high demand nowadays for various portable electronic devices, electric and hybrid vehicles and also for stand-alone energy storage systems for storing energy from intermittent renewable energy sources, research and development of new materials for Na^+ ion conducting electrolytes and compatible electrodes is highly important for the battery industry.

Although sodium and lithium are chemically similar, a major challenge in commercial production of the SIBs is the relatively lower room temperature ionic conductivity of

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sodium-ion conducting electrolytes, particularly in solid state, due to the larger size of sodium ions compared to that of lithium ions. However, gel-polymer electrolytes would exhibit sufficient conductivity at room temperature for practical applications, mainly due to the increased mobility of ionic species. Lithium-ion-based gel-polymer electrolytes have been widely studied [4–7], but only a few reports are available on sodium-ion conducting gel-polymer electrolytes [8–12]. The sodium-ion conducting gel-polymer electrolytes comprise high dielectric constant plasticizers/solvents with various sodium salts immobilized in a polymer matrix. Polymer host provides the mechanical/dimensional stability, whereas solvent/salt solution facilitates the process of ion conduction.

Most of the sodium-ion conducting gel-polymer electrolytes studied in the past were based on poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) co-polymer [8, 9, 11]. In 2010, Kumar et al. [8] studied a PVdF-HFP-based gel-polymer electrolyte, in which sodium triflate ($NaCF_3SO_3$) was dissolved in a room temperature ionic liquid namely 1-ethyl 3-methyl imidazolium trifluoro-methane sulfonate (EMI-triflate). For the optimized composition, they reported a conductivity of 5.74 mS cm^{-1} and the Na^+ ion transference number of 0.23 at room temperature. Another nanocomposite gel-polymer electrolyte (PVdF-HFP)-$NaCF_3SO_3$-EC-PC + x wt% SiO_2 (x = 0, 3, 5, 10, 15, 20 and 25) was also studied by the same group in 2011, and the ionic conductivity was optimized to 4.1 mS cm^{-1} for the composition incorporated with 3 wt% SiO_2 at room temperature [9]. According to the same group, poly(methyl methacrylate) (PMMA)-based gel-polymer electrolyte, PMMA-$NaClO_4$-EC-PC, dispersed with 4 wt% SiO_2 nanofiller showed the highest conductivity of 3.4 mS cm^{-1} at 20 °C [10]. These electrolytes are transparent and free-standing films and the temperature dependence of conductivity showed Arrhenius behavior. Na^+ ion transference number was found to be 0.23 for both filler-free and filler-added electrolytes. In 2015, Yang et al. [11] studied a PVdF-HFP-based sodium-ion conducting gel-polymer electrolyte and found an optimized conductivity of 0.6 mS cm^{-1} at room temperature. They also reported that the conductivity variation with temperature is Arrhenius type and the Na^+ ion transference number is 0.3.

In the present work, several poly(acrylonitrile) (PAN)-based gel-polymer electrolytes, PAN-$NaClO_4$-EC-PC, have been synthesized by systematically varying the weight ratios of PAN, $NaClO_4$, EC and PC. PAN is chosen as the host polymer due to its low thermal resistance and flame-retardant property [13]. To the best of our knowledge, there are no reports available in the literature on PAN-based sodium-ion conducting gel-polymer electrolytes. Electrical and thermal properties of these gel-polymer electrolytes have been studied to optimize the composition. Reasonably good room temperature conductivity was obtained for the optimized composition, and these gel-polymer electrolytes have been found to be thermally stable for practical applications in SIBs.

Experimental

Poly-acrylonitrile (molecular weight, 1.5×10^5) from Sigma-Aldrich (USA), $NaClO_4$ (anhydrous, 98%) from Strem Chemicals (USA), and EC (99%) and PC (99%) both from Alfa Aesar (UK) were used as received. In order to prepare PAN-$NaClO_4$-EC-PC gel-polymer electrolytes, required quantities of EC and PC were first dissolved by magnetically stirring for about 1–2 h at room temperature. Then the required amount of $NaClO_4$ was added and stirred again at room temperature for about 3–4 h until the salt homogeneously dissolves into the EC-PC mixture. Finally, the required amount of PAN was added and magnetically stirred by at around 100 °C for 4–5 h until a clear transparent gel is obtained.

A computer-controlled EZstat Pro Potentiostat-Galvanostat (0.01 Hz–10 kHz) from Nuvant Systems Inc., Indiana, USA, was used for impedance measurement on disk-shaped samples sandwiched between two spring-loaded stainless steel blocking electrodes separated by a non-conducting spacer of diameter ~4 mm and thickness ~3 mm. The temperature of the sample was varied from 25 to 75 °C, and the measurements were made at 10 °C intervals. The ionic conductivity values were extracted from the complex impedance data. For the weight loss studies, Thermo-Gravimetric Analyzer (TGA) model TG92 from Setaram Instrumentation, France, was used with a heating rate of 10 °C min^{-1} from RT to 350 °C. Aluminum pans were used to contain ~5 mg of the gel-polymer electrolyte samples under static nitrogen gas environment.

Results and discussion

Figure 1a shows the conductivity variation with inverse temperature (σ vs 1/T) for five different samples (nos. 1, 2, 3, 4, and 5), which have been prepared initially by systematically varying the weight ratios of (PAN + $NaClO_4$) to (EC + PC). Here, EC and PC, which are solid and liquid respectively at room temperature, act both as solvent and plasticizer to dissolve the ionic salt and also to soften the polymer chains. Weight compositions of all the samples studied in this work are shown in Table 1. Figure 1b shows the respective conductivity isotherms at various temperatures. It can clearly be seen that, all the gel-polymer electrolytes studied in this work showed Arrhenius behavior of conductivity variation with inverse temperature. Increase in conductivity with temperature is believed to be due to the expansion of the polymer matrix leading to increase in free-volume. The increased free-volume

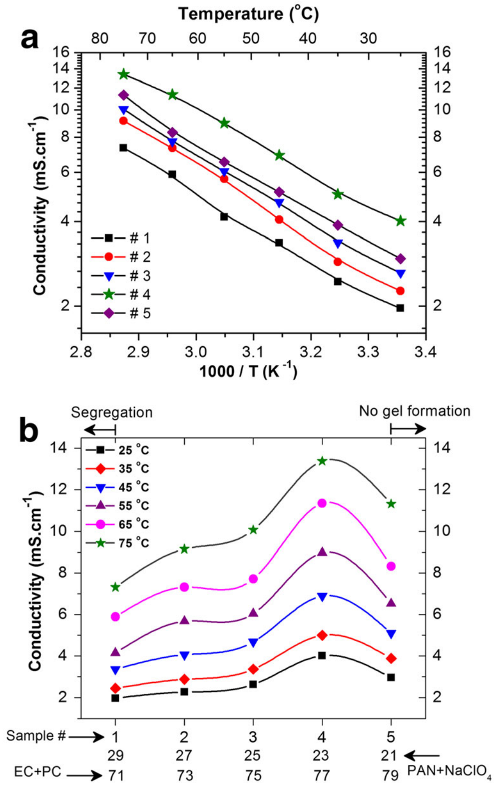

Fig. 1 **a** Conductivity variation with inverse temperature. **b** Conductivity isotherms, for sample nos. 1, 2, 3, 4, and 5

in turn promotes the mobility of the polymer segments and ionic species, resulting in higher conductivity. In general, σ vs 1/T variation for gel-polymer electrolytes show curved behavior, but we observe Arrhenius behavior for the present system of samples, possibly due to the fact that the process of ion conduction is governed by the nature of co-solvent mixture EC-PC. There are a few other gel-polymer systems published in the literature which showed Arrhenius behavior rather than Vogel-Tammen-Fulcher (VTF), for example PMMA-NaClO$_4$-EC-PC system studied by Kumar et al. [10]. As shown in Fig. 1b, our attempt to prepare the gel-polymer electrolytes with (PAN + NaClO$_4$) is to (EC + PC) weight ratio greater than 29:71 was not successful, mainly due to the segregation of ionic salt from the polymer matrix. The degree of the segregation is too high that it is seen by naked eye. Also, the gels could not be formed with (PAN + NaClO$_4$) to (EC + PC) weight ratio less than 21:79. Obviously, sample no. 4 (9PAN-14NaClO$_4$-40EC-37PC) showed the best conductivity values at all temperatures and its conductivity is 4.0 mS cm^{-1} at room temperature.

In order to further enhance the conductivity of sample no. 4, the PAN to NaClO$_4$ weight ratio while keeping the amount of EC and PC fixed at constant values was changed. Sample nos. 6 and 7 (see Table 1) were prepared in this way, and as shown in Fig. 2, sample no. 7 showed the maximum conductivity at all experimental temperatures. Our attempts to prepare samples with PAN wt.% less than 7 and higher than 11 were not successful, because of the difficulties in forming the gels. As an attempt to have further conductivity enhancement, we have chosen the weight composition of sample no. 7 and tried to optimize the weight ratio of EC and PC by keeping the amounts of PAN and NaClO$_4$ fixed at constant values. Samples 8, 9, 10, and 11 shown in Table 1 were prepared in this way and the conductivity variation of these samples with inverse temperature (see Fig. 3a) were extracted from the impedance data taken during the heating cycle. Conductivity isotherms for the same samples (nos. 7, 8, 9, 10, and 11) are shown in Fig. 3b, and it can clearly be seen that sample no. 7 (11PAN-12NaClO$_4$-40EC-37PC) is the best conducting gel-electrolyte sample among all the samples developed in this work. We believe that the optimized conductivity of the sample no. 7 is due to the highest degree of ionic dissociation and increased mobility of ions caused by the higher weight percentages of EC (40%) and PC (37%). PC is functioning as the solvent and the liquid plasticizer in the gel-polymer

Table 1 Compositions of all PAN-NaClO4-EC-PC gel-polymer electrolyte samples

Sample no.	PAN (wt%)	NaClO$_4$ (wt%)	EC (wt%)	PC (wt%)	PAN + NaClO$_4$(wt%)	EC + PC (wt%)
1	12	17	37	34	29	71
2	11	16	38	35	27	73
3	10	15	39	36	25	75
4	9	14	40	37	23	77
5	8	13	41	38	21	79
6	7	16	40	37	23	77
7	11	12	40	37	23	77
8	11	12	38	39	23	77
9	11	12	36	41	23	77
10	11	12	42	35	23	77
11	11	12	44	33	23	77

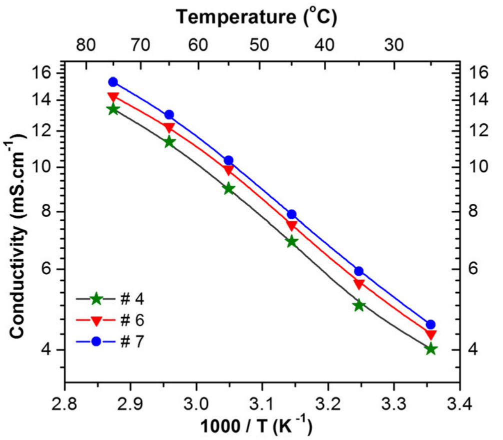

Fig. 2 Conductivity variation with inverse temperature for sample nos. 4, 6, and 7

electrolytes and the sample showing optimized conductivity has 37 wt.% PC. Excessive amount of PC will help to improve ionic conductivity, but will hinder the formation of gels. However, moderate or lower amount of PC will lead to segregation within the gel. It is strongly believed that the optimized composition (37 wt.% PC) forms better conducting pathways and optimized ionic dissociation leading to highest ionic conduction.

Figure 4 compares the optimum room temperature conductivity values of present PAN-based gel-electrolytes with some other Na$^+$ ion conducting gel-polymer electrolytes available in the literature. The optimized composition (11PAN-12NaClO$_4$-40EC-37PC) shows a conductivity value of 4.5 mS cm^{-1} at room temperature, whereas an electrolyte (PVDF-HFP)-NaCF$_3$SO$_3$-EC-PC-SiO$_2$ (labeled as “A” in Fig. 4) published by Hashmi et al. [9] showed 4.1 mS cm^{-1}, electrolyte (PVDF-HFP)-NaCF$_3$SO$_3$-EMI (labeled as “B” in Fig. 4) studied by the same group Hashmi et al. [8] showed 5.74 mS cm^{-1}, electrolyte (PVDF-HFP)-NaClO$_4$-EC-DMC-DEC (labeled as “C” in Fig. 4) studied by Yang et al. [11] showed 0.6 mS cm^{-1}, and the electrolyte PMMA-NaClO$_4$-EC-PC-SiO$_2$ (labeled as “D” in Fig.4) studied by Hashmi et al. [10] showed 3.4 mS cm^{-1}. It would be more appropriate to compare the conductivity of the optimized PAN-based sodium-ion conducting gel-polymer electrolytes with that of lithium-ion conducting systems. For example, 21PAN-8LiClO$_4$-33PC-38BL showed a conductivity value of 3.71 mS cm^{-1} at 20 °C [14]. Almost comparable conductivity values of these sodium and lithium systems is due to the increased mobility of mobile ions in the gel-polymer matrix. Yang et al. [11] have recently studied a PVDF-HFP-based gel-polymer electrolyte system and also reported almost similar conductivity values for both sodium and lithium systems incorporated with NaClO$_4$ and LiClO$_4$ ionic salts, respectively.

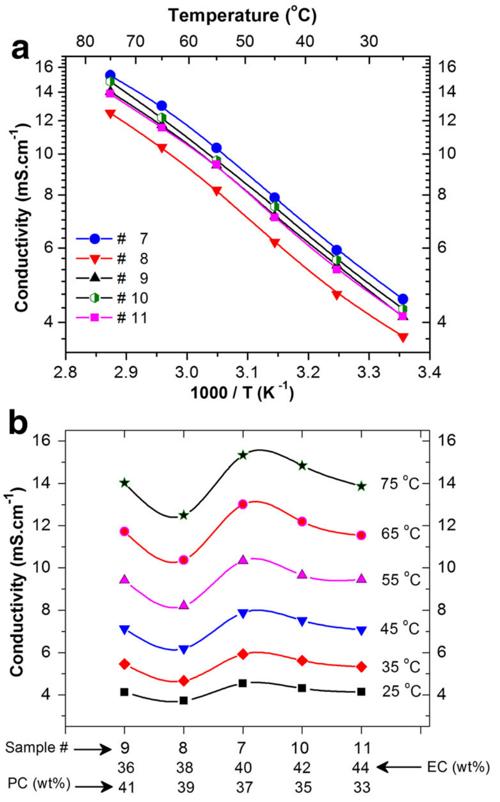

Fig. 3 **a** Conductivity variation with inverse temperature. **b** Conductivity isotherms, for sample nos. 7, 8, 9, 10, and 11

Activation energy (E$_a$) values have been estimated for all the samples and are given in Table 2 along with their room temperature conductivity values. Activation energy is actually a combination of energy of the defect formation and the energy of defect migration within the polymer chains [11]. As in Table 2, E_a essentially remains constant showing only a slight change for different sample compositions. This implies that the change in conductivity with composition is mainly due to the amount of ionic dissociation, which primarily depends on the concentration of EC and PC. PC can contribute for better dissociation of ionic salt due to its higher dielectric constant compared to that of EC [15]. As has been reported in the

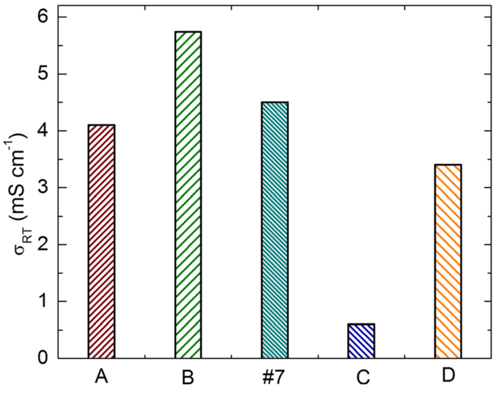

Fig. 4 Comparison of room temperature conductivity values, (*A*) (PVdF-HFP)-NaCF$_3$SO$_3$-EC-PC-SiO$_2$ [9], (*B*) (PVdF-HFP)-NaCF$_3$SO$_3$-EMI [8], (*C*) (PVdF-HFP)-NaClO$_4$-EC-DMC-DEC [11], (*D*) PMMA-NaClO$_4$-EC-PC-SiO$_2$ [10], and our optimized composition *(no.7)*

Table 2 Conductivity and activation energy values for PAN-$NaClO_4$-EC-PC gel-polymer electrolyte samples

Sample no.	σ_{RT} (mS cm^{-1})	E_a (kJ mol^{-1})
1	2.0	2.3
2	2.3	2.5
3	2.6	2.3
4	4.0	2.2
5	3.0	2.3
6	4.3	2.1
7	4.5	2.2
8	3.7	2.2
9	4.1	2.1
10	4.3	2.2
11	4.1	2.1

literature, the identical of the activation energies for gel-polymer electrolytes [16–18] is due to a single activation process which depends on the functional groups of the solvent family actually governing the ionic motion. For low and moderate concentrations of salts, activation energy is almost independent of the salt concentration or the type of the salt.

As listed in Table 2, the activation energy for sample no. 7 is 2.2 kJ mol^{-1} and all the other compositions showed essentially same and low values for their activation energies. The low value of the activation energy is another indication of amorphous nature of these gel-polymer electrolytes as lower activation energies are always associated with better ion transport [11]. The activation energy of the optimized electrolyte (sample no. 7) can be compared with that of gel-polymer electrolytes based on PVdF-HFP polymer host showing Ea of 4.6 kJ mol^{-1} and the commercial separator, Celgard 2730 saturated with polymer electrolyte showing Ea of 5.7 kJ mol^{-1} [11]. These two gel-polymer electrolytes in the literature showed room temperature conductivity values of 0.60 and 0.16 mS cm^{-1}, respectively. Hopping of ionic species between the coordinating sites, better ionic dissociation due to the optimized EC:PC concentration and the resulting segmental motion of the PAN polymer chains contribute to the optimum ionic conductivity observed in our present study.

Thermo-gravimetric analysis is one of the best techniques to study the thermal stability of these gel-polymer electrolytes in a desired temperature range. TGA studies were performed on two sample compositions (sample nos. 1 and 7), which are the lowest and highest conducting samples respectively among all the 11 samples studied in the present work. Percentage weight loss is shown in Fig. 5 as a function of temperature. As observed, there is no noticeable weight loss of the gel-polymer electrolytes up to 100 °C indicating that the thermal stability is met for practical applications. When the temperature is increased above 100 °C, there is noticeable weight loss, and obviously rate of weight loss is higher for sample no. 7 than sample no. 1. This could be due to the higher amount of EC and PC present in sample no. 7 compared to that of sample no. 1, and hence the evaporization of EC and PC. These PAN-based polymer electrolytes studied in this work have better thermal stability compared to recently studied PVdF-HFP-based gel-polymer electrolytes, which showed weight loss even at 65 °C [11]. Overall, our best conducting sample composition (11PAN-12$NaClO_4$-40EC-37PC) showed reasonably good room temperature conductivity (σ_{RT} = 4.5 mS cm^{-1}) and also has better thermal stability for practical applications in rechargeable SIBs. Very recently, several techniques have been introduced for the development of lithium-ion conducting gel-polymer electrolytes for secondary lithium-ion batteries. For example, Li et al. [19] have recently published a new composite gel-polymer electrolyte synthesized with non-woven fabric (NWF) and methyl cellulose (MC) with improved mechanical properties as well as outstanding thermal and electrochemical stabilities. These electrolytes have been prepared by a tape casting process followed by the absorption of liquid electrolyte. A few other reports are also available in the literature on these types of lithium-ion conducting gel-polymer electrolytes reinforced with NWF or glass fiber mats [20, 21]. These research directions would pave the way for developing sodium-ion conducting gel-polymer electrolytes.

Conclusions

A new set of PAN-based Na^+ ion conducting gel-polymer electrolytes have been synthesized and characterized to optimize the ionic conductivity. Room temperature conductivity value of 4.5 mS cm^{-1} was obtained for the composition 11PAN-12$NaClO_4$-40EC-37PC and the activation energies remained almost constant for all the compositions studied suggesting that the activation process is governed by the nature of the co-solvent (EC/PC) rather than the type of the salt

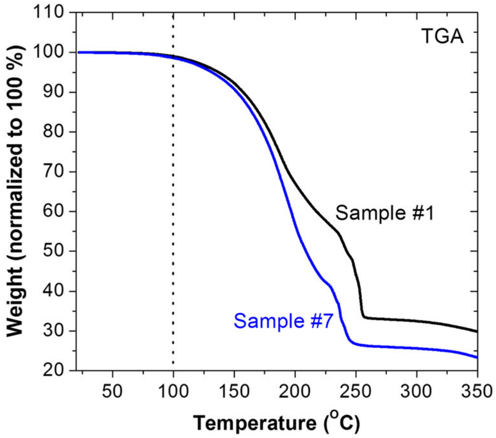

Fig. 5 Weight loss as a function of time for sample nos. 1 and 7

or the salt concentration. Variation of ionic conductivity with inverse temperature showed Arrhenius behavior. Thermogravimetric analysis revealed that there is no noticeable weight loss of these electrolytes at temperatures up to 100 °C and hence these electrolytes are thermally stable for operating temperatures up to 100 °C. Overall, our optimized composition has the high potential for practical applications because of its high room temperature conductivity and better thermal stability.

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