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Novel Gel-Polymer Electrolytes for Sodium-Ion Secondary Batteries - An Electrochemical Impedance Spectroscopic Studies

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Abstract. Global lithium deposits have been consumed a lot because of the heavy usage of lithium-ion batteries (LIBs) in almost all portable electronic devices and in automobiles. Due to the very limited global lithium resources, the so-called '*batteries beyond lithium-ion*' such as sodium-ion batteries (SIBs) are becoming popular, particularly in the R&D level. One of the common problems in the commercial level production of SIBs is the synthesis of suitable electrolytes with sufficient ambient temperature ionic conductivities. In this work, a set of novel gel-polymer electrolytes (GPEs) based on poly (methyl methacrylate) (PMMA) host polymer have been synthesized and characterized by electrochemical impedance spectroscopic (EIS), DC polarization and cyclic voltammetric (CV) techniques. The optimized PMMA-$NaClO_4$-EC-DMC GPE composition (10:14:38:38 wt.%) showed an ambient temperature ionic conductivity of 8.4 mS cm^{-1}. Ionic conductivity vs inverse temperature showed Arrhenius behavior with almost same activation energies of 0.16 eV for all the compositions studied. DC polarization test on SS/GPE/SS configuration showed that the best conducting composition is dominantly an ionic conductor ($t_{ion} \sim 0.998$) with negligible electronic conductivity, which is highly desirable to avoid short circuits within the cell. The CV test on best conducting composition revealed that the electrochemical stability window (ESW) of these GPEs is about 4 volts (- 2 to + 2 volts). This optimized composition with highest ambient temperature ionic conductivity and negligible electronic conductivity seems to be a promising candidate for practical applications in sodium-ion secondary batteries.

Introduction

Lithium-ion batteries (LIBs) are inevitable for portable electronics as well as automobile applications due to their high energy density and several other advantages [1-2]. On the other hand, global lithium resources are limited and also consumed heavily from 1991 after the commercialization of first LIB by the SONY corporation. This led to the exponential growth of prices of lithium raw materials. Present R&D works of the battery research community is being mainly focused on new battery chemistries which are cheaper alternatives to LIBs, for example sodium-ion batteries (SIBs). Although sodium is abundant in the Earth and hence cheaply available, one of the major problems with SIB technology is the low ambient temperature ionic conductivity of the electrolytes, especially in the solid state [3-4]. This is obviously due to the larger size of Na^+ ions compared to that of Li^+ ions. To overcome this problem, various types of electrolytes such as organic liquids, aqueous liquids, ionic liquids and gel-polymer electrolytes (GPEs) are being heavily studied nowadays. Among these, gel-polymer electrolytes are much preferred because of their intermediate nature showing the properties somewhat in the middle of solid and liquid electrolytes. Their quasi-solid state nature helps to enhance the mobility of Na^+ ions leading to better ambient temperature ionic conductivities and at the same time helps to avoid electrolyte leakage problems.

Among Na^+ ion conducting GPEs reported in the literature, there are a few reports on PMMA polymer host based electrolytes as well [4-6], but not on PMMA-$NaClO_4$-EC-DMC system incorporating EC (Ethylene Carbonate) and DMC (Dimethyl Carbonate) as the plasticizer and the solvent, respectively. In this work, several different compositions of PMMA-$NaClO_4$-EC-DMC GPEs have been synthesized and characterized by electrochemical impedance spectroscopic (EIS), DC polarization and cyclic voltammetric (CV) techniques. PMMA was chosen because of its ability to entrap the liquid part of the electrolytes within the polymer chain segments [5]. It has been found that the GPE composition 10PMMA-14$NaClO_4$-38EC-38DMC (wt.%) showed best ambient temperature ionic conductivity among several different compositions studied in this work.

Materials and Methods

Five different compositions of PMMA-$NaClO_4$-EC-DMC GPEs have been synthesized as listed in Table 1. PMMA, $NaClO_4$, EC and DMC, all purchased from Sigma-Aldrich, are the polymer host, ionic salt, plasticizer and the solvent, respectively. For the synthesis of GPEs, required amount of ionic salt ($NaClO_4$), EC and DMC were magnetically stirred at room temperature for 3 hours, then the required amount of PMMA was added and stirred again for 7 hours at 40 ºC until a clear homogenous gel sample was obtained.

Metrohm Autolab (PGSTAT 128N) impedance analyzer in the frequency range from 1 Hz to 0.1 MHz was used for impedance measurements on disc shaped samples sandwiched between two spring-loaded stainless steel blocking electrodes (SS/GPE/SS) separated by an insulating spacer. The temperature of the samples was varied from 25 to 75 °C and the impedance data were recorded at 10 °C intervals on heating. The ionic conductivity for each samples were estimated by finding the bulk resistances in the respective Nyquist plots. DC polarization test was performed at room temperature on best conducting sample under an applied voltage of 1V with a scan rate of 5 mV s^{-1}; stainless steel (SS) blocking electrodes were used to assemble the cell. The electrochemical window of the best conducting sample was found from the CV studies performed with a scan rate of 5 mVs^{-1} for a cell configuration of SS/GPE/SS.

Table 1: Sample compositions of five different PMMA based GPEs synthesized in this work.

Sample	**PMMA (wt%)**	**$NaClO_4$ (wt%)**	**EC (wt%)**	**DMC (wt%)**
A	16	08	38	38
B	14	10	38	38
C	12	12	38	38
D	10	14	38	38
E	08	16	38	38

Results and Discussion

As shown in Table 1, all five GPE compositions were synthesized by systematically varying the EO/Na^+ ratio, while keeping the content of EC and DMC fixed at 38 wt.%. EIS data was recorded by using Metrohm Autolab (PGSTAT 128N) impedance analyzer with an applied ac signal of 10 mV in the frequency range of 1 Hz to 0.1 MHz. Fig.1a shows the Nyquist plots at ambient temperature for all the GPE compositions (A, B, C, D and E). The equation (1) was used to estimate the conductivity values (σ) by using the bulk resistance values (R_b) extracted from the respective Nyquist plots. R_b values were obtained from the intercept of the respective spikes with the X-axis.

$$\sigma = l/R_b A \tag{1}$$

where l is the thickness and A is the cross-sectional area of the electrolyte sample sandwiched between a non-conducting spacer.

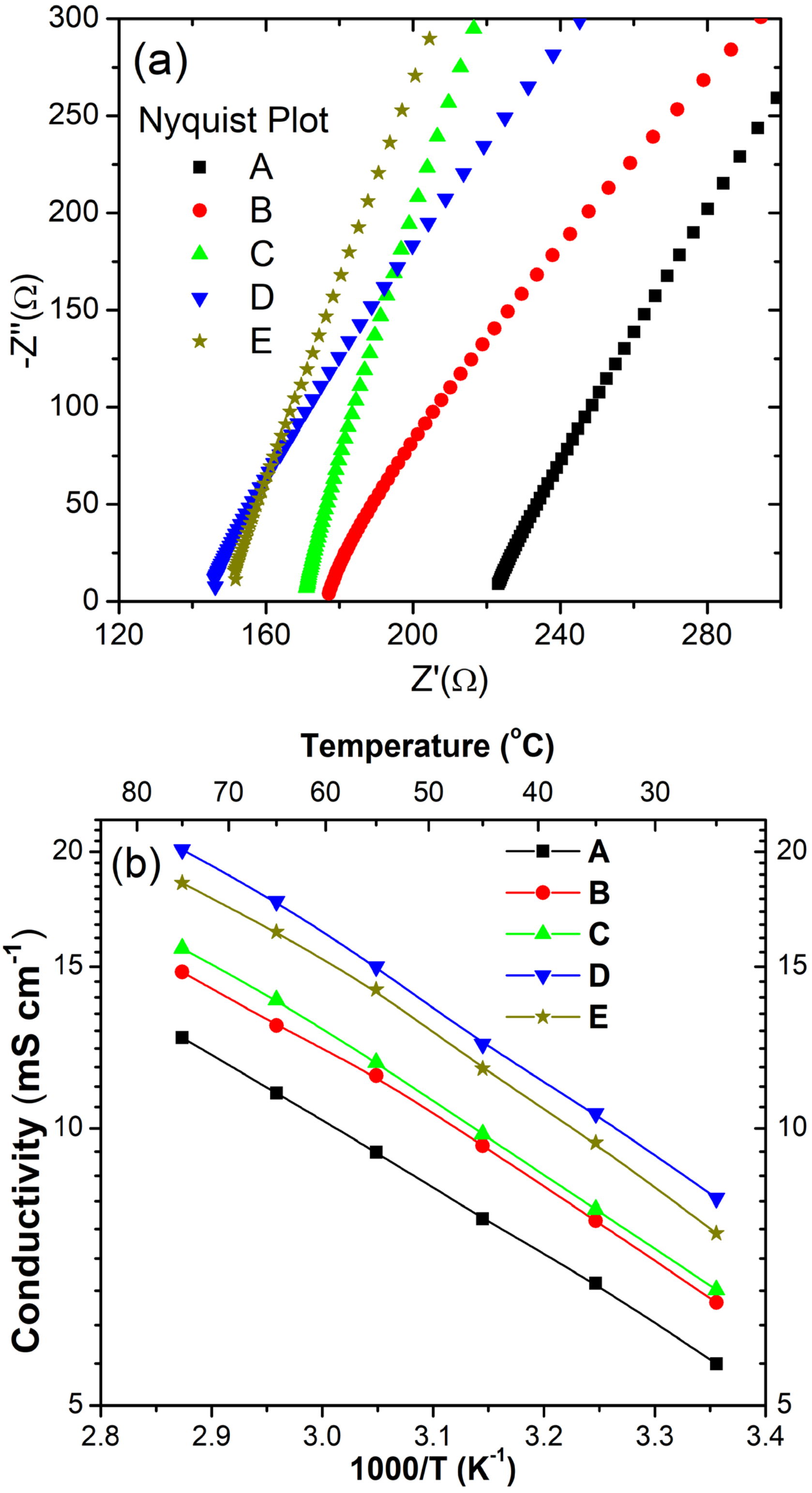

Figure 1: (a) Nyquist plots at RT, and (b) σ vs 1/T plots, for PMMA-$NaClO_4$-EC-DMC gel-polymer electrolyte samples A, B, C, D and E.

As shown in Fig.1a, Sample D shows the lowest ambient temperature bulk resistance leading to highest conductivity among all the samples studied in this work. Fig.1b shows the conductivity variation with inverse temperature (σ vs 1/T). Obviously, all these GPE samples show Arrhenius behavior of conductivity variation with temperature satisfying the Arrhenius equation given in (2).

$$\sigma(T) = \sigma_0 \, e^{-E_a/kT} \tag{2}$$

where σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann constant.

Activation energies were calculated from the slopes of the respective ln σ vs 1/T plots. The ambient temperature conductivities, pre-exponential factors and the activation energies for all the samples are listed in Table 2. All the GPEs studied in this work showed almost same activation energies (~ 0.15 - 0.16 eV) exhibiting that the activation process is mainly controlled by the concentration of EC and DMC rather than the concentration of polymer host or the ionic salt. Hence, the degree of ionic dissociation would be the prime factor determining the change in conductivity with composition. As listed in Table 2, ambient temperature conductivity and the pre-exponential factor are maximum for Sample D, which are 8.4 mS cm^{-1} and 3.89 S cm^{-1}, respectively. Conductivity increase with temperature (Fig.1b) would be mainly due to the increase in free volume within the polymer chains and the enhanced segmental flexibility leading to increased mobility of ionic species. Conductivity increases with the increase in salt concentration stating from 8 wt.%, but a drop in conductivity is observed for salt concentration higher than 14 wt.% (Tables 1 and 2). This drop could be due to the formation of ion aggregates blocking the mobility of ions. Our attempts to synthesize samples with PMMA content less than 8 wt.% and higher than 16 wt.% were unsuccessful due to the difficulty in the gel formation and the segregation of ionic salt within the polymer matrix, respectively.

Table 2: Conductivity at ambient temperature (σ_{RT}), pre-exponential factor (σ_0) and the activation energy (E_a) of PMMA based GPEs synthesized in this work.

Sample	**σ_{RT} (mS cm^{-1})**	**σ_0 (S cm^{-1})**	**E_a (eV)**
A	5.6	1.60	0.15
B	6.5	2.10	0.15
C	6.7	2.73	0.15
D	8.4	3.89	0.16
E	7.7	3.70	0.16

Arrhenius behavior of conductivity variation was already reported for some other Na^+ ion conducting gel-polymer as well as solid-polymer electrolyte systems [3, 5, 7-9]. In this study, employing PMMA as the polymer host is highly advantageous for the formation and retention of gel. Kumar *et al.*[5] have reported for some other Na^+ ion conducting GPE system that the ability of PMMA to entrap the liquid phase of the electrolyte within the pores of the polymer host is very high resulting in enhanced ionic conductivity. Further, $NaClO_4$ better suits as the ionic salt for electrolytes; anion (ClO_4^-) size is more than double compared to that of the cation (Na^+) and hence the ionic conductivity is dominantly from the Na^+ ion mobility, which is good for battery applications [10].

DC polarization test was performed under an applied voltage of 1 V with SS/GPE/SS configuration and the data is shown in Fig.2b for the best conducting composition (Sample D). Current was measured with time for about 6 hours. Current suddenly drops to almost zero within a few minutes indicating that the electrolyte is a dominant ionic conductor. Ionic transference number was estimated as, $t_{ion} = 0.998$, which is almost close to unity and hence the electronic contribution to conductivity is negligibly small. This is highly beneficial for a good electrolyte to avoid short circuiting within the cell. CV data was also recorded on Sample D and shown in Fig.2b. It shows that the electrochemical stability window (ESW) of the best conducting composition is about 4 V (-2 to +2 V).

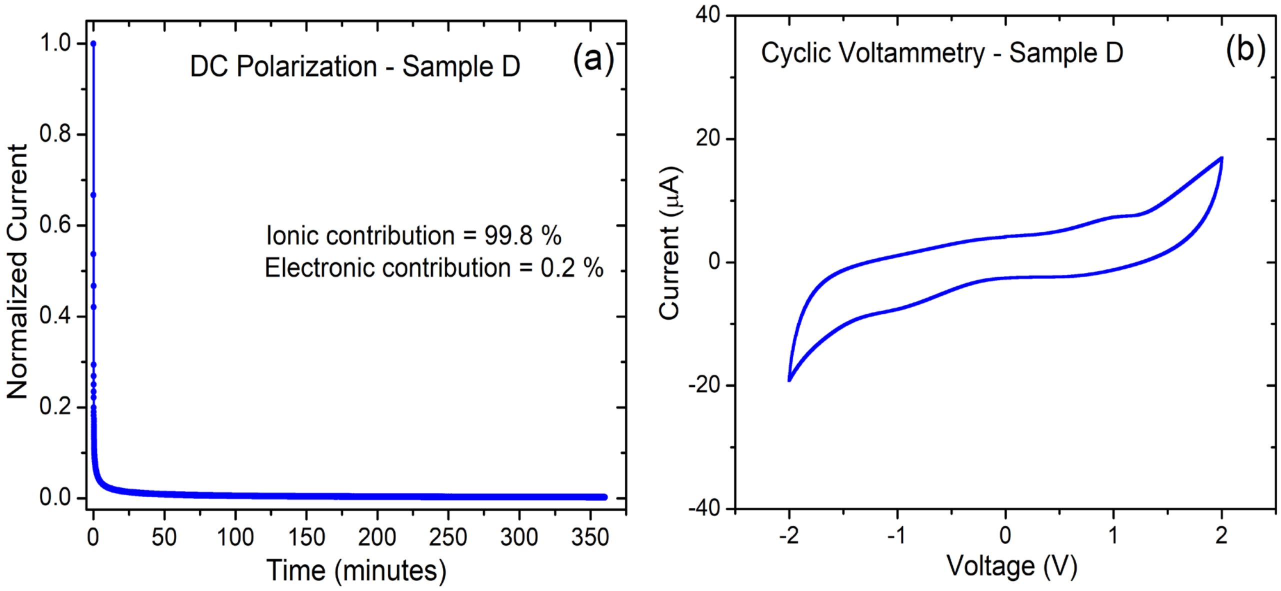

Figure 2: (a) DC polarization under an applied voltage of 1 V, and (b) Cyclic voltammetry; both recorded with a scan rate of 5 mV s^{-1} in the configuration SS/GPE/SS for the best conducting composition (Sample D).

Conclusion

Sodium batteries are emerging as a cheaper alternative to expensive lithium batteries. However, designing a suitable electrolyte is a major obstacle due to the larger size of Na^+ ions compared to that of Li^+ ions. A set of new gel-polymer electrolytes have been synthesized in this work and characterized to study their properties. PMMA was chosen because of its ability to retain the liquid part of the electrolyte within the pores of the polymer chains. The composition 10PMMA-14$NaClO_4$-38EC-38DMC (wt.%) showed maximum ambient temperature ionic conductivity of 8.4 mS cm^{-1}. Variation of ionic conductivity with inverse temperature showed Arrhenius behavior with almost constant activation energies. Electronic contribution to the conductivity is negligibly small for the best conducting composition, which is highly beneficial for the practical applications to avoid short circuiting inside the cells. The electrochemical stability window of the best conducting GPE is found to be about 4 volts (- 2 to + 2 volts). Overall, the properties of the optimized composition seem to be highly suitable for applications in sodium-ion secondary batteries.

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