



# Effect of organic solvent addition on electrochemical properties of ionic liquid based Na<sup>+</sup> conducting gel electrolytes

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## ABSTRACT

A novel sodium ion conducting gel polymer electrolyte comprising room temperature ionic liquid, 1-ethyl-3-methyl imidazolium trifluoro-methane sulfonate (EMITf) incorporated with ethylene carbonate and propylene carbonate and its solution with sodium trifluoromethane sulfonate (NaTf) entrapped in poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) is prepared using solution cast technique. The gel electrolyte is obtained in the form of free-standing transparent film. The gel electrolyte offers electrical conductivity of  $\sim 10^{-3} \text{ S cm}^{-1}$  at  $\sim 30^\circ\text{C}$  with good mechanical, thermal and electrochemical stability window. The electrical conductivity is measured as a function of temperature and found to be consistent with Vogel-Tamman-Fulcher (VTF) relationship in the temperature range from  $30^\circ\text{C}$  to  $75^\circ\text{C}$ .

Sodium ion conduction in the gel electrolyte film is confirmed from cyclic voltammetry and transport number measurements. The value of the sodium ion transport number of the ionic liquid based gel electrolyte is  $\sim 0.19$ . The sodium sulfur battery with the gel electrolytes delivers the first discharge capacity of  $267 \text{ mAh g}^{-1}$  sulfur and then it decreases with repeated charge–discharge cycles.

## 1. Introduction

Gel polymer electrolytes are materials of considerable interest worldwide and are good substitute for liquid electrolytes in various electrochemical devices. The most advantageous features of these electrolytes are their free-standing consistency, high ionic mobility and charge carrier concentration. Apart from various attractive properties, the gel polymer electrolytes suffer from few drawbacks such as poor dimensional stability, interfacial instability towards cathode materials and lower liquid retention capacity. In order to improve their performance characteristics, various approaches have been adopted including the incorporation of the ionic liquids to obtain gel electrolytes [1–4]. Ionic liquids meet the requirements of plasticizing salts and also offer improved thermal and mechanical properties to flexible polymers. Recently few studies have been reported in which EC or the mixture of EC and PC are incorporated into ionic liquid based gel polymer electrolytes [5]. Such modifications lead to a significant improvement in the electrochemical stability, particularly the substantial improvement in the electrode-electrolyte interfacial stability due to good flexibility of the materials.

Particularly, the lithium based batteries, which are mostly reported in literature, suffer from some safety limitations and many other problems [6]. Many researchers have attempted different cell chemistries like sodium, magnesium, zinc etc. as an alternative to obtain a battery

that has high specific energy density, high specific power, cost-effective, safe and environmental friendly [7–15]. These alternatives are not extensively studied and are still in developing stage and needs continued research for establishing them. The lower price of sodium followed by its high natural abundance, non-toxicity, low atomic mass (23.0) and high electrochemical reduction potential ( $-2.71 \text{ V}$  vs. S.H.E) promises it as a good rationale for study of the sodium/polymer battery. When coupled with an appropriate electropositive material, it would be capable of giving a cell of voltage  $> 2 \text{ V}$  [16].

Conventional Sodium-sulfur (Na/S) battery is one of the most promising candidates for energy storage applications developed since the 1980s. Kummer and Weber reported the electrochemical properties of sodium/sulfur cell above  $300^\circ\text{C}$ ., which utilized solid ceramic electrolyte, and both sodium and sulfur electrodes in liquid state. Substantial power is consumed in maintaining high operating temperature above  $300^\circ\text{C}$  and in many times liquid sodium and sulfur are found to induce explosion [17–23].

In order to develop room temperature Na/S batteries, many materials have been studied as anodes or cathodes of the sodium battery. Doeff et al. reported discharge behavior of Na/PEO/ $\text{Na}_x\text{MnO}_2$ , Na/PEO/ $\text{NaCoO}_2$  at  $85^\circ\text{C}$  [24]. Barker et al. has fabricated a hard carbon/ $\text{NaVPO}_4\text{F}$  cell, and explained that reversible specific capacities of the cathode and anode were  $82 \text{ mAh g}^{-1}$  and  $202 \text{ mAh g}^{-1}$  [25]. H-J Ahn et al. has reported the discharge capacity of  $505 \text{ mAh g}^{-1}$  at  $90^\circ\text{C}$  and

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489 mAh g<sup>-1</sup> sulfur at room temperature [26]. Current global research activities towards sodium have revealed the hidden potential of sodium batteries which is still need to be explored at newer levels [27]. Recently a few Na/S batteries have been developed based on gel polymer electrolytes operative at room or ambient temperatures [21,28–30]. In order to develop sodium-sulfur batteries, the electrolyte should have high ionic conductivity below the melting temperatures of sodium (melting point = 97.8 °C) and sulfur (melting point = 110 °C). The disadvantages of sodium metal as a negative electrode is that an aqueous electrolyte cannot be employed as it is a potential fire hazard. It is therefore a need to use room temperature high sodium ion conducting non-aqueous electrolyte suitable for the fabrication of sodium-sulfur batteries [31–38].

The present work reports a novel sodium ion conducting gel polymer electrolyte, which comprises of room temperature ionic liquid, 1-ethyl 3-methyl imidazolium trifluoro-methane sulfonate (EMI-triflate or EMITf) incorporated with ethylene carbonate (EC) and propylene carbonate (PC) and its solution with sodium trifluoromethane sulfonate (Na-triflate or NaTf) entrapped in poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP). In order to characterize the gel polymer electrolyte and to study the thermal, electrical and electrochemical performance, various physical experiments, namely differential scanning calorimetry, complex impedance spectroscopy, ionic conductivity, electrochemical stability, transference number measurement, open circuit voltage and charge-discharge studies have been carried out.

## 2. Experimental

PVdF-HFP (average molecular weight ~ 400,000), 1-ethyl 3-methyl imidazolium trifluoro-methane sulfonate (EMI-triflate or EMITf), sodium triflate (NaTf), ethylene carbonate (EC) and propylene carbonate (PC) and elemental sulfur powder were procured from Aldrich. The ionic liquid EMITf, acetylene black and NaTf were vacuum dried at 100 °C for 12 h prior to use. PVdF-HFP polymer and elemental sulfur was vacuum dried at 60 °C for about 24 h.

### 2.1. Preparation of electrodes

A sulfur cathode was prepared from a suspension of 70 wt% elemental sulfur powder, 20 wt% acetylene black, and 10 wt% (PVdF-HFP)-EMITf-EC-PC-NaTf gel electrolyte in acetonitrile in the form of a slurry. The slurry was mixed for 48 h by attrition ball mill and then cast on stainless steel current collectors. Electrode films were then heated at ~60 °C for ~24 h in a vacuum prior to use. Sodium amalgam, commonly denoted as Na-Hg, is an alloy of mercury with sodium metal and is used as anode.

### 2.2. Preparation of electrolyte

The “solution-cast” technique has been employed to prepare the ionic liquid based sodium ion conducting gel polymer electrolytes. The weight ratio of EMITf, PVdF-HFP and EC-PC mixture was kept at 65:20:15 w/w. The liquid electrolyte consisting of 0.5 M salt solution and PVdF-HFP/acetone solution were then mixed thoroughly at room temperature using magnetic stirrer for 10 h. Finally, the dimensionally stable free standing transparent thick (thickness ~300–400 μm) film of gel electrolyte was obtained.

### 2.3. Instrumentation

Thermal analysis of the gel electrolyte was performed using differential scanning calorimetry (DSC). The DSC was performed with a system of TA Instruments, Model: Q100. The samples were put in sealed aluminum pan and the measurements were carried out from -90 °C to 200 °C at a heating rate of 10 °C min<sup>-1</sup> in a static nitrogen atmosphere. The ionic conductivity measurements of the gel electrolyte film were

carried out by impedance spectroscopic analysis of a cell, in which the electrolyte film was sandwiched between two symmetrical stainless-steel (SS) electrodes. The impedance measurements were performed using a LCR Hi-Tester (HIOKI-3522-50, Japan) over the frequency range from 1 to 100 kHz with a signal level of 10 mV. The ionic conductivity has been evaluated and recorded over a temperature range from 30 to 75 °C.

The total ionic transport number ( $t_{ion}$ ) was evaluated using the d.c. polarization technique. In this technique, a cell SS|electrolyte|SS was polarized by applying a potential of 0.75 V and the resulting potentiostatic current was monitored as a function of time. The cationic (i.e., sodium ion) transport numbers of the ionic liquid based gel polymer electrolyte films were estimated using a combination of a.c. impedance and d.c. polarization techniques, as proposed by Evans et al. [39]. Using an electrochemical analyzer (Model 608C, CH Instruments, USA), voltammetric studies were carried out to evaluate the ‘electrochemical potential window’ of the gel electrolyte and to confirm their ability to conduct the sodium ions. The discharge and charge of the cell were carried out using Arbin Instrument, model BT 2000, USA at specific current (7.5 mA g<sup>-1</sup>) to cut-off voltages of 2.4 V and 1.4 V at room temperature (30 °C).

## 3. Results and discussion

### 3.1. Differential scanning calorimetry

The comparative DSC thermograms for pure PVdF-HFP polymer film and gel polymer electrolyte film are shown in Fig. 1. An endothermic peak, observed at ~140 °C, corresponds to the melting temperature of PVdF-HFP polymer film (Fig. 1a). The immobilization of salt solution containing NaTf/EMITf/EC-PC reduces the melting point to ~90 °C, suggesting that the polymer gel electrolyte can endure a temperature less than ~90 °C. PVdF has glass transition temperature of -35 °C and this peak is not visible in pure PVdF-HFP film. However, a

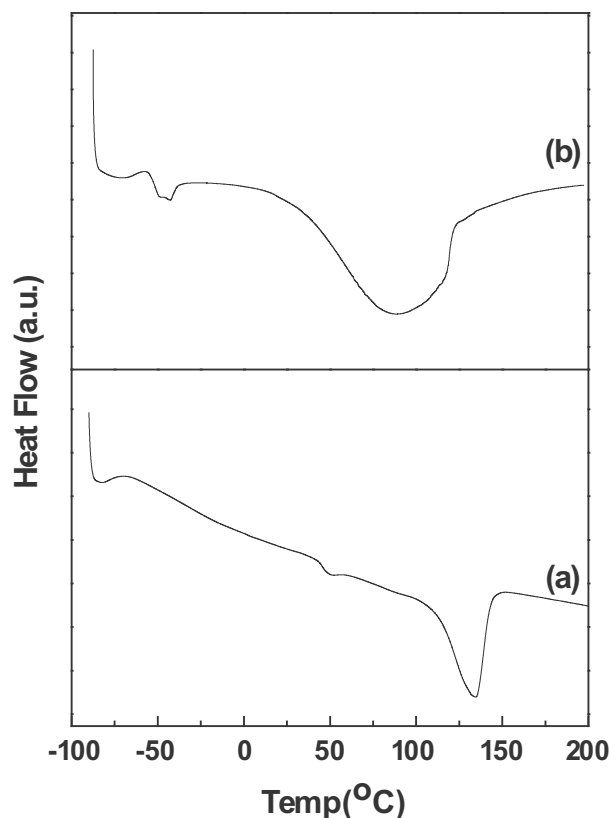


Fig. 1. DSC curves of: pure PVdF-HFP (a); gel polymer electrolyte (b).

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