

# Application of polyacrylonitrile-based polymer electrolytes in rechargeable lithium batteries

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**Abstract** Polyacrylonitrile (PAN)-based polymer electrolytes have obtained considerable attention due to their fascinating characteristics such as appreciable ionic conductivity at ambient temperatures and mechanical stability. This study is based on the system PAN–ethylene carbonate (EC)–propylene carbonate (PC)–lithium trifluoromethanesulfonate ( $\text{LiCF}_3\text{SO}_3$ ). The composition 15 mol% PAN–42 mol% EC–36 mol% PC–7 mol%  $\text{LiCF}_3\text{SO}_3$  has shown a maximum room temperature conductivity of  $1.2 \times 10^{-3} \text{ S cm}^{-1}$ . Also, it was possible to make a thin, transparent film out of that composition. Cells of the form,  $\text{Li/PAN-EC-PC-LiCF}_3\text{SO}_3/\text{polypyrrole (PPy)-alkylsulfonate (AS)}$  were investigated using cyclic voltammetry and continuous charge–discharge tests. When cycled at low scan rates, a higher capacity could be obtained and well-defined peaks were present. The appearance of peaks elucidates the fact that redox reactions occur completely. This well proves the reason for higher capacity. The average specific capacity was about  $43 \text{ Ah kg}^{-1}$ . Cells exhibited a

charge factor close to unity during continuous charging and discharging, indicating the absence of parasitic reactions.

**Keywords** Polyacrylonitrile · Ethylene carbonate · Propylene carbonate · Lithium triflate

## Introduction

Solid polymer electrolytes are known to be ionically conducting solid phases combined with salts, solid polymeric matrix, and solvents [1]. The history of solid polymer electrolytes dates back to 1970s, and since inception, they had poly(ethylene oxide) (PEO) in the skeleton due to its good solvation properties towards alkali metal ions. However, their propensity for crystallization at ambient temperatures, which results in low conducting values, has hindered them from being used for so many applications. Hence, attention has been focused on solid polymer electrolytes based on other polymer matrices. At present, much interest is on polyacrylonitrile (PAN)-based polymer electrolytes due to their liquid-like ionic conductivities at room temperature and fascinating mechanical stability [2]. Moreover, it is possible to make thin films easily. Among the numerous applications, much attention has been received for their use in Li rechargeable cells as electrolytes. Due to their ionic conductivity values and mechanical stability, some tend to categorize PAN-based systems as gel electrolytes. The common concept behind them is encapsulating a liquid electrolyte inside the polymer matrix which serves only as a container for the liquid electrolyte. As such, we have attempted to find a composition consisting of PAN, ethylene carbonate (EC), propylene carbonate (PC), and lithium trifluoromethanesulfonate ( $\text{LiCF}_3\text{SO}_3$ ), which provides a mechanically stable thin film of higher conductivity

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at room temperature. Furthermore, we aimed to determine whether the polymer electrolyte under investigation acts as a conventional solid polymer electrolyte or as a liquid polymer electrolyte. Today, much interest is on Li cells with polymer cathodes [3]. Hence, in this study, an extended investigation was done on cells in the form, Li/PAN–EC–PC–LiCF<sub>3</sub>SO<sub>3</sub>/polypyrrole (PPy)–alkylsulfonate (AS). Cyclic voltammetry studies and continuous charge–discharge tests were carried out to study the performance of the cell.

## Materials and methods

For the electrolyte samples, the composition reported by K. M. Abraham et al. was used as the reference [4]. At first, samples were prepared varying the salt concentration.

A mixture of EC (Aldrich, 98%) and PC (Bie and Berntsen A-S, 99%) of 1:1 (by weight) was dried over molecular sieves for 24 h. Then, the required amount of LiCF<sub>3</sub>SO<sub>3</sub> (3 M) was mixed in and purification was done by percolating through activated alumina. In a certain amount of so-prepared electrolyte, the corresponding quantity of PAN (Aldrich) was dissolved with the aid of magnetic stirring. The mixture composing of PAN–EC–PC–LiCF<sub>3</sub>SO<sub>3</sub> was heated at 140 °C for 1 h in a Buchi model (T0-50) furnace. The resulting homogeneous, viscous, hot mixture was poured between two well-cleaned glass plates and pressed. On cooling, transparent film membranes could be obtained, which were free from bubbles and pinholes. All the preparation steps were carried out inside a glove box (Vacuum Atmospheres) purged with argon (Ar).

A circular-shaped electrolyte membrane of about 1 cm in diameter from each electrolyte sample prepared was used for AC conductivity measurements. It was sandwiched in between two well-polished stainless steel electrodes in a brass sample holder. Assembling was done inside an Ar-filled glove box. Before the measurements were taken, each cell was kept in a heater cabin at 80 °C for 1 h to give a thermal stabilization. AC measurements were done from –20 to 80 °C at 5-°C intervals within the frequency range 1 Hz–1 MHz. To control the temperature, the cells were placed in a custom-built heating element controlled by an Eurotherm. The complex impedance data were gathered using a computer-controlled Solatron SI 1260 impedance analyzer. Diameter and thickness values of the electrolyte membranes were measured by means of a micrometer gauge. This procedure was repeated for each sample. Impedance data analysis was done using the nonlinear least square (NLLS) fitting routine EQUIVCRT developed by B. A. Boukamp [5]. After determining the salt concentration corresponding to the highest room-temperature conductivity, it was used to make samples varying the amount of PAN. The same preparation and analysis steps were carried

out for those samples too. The composition that showed the maximum room-temperature conductivity and a manageable mechanical stability was used for fabrication of the cells.

Pyrrole (Aldrich) was purified by distillation under nitrogen (N<sub>2</sub>) and stored in a refrigerator under dark. Sodium alkylsulfonate (SAS) (Hoechst) was used as received. Galvanostatic polymerization of pyrrole was done on a polished stainless steel dice (of a brass sample holder) in a three-electrode cell where a platinum electrode and a saturated calomel electrode were served as counter and reference electrodes, respectively. The monomer used consisted of 0.2 M pyrrole with 0.05 M SAS. The current density used was 1 mA cm<sup>–2</sup>. The time for polymerization was regulated to obtain a film of thickness of 1 μm upon the assumption that a charge of 240 mC cm<sup>–2</sup> produces a film having thickness 1 μm [6]. The thickness value of PPy film was 1 μm. Polymerization process was done with the use of a computer-controlled galvanostat/potentiostat. Films were thoroughly rinsed with distilled water after deposition to remove any existing monomer molecules.

Cell preparation was done inside a glove box purged with Ar. A circular-shaped pellet was cut from the electrolyte membrane. A lithium electrode of an identical diameter was taken as the anode. A brass sample holder was used to house the cell assembly.

Cyclic voltammetry tests were done in the potential range of 2.2–3.5 V using a computer-controlled potentiostat/galvanostat. While PPy electrode was served as the working electrode, lithium was used as both the counter and the reference electrodes. Cyclic voltammetry studies were performed at low scan rates, as well as at high scan rates. Thereafter, the cell was continuously charged and discharged using a computer-controlled charge–discharge setup.

## Results and discussion

All of the samples made of varying salt concentrations were transparent and homogeneous. This indicates the favorable compatibility of the components [7]. The graph of room-temperature conductivity vs salt concentration was plotted first. It is depicted in Fig. 1.

Room temperature conductivity increases initially with the salt concentration, but it reaches a maximum value at the concentration of 0.87 mol kg<sup>–1</sup>, followed by a decrement thereafter. Appearance of a conductivity maximum reflects the interplay of carrier concentration, mobility, and ion pairing. To explain the above behavior, it is worthwhile to refer to the expression,

$$\sigma = ne\mu$$

where  $\sigma$ ,  $n$ ,  $e$ , and  $\mu$  stand for conductivity, carrier concentration, electron charge, and ion mobility, respectively.

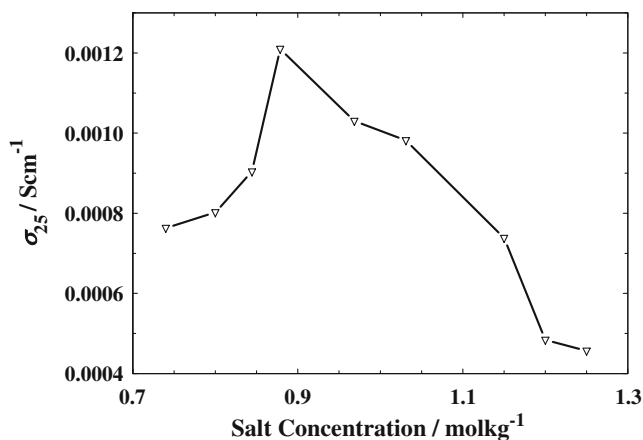


Fig. 1 Variation of room-temperature conductivity with salt concentration

When the salt concentration is increasing, the number of available charge carriers ( $n$ ) becomes higher. As a result, conductivity increases. At high salt concentrations, charge carriers tend to form ion pairs that are neutral in nature. Hence, a conductivity reduction is possible. Apart from that, the viscosity of the electrolyte is believed to increase at high salt concentrations, creating a barrier for the ion motion ( $\mu$ ) [8]. With the reduction of  $\mu$ , conductivity reduces.

Samples were made varying the amount of PAN and keeping the salt concentration at  $0.87 \text{ mol kg}^{-1}$ . At low amounts of PAN, samples were more or less in the liquid state. Due to the lack of mechanical strength, they were difficult to handle. On the other end, samples acquired hard consistency with the increasing PAN amount. The liquid-like and the hard consistencies of electrolytes at low and high amounts of PAN clue that PAN matrix provides dimensional stability.

Room-temperature conductivity variation with the amount of PAN was measured for the samples. It is illustrated in Fig. 2. It is well clear that with the increment of the PAN

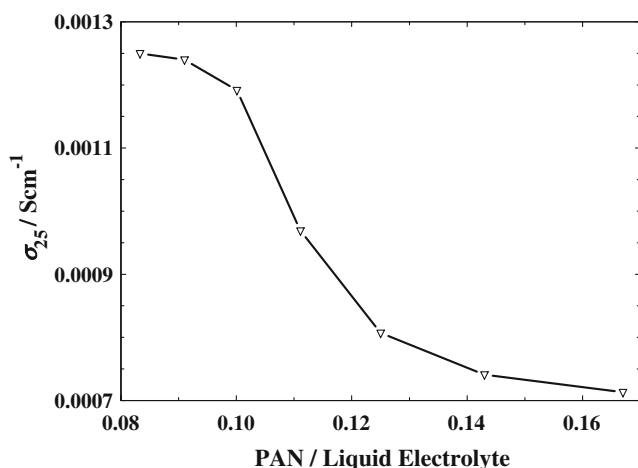


Fig. 2 Variation of room-temperature conductivity with PAN

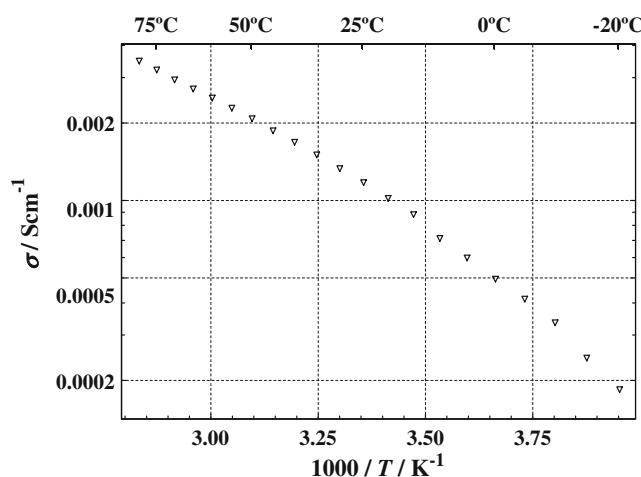


Fig. 3 Conductivity variation of the electrolyte sample with the inverse temperature

amount that room-temperature conductivity is substantially reduced. The variation of the conductivity can be attributed to the fact that, when PAN is introduced to the liquid electrolyte, it makes the ion conduction paths more tortuous by taking up some volume. Thereby, ionic motion is greatly hindered. In other words, at low amounts of PAN, liquid electrolyte constructs local effective pathways in liquid phase for ion conduction. They act as a major medium for ion conduction [9]. Upon the addition of PAN, those solvent channels may get blocked. Then, the ion mobility reduces, resulting in low conductivities. The reduction of conductivity may also be unavoidably affected by increasing interactions between PAN and liquid electrolyte components [10]. Besides, it has been reported that the introduction of PAN may give rise to some separated “islands” of electrolytes by which breaking of continuous conduction pathways would lead to a reduction in conductivity [11].

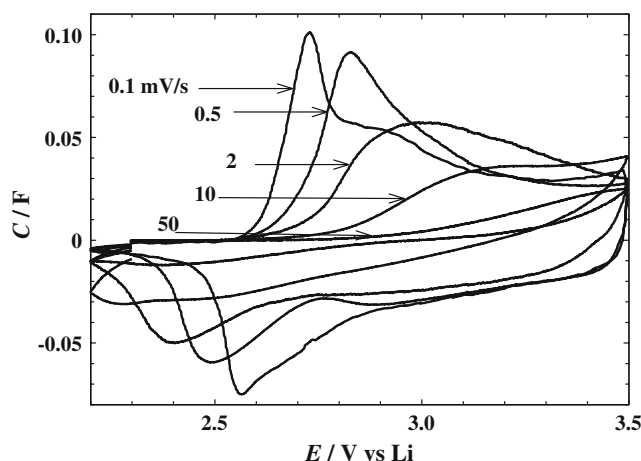
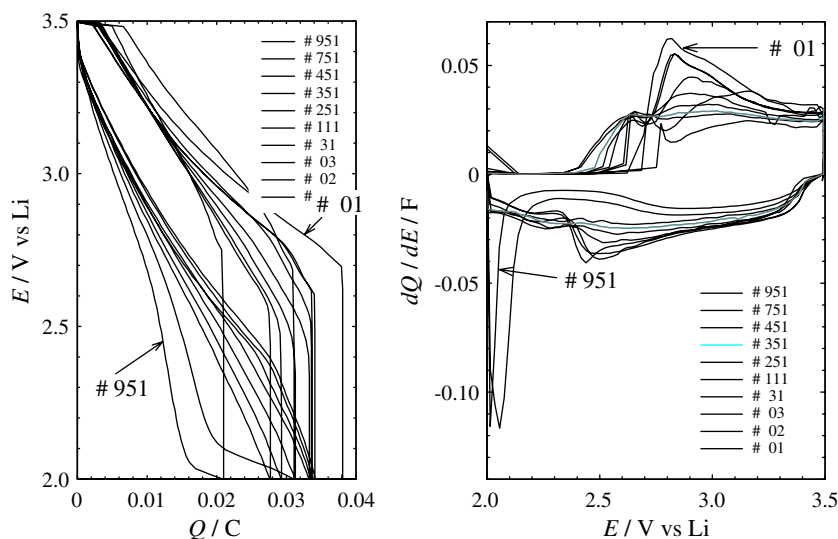


Fig. 4 Cyclic voltammograms obtained for the cell in the form, Li/PAN-EC-PC-LiCF<sub>3</sub>SO<sub>3</sub>/PPy-AS

**Fig. 5** Graphs of potential variation with capacity,  $Q$ , as well as differential capacity,  $dQ/dE$  vs potential



In this study, optimum mechanical properties have been obtained with a PAN amount corresponding to 1/10 of the amount of liquid electrolyte (by weight). The composition, corresponding to the highest room-temperature conductivity of  $1.2 \times 10^{-3} \text{ S cm}^{-1}$ , as well as the acceptable mechanical stability, turned out to be 15.01 mol% PAN–41.84 mol% EC–36.09 mol% PC–7.06 mol%  $\text{LiCF}_3\text{SO}_3$ . This is well comparable to the composition reported by K. M. Abraham et al. with an identical conductivity [12].

Conductivity variation of the electrolyte sample with the inverse temperature is shown in Fig. 3. It followed the Vogel–Tamman–Fulcher (VTF) behavior. This hints that the conduction mechanism is associated with free volume theory.

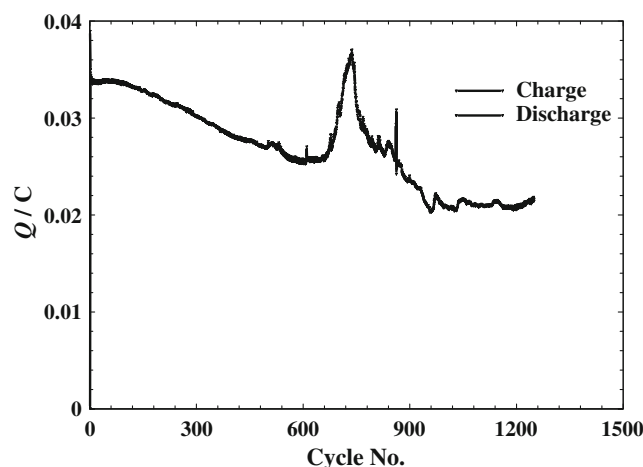
The room-temperature conductivity available in the graph is in the order of  $10^{-3} \text{ S cm}^{-1}$ . This value falls in the range of conductivity values of liquid electrolytes. With the variation of PAN, though the conductivity changes, the values lie in the range of  $10^{-3}$  order of magnitude. However, changing the amount of PAN puts a considerable effect on mechanical properties. These observations lead to the conclusion that PAN plays a great role in providing mechanical stability rather than conductivity. This fact clues that the liquid electrolyte,  $\text{LiCF}_3\text{SO}_3$ , EC, and PC, which is encapsulated in the polymer matrix, PAN, is responsible for the conductivity. By this conclusion, it is possible to report that the system under investigation behaves as a gel-type polymer electrolyte that is assumed to be in between solid and liquid states.

The average open-circuit voltage of the cells in the form of  $\text{Li/PAN-EC-PC-LiCF}_3\text{SO}_3/\text{PPy-AS}$  was in the range 3.0–3.5 V. Resulting cyclic voltammograms are shown in Fig. 4.

One of the clear features in the cyclic voltammograms is that the peaks are shifting with increasing scan rate in such

a way that anodic peaks to higher potentials (anodic side) and cathodic peaks to lower potentials (cathodic side). This gives rise to higher peak separation at high scan rates. Also, the peaks tend to disappear at higher scan rates. Appearance of the peaks symbolizes ion exchange in and out of the polymer electrode, and larger peak separation implies that the redox reactions are becoming slower while losing reversibility. When the scanning rate is very slow, ions have time to fully cooperate with the polymer and also to come out in the reverse scan. Also, these reactions are completed at low potentials. When the scanning is done at very fast rates, complete insertion and rejection takes more time, and therefore, they occur at higher (forward scan) or lower (reverse scan) potentials than in the case for slow scan rates.

Besides, it could be found that higher capacity values are available at low scan rates. This is also related to complete



**Fig. 6** Capacity variation for a cell in the form,  $\text{Li/PAN-EC-PC-LiCF}_3\text{SO}_3/\text{PPy-AS}$

and efficient redox reactions that occur at those scan rates. A negligible amount of charge exists below and around 2.5 V vs Li. It may be due to the nonconducting state of PPy, which becomes conductive around 2.8 V vs Li [13].

Graphs of potential variation with capacity,  $Q$ , as well as differential capacity,  $dQ/dE$  vs potential, are shown in Fig. 5. It should be emphasized that cell capacity measured in coulombs (C) [for practical batteries, often use ampere-hour (Ah)] should not be confused with capacity measured in farads (F). Here, we use the term cell capacity, as it is the general term mentioned in literature. Graphs of differential capacity variation with potential are equivalent to normal cyclic voltammograms.

In each curve in graphs of potential vs capacity, the separation between adjacent charge and discharge cycles is small. This is an indication of better kinetic reversibility of the cells. Major peaks in graphs of  $dQ/dE$  vs  $E$  indicate that a considerable amount of capacity has been found around 2.6 V vs Li. It is the potential around which PPy switches from nonconducting state to conducting state.

Capacity variation for a cell tested is given in Fig. 6. Sometimes, it has resulted in sudden capacity increments—or “spikes.” This happens due to an oxidation reaction, probably in the electrolyte. This reaction is not fully reversible. However, a proper cell function is obtained as the discharge capacity of the following cycle increases. This is equivalent to the soft dendrites often described for polymer electrolytes. Simply, it is described as the propensity of polymer electrolytes for self-healing. From the results, it is seen that the system under study also has that property. The extra capacity resulting from this is usually visualized as a new peak in the graph of derivative capacity vs potential. It is interesting to note that same capacity values obtained from cyclic voltammetry studies with low scan rates are available even with continuous charge–discharge cycling. Cells sometimes show capacity increment during cycling. It may be due to introduction of imperfections and/or improved contacts. Sometimes, initial capacity decrements followed by capacity increments and then capacity decrement are seen. Such occurrence can be reasonably attributed to variation of contacts and decomposition of components. Amongst the most specified characteristics is the retention of charge factor, which is defined as the ratio between the charge and the discharge capacities close to unity. This indicates the absence of

parasitic reactions, which may cause higher charge capacities than discharge capacities. Also, it can be used to elucidate that cells have sufficient electrochemical stability and reversibility.

## Conclusion

In forming free-standing films, PAN plays a great role. The composition 15 mol% PAN–42 mol% EC–36 mol% PC–7 mol%  $\text{LiCF}_3\text{SO}_3$  is found to give an appealing conductivity value of  $1.2 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature. According to the VTF behavior of conductivity variation and inverse temperature, this system can be considered as a gel polymer electrolyte. It has the ability to serve as an electrolyte in lithium polymer rechargeable cells. It may be possible to use the same composition for applications such as artificial muscles, super capacitors, etc.

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## References

1. Bruce PG, Vincent CA (1983) *J Chem Soc Faraday Trans* 89 (17):3187
2. Croce F, Gerace F, Passerini GDS, Appatechchi GB, Scrosati B (1994) *Electrochim Acta* 39/14:2187
3. Kakuda S, Momma T, Osaka T, Appatechchi GB, Scrosati B (1995) *J Electrochem Soc* 142/1:L1
4. Abraham KM, Alamgir MA (1990) *J Electrochem Soc* 137/5:1657
5. Boukamp BA (1989) *Equivalent circuit users manual*, 2nd edn. University of Twente, Enschede
6. Diaz AF, Castillo JI (1980) *J Chem Soc Chem Commun* 397
7. Sureshini AM, Nishimoto A, Watanabe M (1996) *Solid State Ionics* 86–88:385
8. Croce F, Gerace F, Dautzenberg G, Passerini S, Appatechchi GB, Scrosati B (1994) *Electrochim Acta* 39/14:2187
9. Kim DW, Kim YR, Park JK, Moon SI (1998) *Solid State Ionics* 106:329
10. Wang Z, Huang B, Huang H, Chen L, Xue R, Wang F (1996) *Electrochim Acta* 41/9:1443
11. Bohnke O, Frand G, Rezrazi M, Rousselot C, Truche C (1993) *Solid State Ionics* 66:97
12. Abraham KM, Alamgir MA, US. Patent No. 5219679
13. Skaarup S, West K, Christiansen BZ, Careem MA, Senadeera GKR (1994) *Solid State Ionics* 72:108