



Short Communication

Determination of electrochemical stability window of a polyacrylonitrile based polymer system for different electrodes

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Abstract

Solid polymer electrolytes are considered to be very appealing candidates for numerous applications such as batteries, artificial muscles and super capacitors. For applications, the voltage limits between the oxidation and reduction are very important. The voltage limits are taken as the positions where oxidation and reduction occurs. Those two positions can be traced using a cyclic voltammogram. The solid polymer electrolyte under investigation comprised of polyacrylonitrile (PAN), ethylene carbonate (EC), propylene carbonate (PC) and lithium trifluoromethanesulfoinate ($\text{LiCF}_3\text{SO}_3 - \text{LiTF}$). All the preparation steps were carried out in side an Argon filled glove box. Electrolyte film was sandwiched in a brass sample cell holder in between a Li electrode and one of an inert electrode made of stainless steel, nickel, platinum, copper and aluminium. Lithium was used as the reference and counter electrodes while the inert electrode was used as the working electrode. Cyclic voltammetry measurements were taken in the potential range, 2.0 V – 4.9 V vs Li. A good stability window was seen when the stainless steel electrodes were used.

1. INTRODUCTION

Polymer electrolytes can be recognized as a relative latecomer to the broader field of solid state ionics. The penalty for this is due to the fact that they have to compete with other solid state materials that have already confirmed their excellent properties in the areas of conductivity, transport mechanism, stability and reactivity towards applications. In fact, liquid polymer electrolytes exhibit better conductivity values than solid polymer electrolytes. However, former is having many problems in handling. Those problems

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underestimate their contribution in applications. As a result, much attention is now on solid polymer electrolytes. These are consisted with of an ionic salt dissolved in a solid coordinating polymeric solvent [1]. They have been tested for their ability to use for various applications. Apart from the conductivity values, the electrochemical stability of the systems is of prime importance almost for all applications [2]. Without any disturbance, it should be able to obtain a constant voltage for a long time. Unfortunately, the amount of research done on this aspect is very little. In this study, our objective was to investigate the electrochemical stability of a polyacrylonitrile (PAN) based solid polymer electrolyte using different types of inert electrodes.

2. EXPERIMENTAL

Preparation of the electrolyte was done according to the hot pressed method [3]. The composition selected was 15 mol% PAN: 42 mol% : EC: 36 mol% PC: 7 mol% LiTF. 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 hours. LiTF was mixed and purification was done percolating through activated alumina. PAN (ALDRICH) was dissolved in using magnetic stirring. The mixture was heated for 1 hr at 140 °C. The resulting homogeneous and hot mixture was poured in between two well cleaned glass plates and pressed. On cooling, a transparent film membrane could be obtained which was free from bubbles. All the preparation steps were carried out inside an Argon filled glove box.

Cells were assembled in brass sample holders in side a glove box placing the electrolyte in between a lithium electrode and an inert electrode selected. While lithium was used as the counter and reference electrodes, the inert electrode was used as the working electrode. The cell assembly was quite similar to the normal three electrode electrochemical cell. Cyclic voltammetry measurements were taken in the potential range, 2.0 V – 4.9 V vs Li using a computer controlled potentiostat / galvanostat. Sweep rates were at a scan rate 1 mV / s. The experiment was performed at room temperature.

3. RESULTS AND DISCUSSION

The anodic (oxidation) and cathodic (reduction) potential limits in the cyclic voltammogram have been taken as the values at which current passes through the cell. The region, which is bounded by these two values, is known as the electrochemical stability window.

Fig. 1 illustrates the cyclic voltammogram for the electrolyte on platinum electrode. Oxidation seems to occur at potentials beyond 4.2 V vs Li. After initiation of the oxidation, current has constantly increased upto 4.9 V vs Li. It has been reported a similar oxidation stability window upto 4.4 V vs Li on platinum for an electrolyte comprising, PAN : PC : LiAsF₆ [4].

The behaviour of the electrolyte on copper electrodes is shown in Fig. 2. Oxidation process is seemed to occur at a potential around 3.7 V vs Li. With the observation of the corrosion layer, it can be guessed that the corrosion product may be $\text{Cu}(\text{CF}_3\text{SO}_3)_2$. Once the oxidation begins, the resulting current exists even in the reverse scan. The corrosion may be getting dissolved slightly allowing further reactions. Also, Cu electrodes may get dissolved as reported by some researchers [5]. A small reduction peak can be seen at 2.6 V vs Li. It may be due to oxidation of Cu to Cu^{2+} . It was not possible to take measurements up to 4.9 V. The attempt resulted unusual patterns of the voltammograms which may be due to some reactions occurred in that potential range.

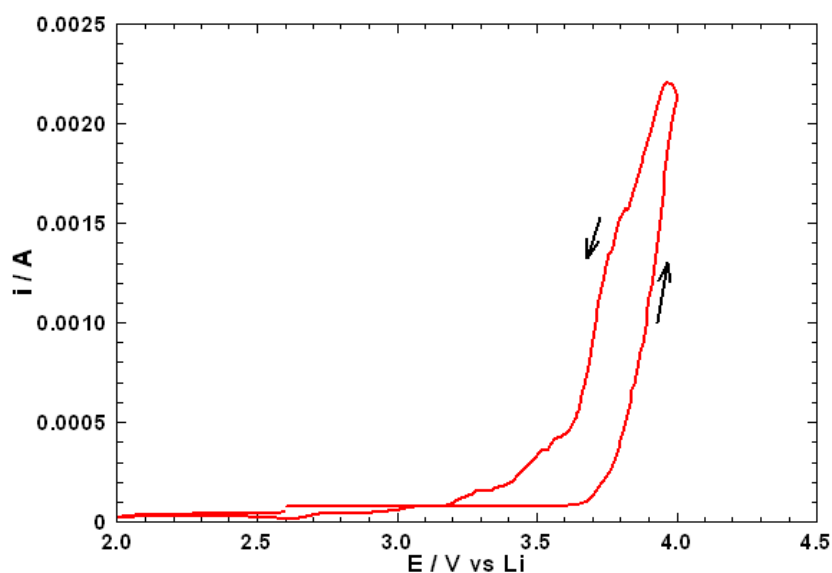


Fig. 1 Cyclic voltammogram with platinum inert electrode

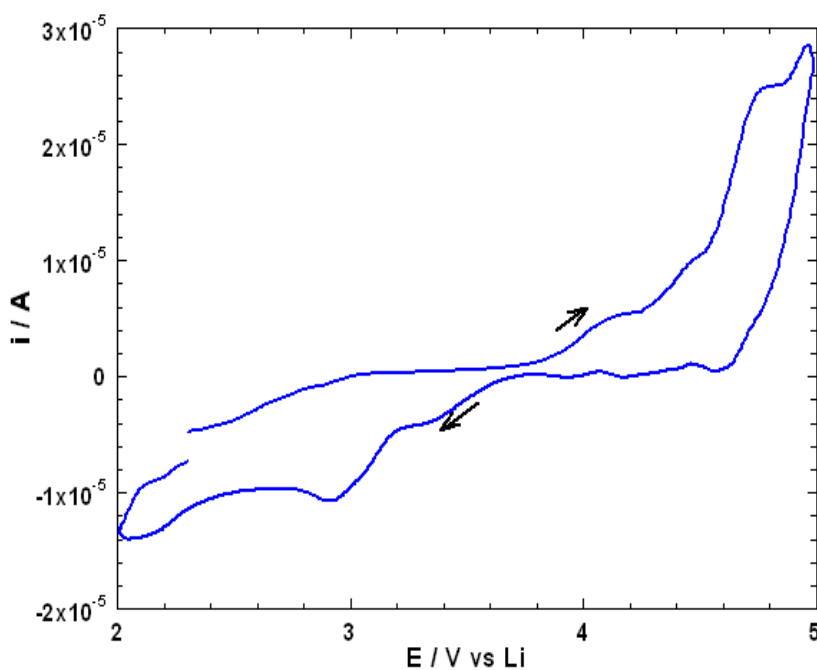


Fig. 2 Cyclic voltammogram with Cu inert electrode

Fig. 3 shows the cyclic voltammogram for the same electrolyte on nickel electrode. An oxidation reaction is seemed to initiate around 3.6 V vs Li. As with Cu, it was not possible to do measurements up to 4.9 V due to unwanted reactions took place. It is hence seen that the electrochemical stability window exists up to 3.6 V vs Li which is an acceptable value for some applications.

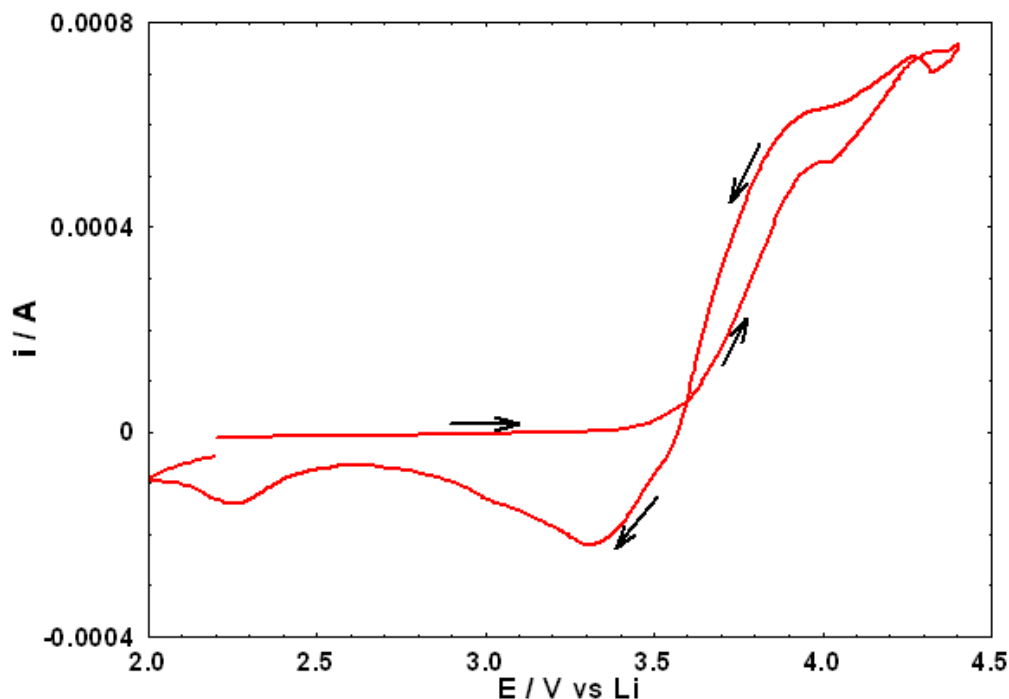


Fig. 3 Cyclic voltammogram with nickel inert electrode

Fig. 4 illustrates the stability of the electrolyte on aluminium electrode. Around 3.5 V vs Li, the process of oxidation begins. Up to about 4.6 V, resulting current increases gradually but beyond 4.6 V, it shows a significant increase. This is believed to be the breakdown voltage of the aluminium passivating layer. As with other cases, the corrosion product here is not passivating aluminium. Rather, it may get dissolved in the electrolyte. Continuation of high current even in the reverse scan is attributed to the fact that one of the passivation film on aluminium is broken down and hence aluminium corrodes at potentials above 2.9 V vs Li. On Cu, Ni and Al electrodes, it is seen that oxidation starts at lower voltages. It may be due to metal corrosion reactions [6].

As shown in Fig. 5, the electrolyte is stable on stainless steel in the potential range, 2.0 V – 4.0 V vs Li. Once the formation of the passivation film is stabilized, the stability window reduces to 2.0 V – 3.8 V vs Li.

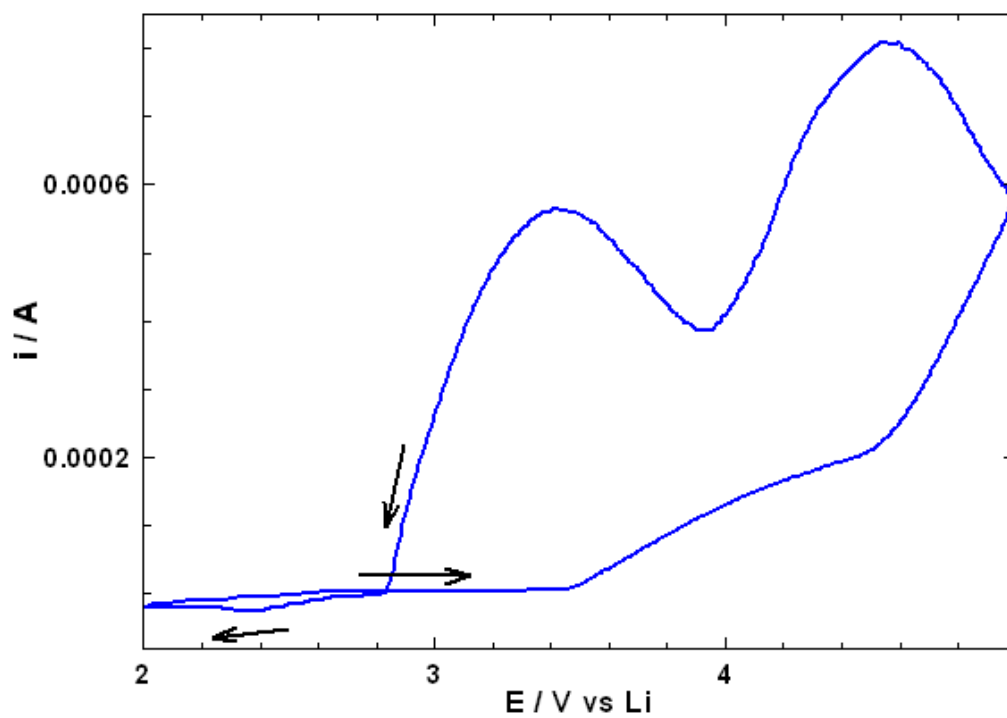


Fig. 4 Cyclic voltammogram with aluminium inert electrode

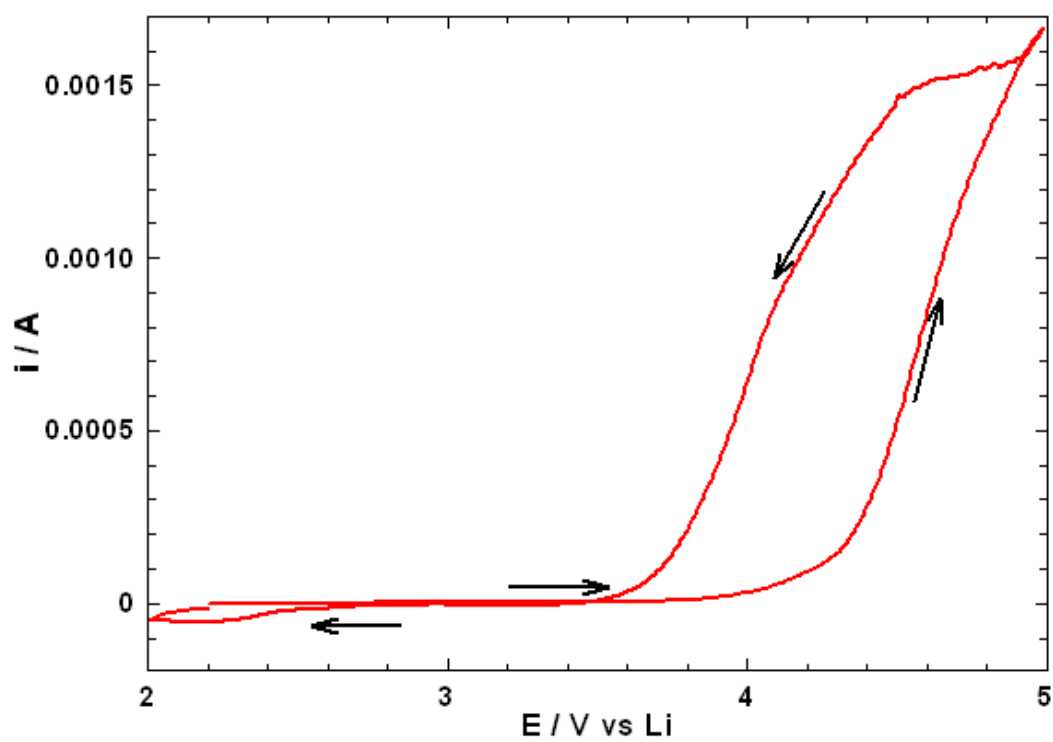


Fig. 5 Cyclic voltammogram with stainless steel inert electrode

4. CONCLUSION

With the observations, it is clear that the electrolyte is stable up to about 4.0 V with platinum and stainless steel. With aluminium, copper and nickel electrodes, proper functioning is accepted up to about 3.5 V. In this study, cyclic voltammtery curves were obtained at a scan rate of 1 mV /s. If this value was lower, it would be possible to observe the oxidation at a higher voltage and reduction at a lower potential. The reason is at low scan rates, there is ample time for the electrochemical reactions to occur. As a result, a wider stability window may be observed. Due to the same reason, at fast scan rates, a narrow electrochemical stability window may be seen. Furthermore, the stability windows have been determined for a short period of time. As a further study, the same experiment can be done for a longer period of time.

ACKNOWLEDGEMENT

We wish to extend our sincere thanks to Prof. Steen Skaarup and Prof. Keld West at Technical University of Denmark for their support. We would like to acknowledge International Program for Physical Sciences (IPPS), Uppsala, Sweden for offering financial assistance by means of fellowships and equipments. Our thanks are also due to the University of Peradeniya.

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