

Short communication

Organic polymer gel electrolyte for Li-ion batteries

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Abstract

The present paper describes a novel synthesis of organic polymer gel electrolyte for Li-ion cell, comprising of Polyethylene oxide (PEO), LiClO_4 , LiOH , Li_2SO_4 and dimethyl formamide (DMF). The gel was obtained with a specific weight ratio of these components after appropriate heat treatment. The gel when layered over graphite plate and LiCoO_2 cathode, it forms laboratory model Li-ion cell. The cell shows an OCP value of 3.624 V at 298 K.

The galvanostatic charge/discharge tests show performances comparable to liquid electrolyte system.

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1. Introduction

The secondary liquid-electrolyte based lithium-ion battery is well accepted in the commercial market. But, their manufacturing cannot fulfill the present demand arises by a growing electronic market. As the electronic goods are becoming smaller, thinner, though they need high energy density battery, flexible and powerful batteries are urgently needed. Therefore, lightweight lithium-ion battery technology may fulfill the present requirement. Organic solid polymers electrolyte (SPE) based on PEO have become a very important electrolyte material for lithium-ion battery technology [1,2]. Because, use of SPE in lithium-ion battery has several advantages: (i) volatile organic solvent is not incorporated, (ii) dendrite formation at the lithium electrode can be minimized, (iii) batteries can be made of any size and shape and (iv) light weight and high energy density battery can be made. It should be noted that the present lithium-ion battery technology based on solid polymer electrolyte is incapable of functioning efficiently at ambient temperature because of the lack

of polymer electrolyte with high ionic conductivity. The high crystallinity of PEO at room temperature is the main reason for such poor ionic conductivity and poor mechanical strength [3]. Recently there are many reports on the improvement of ionic conductivity as well as the mechanical strength after grafting PEO in to various polymers [4–20]. In this paper, we report a very simple method to synthesize an organic polymer gel based on PEO with different additives that has comparable performances to liquid electrolyte system.

2. Experimental

Organic polymer gel electrolyte was prepared by heating the homogeneous mixture of LiClO_4 , LiOH , Li_2SO_4 , DMF and polyethylene oxide at 50 °C for 20 min. Initially, solid LiClO_4 salt was added to DMF to obtain 1 M clear solution. In the next step, the DMF solution was saturated with LiOH and Li_2SO_4 at the same temperature and finally PEO powder was added to it with constant stirring. The whole solution was heated at 50 °C for 20 min before it was casted in a tape form. The electrochemical stability of the polymer gel electrolyte was examined by cyclic voltammetry technique using a potentiostat/galvanostat (PAR, model VersaStat™

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II). The current–potential curve was recorded in between the potential window of 0.0–4.0 V versus lithium metal at a sweep rate of 1 mV s^{-1} . LiCoO_2 cathode powder was synthesized by well-known citrate–nitrate method. In this method, the proportionate amount of Li_2CO_3 and $\text{Co}(\text{NO}_3)_3$ salts were dissolved in citric acid solution. The whole solution was stirred at 120°C for 2 h until a gel is formed, which produced the precursor powder after auto-combustion. The citrate/nitrate ratio for this synthesis was mentioned at 0.7. The precursor powder was then calcined at 600°C for 12 h and used as a cathode material for the Li-ion cell. A rectangle shaped graphite sheet (4 cm^2) was used to prepare lithium intercalated graphite (LiC_x) electrode. The intercalation was carried out inside an inert gas chamber using lithium metal as an anode and LiClO_4 in DMF as an electrolyte. Finally the cell (capacity 5 mAh) with the configuration, $\text{LiC}_x/\text{polymer gel electrolyte}/\text{LiCoO}_2$, was assembled inside a laboratory-made inert gas chamber after sand-witching the polymer gel electrolyte in between LiCoO_2 cathode and LiC_x anode. The thickness of the polymer gel electrolyte was measured by using micrometer (Mitutoyo, Japan) and kept at $3000 \mu\text{m}$ by putting a rubber gasket in between cathode and anode. The electrochemical performance of this cell was recorded using a potentiostat/galvanostat (PAR, model VersaStat™ II). The cell was cycled between the potential windows of 2.5–4.0 V and the charging current and discharging current were 3 and 0.45 mA, respectively.

3. Results and discussion

3.1. Ionic conductivity

The polymer gel electrolyte, as obtained, was transparent at room temperature. The conductivity of the polymer gel was measured by two-probe dc method at different temperature. The conductivity value of the gel polymer electrolyte measured at room is about $10^{-4} \text{ S cm}^{-1}$, which is comparable to that of liquid electrolyte. The conductivity values gradually increases with increase of temperature and follow the same trend as observed for other polymer electrolytes [1]. The activation energy of ion conduction (E_a) is calculated to be approximately $4.01 \text{ kcal mol}^{-1}$ from the Arrhenius plot, shown in Fig. 1. Similar activation energy value is reported for an improved polymer electrolyte with 50 wt% PEGDME as plasticizer [1].

3.2. Electrochemical stability

The cyclic voltammetry of the solid polymer gel is shown in Fig. 2. In the anodic scan, no significant oxidative degradation is observed up to 3.6 V. Some discrepancy is observed beyond the potential of 3.6 V versus Li in the anodic direction. This might be due to some unexpected chemical reaction, which need further clarification. If the oxidative degradation of the polymer gel is expected then, there should be an

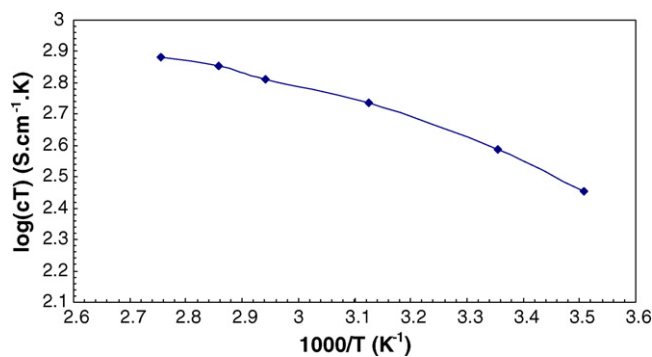


Fig. 1. Arrhenius plot of the polymer gel electrolyte.

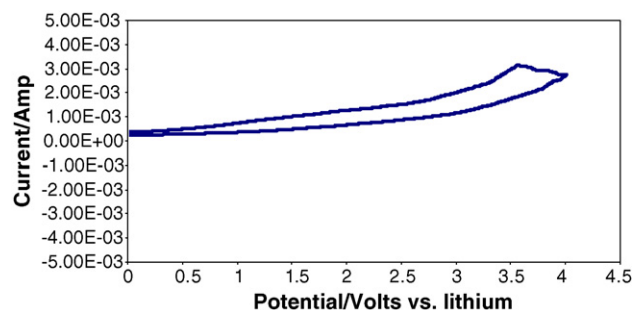


Fig. 2. Cyclic voltammogram for the polymer gel at 298 K. Sweep rate = 1 mV s^{-1} .

increase in anodic current. Therefore, oxidative degradation of the polymer gel may be avoided. This might be explaining the reason for obtaining 3.6 V (versus Li) open-circuit potential for the cell.

3.3. Battery performances

Fig. 3 shows the galvanostatic charge–discharge profile of the cell mentioned above. In this experiment, the voltage was limited to a maximum value of 4.0 V versus Li during charging and to a minimum value of 2.5 V versus Li during discharging process. The cell was charged using various current, though a single plot using 3 mA current is shown in Fig. 3. It is noted that the cell requires more than 2 mA cur-

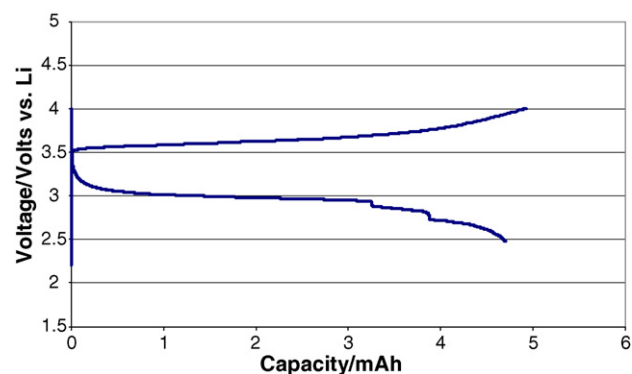


Fig. 3. Charge–discharge pattern of $\text{LiC}_x/\text{polymer gel electrolyte}/\text{LiCoO}_2$ cell; charging current = 3 mA and discharging current = 0.45 mA.

rent for proper charging under the mentioned configuration. Requirement of such high current density for the charging process might be because of the use of thick polymer electrolyte in the cell. Since SPE based lithium-ion battery does not require any extra separators, reducing the thickness of the gel electrolyte in the cell can minimize the charging current density. A cell with minimum thickness of the gel electrolyte restricts us to make a direct comparison with a cell based on liquid electrolyte. The cell was discharged at a current of 0.45 mA, once the cell voltage reaches to 4.0 V versus Li and the discharge pattern is shown in Fig. 2. Nearly 96% of its charge capacity has been delivered in the first cycle and it will be interesting to know how does it retains its capacity upon cycling, which is under investigation.

4. Conclusions

A solid polymer gel based on polyethylene oxide (PEO) is developed having compatible ionic conductivity than liquid electrolyte. A cell, LiC_x /polymer gel electrolyte/ LiCoO_2 , fabricated after sandwiching the synthesized polymer gel in between lithium intercalated graphite sheet and LiCoO_2 , showed 100% reversible behavior when cycled in between 2.5 and 4.0 V versus lithium. An optimization of the polymer gel may find itself in solid lithium-polymer gel battery that operates at room temperature.

Acknowledgement

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