

Cycling performance of lithium-ion polymer batteries assembled using in-situ chemical cross-linking without a free radical initiator



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ABSTRACT

We present a cross-linked gel polymer electrolyte for lithium-ion polymer batteries that can be easily synthesised without any initiators. The gel polymer electrolyte has a high ionic conductivity comparable to a liquid electrolyte, as well as favourable interfacial characteristics between the electrodes and the electrolyte during cycling. The lithium-ion polymer batteries assembled with cross-linked gel polymer electrolyte exhibit improved capacity retention and good rate capability.

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1. Introduction

Due to their high energy density and long cycle life, lithium-ion batteries have become the dominant power sources for portable electronic devices and electric vehicles [1,2]. However, safety issues still prevent full utilisation of these batteries. The high flammability of the organic solvents used in liquid electrolytes can lead to fires and explosions when short circuits or local overheating accidentally occurs. Therefore, there is a pressing need for safer, more reliable electrolyte systems, and polymer electrolytes are promising candidates in this regard [3–10]. Solid polymer electrolytes based on poly(ethylene oxide) are the most common examples. However, their low ionic conductivities, ranging from 10^{-8} to 10^{-5} S cm^{-1} , preclude their practical application for use in rechargeable lithium batteries at ambient temperatures. Accordingly, the most relevant research has focused on gel polymer electrolytes that exhibit higher ionic conductivities at room temperature. Such gel polymer electrolytes encapsulate a large number of liquid electrolytes in host polymers, such as polyacrylonitrile, poly(vinylidene fluoride-co-hexafluoropropylene) and poly(methyl methacrylate), and their ionic conductivities usually exceed 10^{-3} S cm^{-1} , which is necessary for practical battery applications. Nevertheless, most efforts to increase the ionic conductivity by incorporating larger numbers of liquid electrolytes have been detrimental to their mechanical properties. An in-situ chemical cross-linking method with a multi-functional acrylate has been used to overcome this problem [11–16]; this technique has been applied to the manufacture of commercialized lithium-ion

polymer batteries. In this process, an electrolyte solution containing cross-linking agents is injected into a lithium-ion cell, and gelation is carried out by heating the cell. However, this method has inherent disadvantages. The thermal curing procedure generally uses free radical initiators and must occur at an elevated temperature, which may induce thermal decomposition of the salt, formation of bubbles in the gel electrolyte due to gas evolution by thermal decomposition of initiator such as azobisisobutyronitrile (AIBN) and solvent evaporation. These factors can ultimately lead to degradation in battery performance [17,18]. Thus, there is great interest in an in-situ cross-linking approach that does not require the use of thermal initiators.

In this study, a cross-linked gel polymer electrolyte was synthesised without any initiators. As cross-linking agents, we used polyethyleneimine (PEI) with amine groups and poly(ethylene glycol) diglycidyl ether (PEGDE) with epoxy groups. Previously, our group has reported the cross-linking reaction of PEI with PEGDE for applications in dye-sensitised solar cells [19,20]. In this paper, the cycling performance of lithium-ion polymer batteries assembled by in-situ chemical cross-linking was investigated and compared with that of liquid electrolyte-based lithium-ion batteries. Our results confirmed the superior performance of the cross-linked gel polymer electrolyte compared with liquid electrolyte.

2. Experimental

2.1. Materials

PEI (branched, $M_n = 10,000$) and PEGDE ($M_n = 500$) (Aldrich Chemical Co.) underwent vacuum drying at 90 °C for 4 h and 50 °C for

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4 h, respectively. A liquid electrolyte, which consisted of 1.3 M LiPF₆ in ethylene carbonate(EC)/propylene carbonate(PC)/ethyl propionate(EP) (3:1:6 by volume, battery grade) containing 3 wt.% fluoroethylene carbonate (FEC), was kindly supplied by Panax-Etec. Co., and was used without further treatment. The water content in the liquid electrolyte was determined to be less than 20 ppm by Karl Fisher titration.

2.2. Preparation of the gel polymer electrolytes and cell assembly

Fig. 1 illustrates the synthetic scheme of the cross-linked gel polymer electrolyte. The gel electrolyte precursor consisted of PEI, PEGDE and the liquid electrolyte. A mixture of PEI and PEGDE was added to the liquid electrolyte at a concentration of 1 wt.%, and the solution was stored at ambient temperature. The ratio of PEI to PEGDE was fixed to be 7:3 by weight. After 12 h, fluorinated carbamate was obtained through a reaction between PEI and FEC, as shown in Fig. 1(a). To induce the cross-linking reaction of fluorinated carbamate with reactive epoxy groups in PEGDE, the solution was heated to 65 °C and maintained at that temperature for 4 h. The cross-linked gel polymer electrolyte was then obtained by the ring-opening reaction of PEGDE with fluorinated carbamate (Fig. 1(b)). Note that no gas was evolved in the gel polymer electrolyte during the cross-linking reaction at 65 °C. The LiCoO₂ electrode was prepared by coating an n-methyl pyrrolidone (NMP)-based slurry containing LiCoO₂ (Japan Chemical), poly(vinylidene fluoride) (PVdF) and super-P carbon (MMM Co.) (85:7.5:7.5 by weight) onto

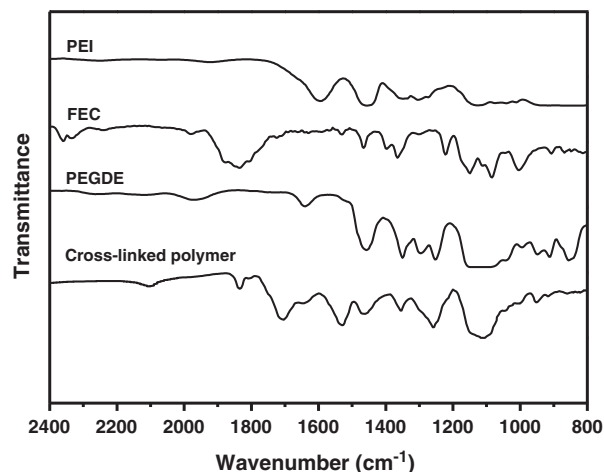
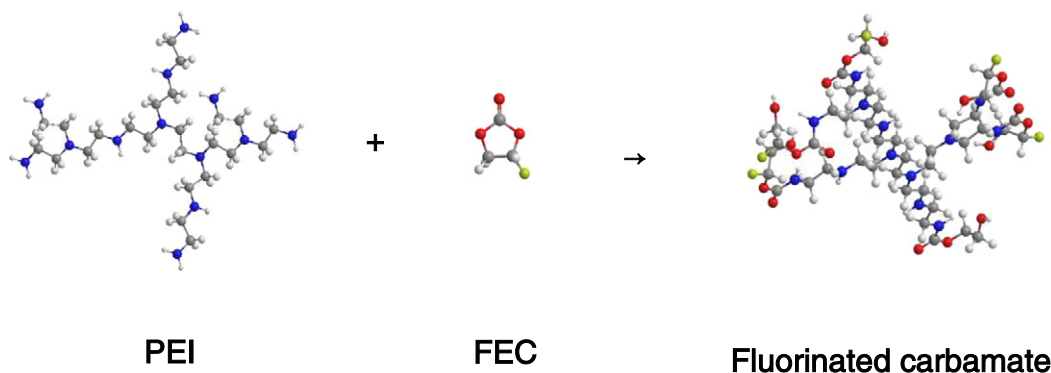


Fig. 2. FT-IR spectra of PEI, FEC, PEGDE and cross-linked polymers obtained from the thermal cross-linking reaction of the PEI, FEC and PEGDE mixture.

an aluminium foil. Its active mass loading corresponded to a capacity of about 2.6 mAh cm⁻². The carbon electrode was prepared in a similar manner by coating an NMP-based slurry of mesocarbon microbeads (MCMB, Osaka gas), PVdF and super-P carbon (88:8:4 by weight) onto

(a) First step



(b) Second step

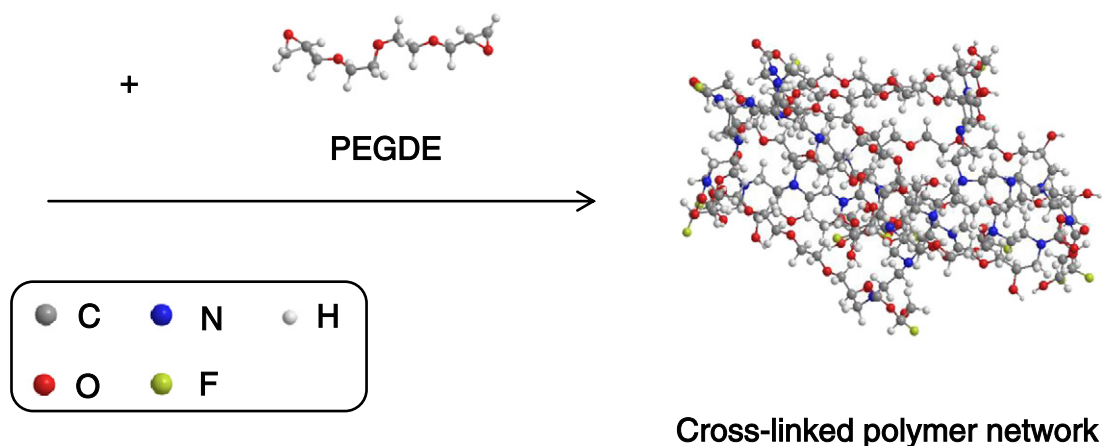


Fig. 1. Reaction scheme for synthesis of a cross-linked polymer network. (a) Fluorinated carbamate synthesised from the reaction between PEI and FEC, and (b) cross-linked polymer network obtained by ring-opening reaction between fluorinated carbamate and PEGDE.

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