



# Gel polymer electrolyte based on p(acrylonitrile-maleic anhydride) for lithium ion battery

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## ABSTRACT

A polymer matrix of poly(acrylonitrile-maleic anhydride) (P(AN-MAH)) is used to prepare a novel porous membranes by phase inversion. The membranes are immersed into liquid electrolyte to form gel polymer electrolyte (GPE) used in lithium ion batteries (LIBs). The results indicate that P(AN-MAH) is successfully synthesized and the membrane of P(AN-MAH) copolymer with adding mass ratios of AN:MAH = 4:1 exhibits superior pore structure and better thermal stability compared with that of pure PAN membrane, which endows the corresponding GPE with excellent comprehensive performances: the considerable ionic conductivity ( $3.03 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature), fine compatibility between GPE and electrode, eminent lithium transference number ( $t_{\text{Li}^+} = 0.57$ ), and high enough electrochemical stability potential (up to 5.4 V (vs. Li/Li<sup>+</sup>)). Accordingly, in constant current charging/discharging cycle, the prepared battery for the GPE also presents excellent initial discharge capacity, C-rate and cycling performances.

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## 1. Introduction

With the continuous development of science and technology, lithium ion batteries (LIBs) with high energy density, high working potential, quick charging-discharging advantages are favored by new energy technology and widely used in cell phones, computers, cameras, etc. [1,2]. It is generally known that the LIBs are commonly composed of four parts: cathode, anode, liquid electrolyte and separator, in which electrolyte directly affects the performances of battery [3,4]. The liquid electrolyte is widely used in LIBs because of its low cost, high ionic conductivity and good compatibility with electrodes [5,6]. However, some shortcomings such as liquid leakage, flammability and explosion may bring unsafe factors and cannot be neglected [7–9]. In addition, solid state polymer electrolytes (SPEs) have also been intensively researched because it can not only solve security problems, but also increase the flexibility of design for the cells with unique shape and size [10,11].

Nevertheless, the lower ionic conductivity of SPEs always restrains its development [12,13]. Over recent years, gel polymer electrolytes (GPEs) formed by immobilizing organic liquid electrolyte into polymer matrices, have advantages with high ionic conductivity and well compatibility with electrodes compared to SPEs the to meet application performance in batteries [14–16]. Gel is a special state of matter that holds both the cohesive properties of solids and the diffusive transport properties of liquids, which makes it have outstanding liquid electrolyte retention ability, so GPEs can effectively solve the security problem caused by liquid electrolyte leakage to a certain extent [17,18]. However, when liquid electrolyte is immersed in the polymer matrix, the polymer segment expands to form a single homogeneous gel state, which hinders the movement of ions to a certain extent compared with the liquid electrolyte. Therefore, a lot of research is needed to improve the overall performance of GPEs [19]. Presently, for GPEs, the widely studied polymer matrices include polyethylene oxide (PEO) [20,21], polyacrylonitrile (PAN) [22–24], poly(vinylidene fluoride) (PVDF) [25,26] and poly(methyl methacrylate) (PMMA) [27,28]. Compared with other polymers based GPE, since PAN based GPE system was first studied by Feullade and Perche in 1975s, GPEs with PAN matrix have been extensively studied because of its advantages of good

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chemical and high stability [29,30]. More importantly, in GPE based PAN, cationic or anionic conductors, generally accepts the electrolytic solution [31]. The solvent molecules are intimately wrapped inside the PAN polymer matrix, similar to the liquid electrolyte conducting ion mechanism, so the ionic conductivity is up to  $10^{-3} \text{ S cm}^{-1}$  [32,33]. Additionally, the PAN matrix also can simply form homogeneous membranes and has good mechanical strength. However, the compatibility of GPE based PAN with lithium metal electrode is poor, which is attributed to the interaction of strong polar groups of  $-\text{C}\equiv\text{N}$  in the PAN chains [34]. Besides, the lithium ion transference number of GPE based PAN is not high, so that the corresponding electrochemical performances do not meet the actual needs, which restricts its further development. It is found that the shortcomings of PAN can be overcome by polymerization with other monomers in previous studies [35–38].

The literature survey indicates that maleic anhydride (MAH) containing a five-membered ring with strong negatively charged groups, is a unique co-monomer due to the difficulty of homopolymerization, yet it is not difficult to form copolymers with other monomers [39–42]. Therefore, when MAH is introduced into PAN chains, the negative groups disrupt the interaction between  $-\text{C}\equiv\text{N}$  in PAN, forming a kind of random copolymerization product, and the steric effects of MAH may weaken the electrostatic interaction between polar groups  $-\text{C}\equiv\text{N}$  with lithium metal electrodes to some extent, resulting in good compatibility with lithium electrode [43–45]. In addition, the introduction of MAH can increase the lithium ion transference number. This can be attributed to the strong negatively charged groups may hinder movement of negative ions, resulting in a high effective current for lithium ions. Furthermore, the introduction of MAH also reduce the brittleness of the PAN matrix [46,47]. Through the above overview, AN and MAH are selected to synthesize poly(acrylonitrile-maleic anhydride) (P(AN-MAH)) copolymer. Meanwhile, the performances improvement of P(AN-MAH) based GPE is worth to be expected compared with pure PAN based one.

## 2. Experimental

### 2.1. Materials

*N,N*-dimethylformamide (DMF), Acrylonitrile (AN), maleic anhydride (MAH), 2, 2'-Azobis(2-methylpropionitrile) (AIBN), dimethyl sulfoxide (DMSO), methanol, lithium perchlorate ( $\text{LiClO}_4$ ) and *n*-butanol were purchased from Chengdu Kelong Chemical Reagent Company. Lithium iron phosphate ( $\text{LiFeO}_4$  (LFP)) was obtained from Deyang Weixun Company; Carbon black and LA-132 binder (a polyacrylonitrile copolymer) obtained from Indigo Power Sources, Battery grade. Liquid electrolyte (1 mol/L) with  $\text{LiPF}_6$  in EC/DMC/EMC (ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate, 1/1/1, w/w/w, LBC305–01, battery grade) were supplied by Shenzhen Poxon Company.

### 2.2. Synthesis of P(AN-MAH)

P(AN-MAH) was synthesized by solution polymerization. Before reaction, AN was distilled to remove the aggregation inhibitor. The purified AN and MAH, as two reaction monomers, were added into a solution consisting of DMSO (66.2 ml) and deionized water (8.1 ml) in a three-neck glass reactor. Then 1 wt.% AIBN, as a free-radical initiator, was added into the reactor under stirring at  $60^\circ\text{C}$  and the whole process of polymerization was carried out under continuous  $\text{N}_2$  flow for 2 h. The resulting product was precipitated with methanol, and then washed with acetone to remove other soluble impurities. Finally, the P(AN-MAH) copolymer of white powder was obtained by transferring into a vacuum

oven for 24 h to remove residual solvent. The obtained copolymers of P(AN-MAH) were prepared with different adding mass ratio of AN/MAH = 1/0, 6/1, 4/1, 2/1, and these polymers are marked as P(AN-MAH)-1-0, P(AN-MAH)-6-1, P(AN-MAH)-4-1 and P(AN-MAH)-2-1, respectively. Scheme 1 is shown the ideal synthetic route of P(AN-MAH) polymers.

### 2.3. Preparation of GPE based on P(AN-MAH)

P(AN-MAH) membranes were prepared by phase inversion, and the principle is shown in Scheme 2. P(AN-MAH) (200 mg) was dissolved in DMF (1.89 ml) to obtain a homogeneous solution at  $60^\circ\text{C}$  under vigorously stirred for 30 min. The non-woven fabric as supporting skeleton was firstly paved on a glass plate coated, and then the solution was evenly poured onto non-woven fabric. The glass plate coated was slowly immersed into deionized water, and after more than ten seconds one kind of white membrane appeared on glass. The membrane was taken off and then dried in the electric blast oven at  $60^\circ\text{C}$  for 2 h. At last, the resulting membrane was dried in a vacuum oven for 12 h and punched into circular pieces (diameter: 19 mm). Finally, the pieces were transferred into the glove box (Ar atmosphere, both  $\text{H}_2\text{O}$  and  $\text{O}_2$  content < 1 ppm), and immersed in liquid electrolyte for 30 min to obtain GPEs. The GPEs are named as GPE-1-0 GPE-6-1, GPE-4-1 and GPE-2-1, respectively.

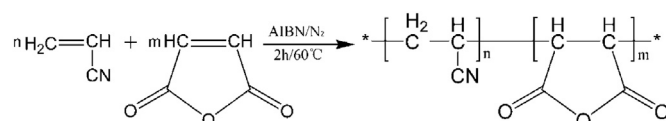
### 2.4. Preparation of electrode

The preparation of cathode round piece was carried out by mixing 85 wt.% LFP powder, 10 wt.% carbon black, and 5 wt.% LA-132 binder with a mortar and pestle to form a slurry. The slurry was evenly coated on aluminum foil, using a 50 mm depth scraper and dried at room temperature. Then the prepared cathode further dried in an electric blast oven at  $60^\circ\text{C}$  for 2 h. Last, the resulting cathode pieces, punched into small circular (diameter: 14 mm, mass loading of LFP:  $2.8 \text{ mg/cm}^2$ ), were dried in a vacuum oven at  $70^\circ\text{C}$  for 24 h and weighed for storage.

### 2.5. Methods of characterization

Fourier transform infrared spectroscopy (FTIR) spectra were recorded by the Perkin Elmer FTIR spectrometer in the wavenumber range of  $400\text{--}4000 \text{ cm}^{-1}$  with a nominal resolution of  $2 \text{ cm}^{-1}$ , which is measured by absorption spectrum. The thermal stabilities of copolymer were obtained by measuring thermogravimetric analysis (TGA, Mettler-Toledo SDTA851e) under  $\text{N}_2$  atmosphere from room temperature to  $500^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ . The microscopic morphology of porous membranes was observed by scanning electron microscopy (SEM, ZEISS EVO MA15). Before testing SEM, the gold was plated on all samples.

The liquid electrolyte uptake ( $\eta$ ) of porous membranes was tested as follows. The dry membranes after weighing were immersed in an electrolyte of 1 mol/L  $\text{LiClO}_4$  to activate for 1 h, and then the surface liquid was blotted dry by filter paper, weigh again. The liquid electrolyte uptake ( $\eta$ ) of membranes was calculated by Eq. (1):



Scheme 1. Synthetic reaction principle of P(AN-MAH) copolymer.

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