



## Gel polymer electrolytes for lithium ion batteries: Fabrication, characterization and performance

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### ABSTRACT

Gel polymer electrolytes (GPEs) with characteristics of both solid and liquid electrolytes have received increasing attentions. Several polymer matrices have been employed as hosts for GPEs in order to investigate their possible applications in lithium ion batteries (LIBs). Herein, we review some crucial physico-chemical and electrochemical properties of GPEs for LIBs as well as the characterization techniques for their evaluation. Then, the different preparation and modification methods of GPEs are summarized. Meanwhile, the effects of preparation on the performance of electrolytes are discussed. Finally, future directions of GPEs are pointed out.

### 1. Introduction

Owing to the advantageous performance, lithium ion batteries (LIBs) commercialized by Sony Corporation in 1991 have gained a dominant position in the market of energy storage for portable devices as well as implantable medical applications, and meanwhile show better application prospects in large-scale electrochemical energy storage applications which are crucial for the development of electric vehicle (EV) systems and carbon-free clean energy (solar, wind, wave, geothermal energy, etc.) in smart grids [1–6]. However, intrinsic security issues for commercial LIBs (Fig. 1) related to organic liquid electrolytes (lithium salts dissolve into organic liquid carbonate solvents) and polyolefin microporous separators must be confronted with [7]. When overheated due to overcharging, abuse, internal short-circuit, manufacturing defects, physical damage, or other failure mechanisms, the organic liquid solutions in LIBs generate highly flammable plumes including CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and so on which will directly cause catastrophic thermal accidents of LIBs [8]. Along with extensive applications of large capacity LIB modules in EVs and smart grids, the quest for safer and more reliable electrolyte systems is therefore urgent. So polymer electrolytes (PEs), inorganic lithium ion conductors (ILICs) and ionic liquids (ILs) have been extensively explored for LIB systems in order to substitute the conventional flammable organic liquid electrolytes, and their development is still in progress [9–11].

Since Armand proposed the first PEO/Li<sup>+</sup> solid polymer electrolyte (SPE) system ( $\sim 10^{-5}$  S cm<sup>-1</sup> at 40–60 °C) for lithium batteries in 1978 [12], polymer electrolytes have attracted widespread attentions due to the superior features such as free standing, shape versatility, security, flexibility, lightweight, reliability and so on [13–18]. Though safety and reliability are improved greatly, the wide range applications of SPEs in commercial LIBs still have a long way to go owing to the low ionic conductivity (mostly ranging from 10<sup>-8</sup> to 10<sup>-5</sup> S cm<sup>-1</sup> at ambient temperature). To improve the ionic conductivity of PEs, the most effective approach is to add low molecular weight plasticizers/organic liquid electrolytes to form a gel polymer electrolyte. The phenomenon of gelation can lower the ambient-temperature region of operations and also increase the amorphous phase of the polymer host. And the ionic conductivity of gel PEs can be improved greatly to the same level of liquid electrolytes for LIBs. The research on gel polymer electrolytes (GPEs) for lithium batteries started when Feuillade and Perch prepared a plasticized PAN with an aprotic solution containing an alkali metal salt in 1975 [19]. In 1994, Bellcore (now Telcordia) firstly reported coke/GPE/LiMn<sub>2</sub>O<sub>4</sub> LIBs, whose electrolytes consisted of P(VDF-HFP) copolymer matrix gelled by a solution of LiPF<sub>6</sub> in EC/DMC [20]. Recently, the development of GPEs has been very rapid.

From a practical point of view, GPEs for LIBs should satisfy certain performance requirements including high ionic conductivity, appreciable Li<sup>+</sup> ion transference number, excellent chemical stability, good thermal stability, wide electrochemical stability window and good

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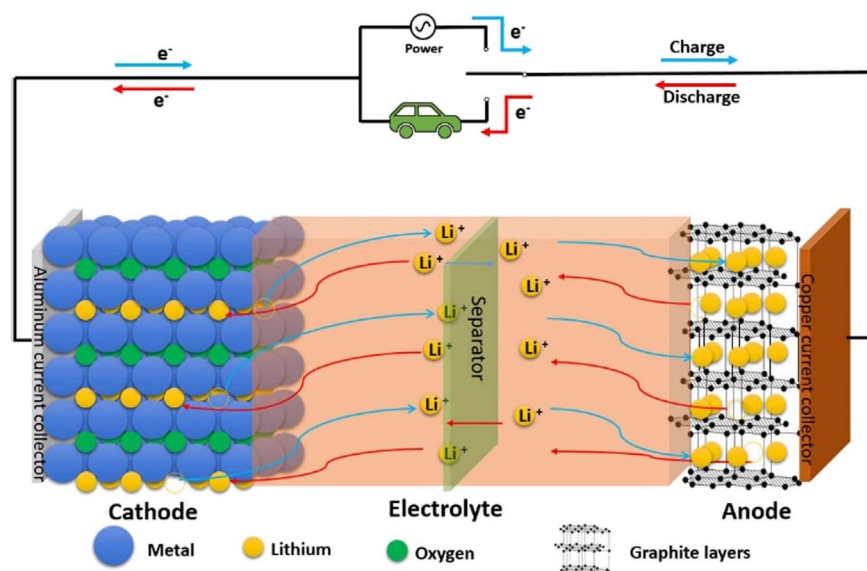


Fig. 1. Schematic of the working mechanism of a lithium-ion battery.

mechanical performance. Till now, numerous GPE systems (Table 1) have been developed and characterized in order to realize their future applications. However, the deterioration of mechanical strength caused by the incorporation of organic liquid electrolyte into the polymer matrix and high cost currently limit wide applications of GPEs in LIBs [21].

In this review, we initially discuss the critical physico-chemical and electrochemical properties of GPEs as well as the characterization techniques for their evaluation. Then, the different preparation and modification methods of GPEs are summarized. Meanwhile, the effects of preparation on the performance of electrolytes are also discussed. Some future research directions are pointed out in the end.

## 2. Physico-chemical and electrochemical properties of GPEs

Some crucial physico-chemical and electrochemical properties of GPEs are discussed in this section. Meanwhile, characterization techniques or detection methods for their evaluation are introduced.

### 2.1. Physico-chemical properties

#### 2.1.1. Chemical structure identification

In order to verify whether the ideal polymer electrolyte is fabricated successfully, chemical structure identification of synthetic polymer electrolyte is necessary. The common techniques include X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, mass spectrometry, nuclear magnetic resonance spectroscopy (NMR) and so on.

XRD is a versatile, non-destructive analytical technique. It is always used to determine the crystallinity of a prepared polymer and to identify the amorphous phase in a polymer membrane. Crystallinity in a polymer or amorphous phase in a polymer membrane will affect the ionic conductivity and mechanical strength of the prepared GPE. Fig. 2a shows the X-ray diffraction pattern of HEC and modified HEC-based polymer [66]. Shown as XRD pattern (Fig. 2a), the wide peak at  $2\theta = 20^\circ$  shows that HEC is semi-crystalline. After the addition of a plasticizer, the diffraction peaks of gelled polymer membrane are wider compared to the bare HEC sample. It indicates the GPE is more amorphous than the HEC sample. The addition of Li salt does not affect the structure of HEC, which suggests that Li salt is completely dissolved in the polymer.

The types of chemical bonds and functional groups in a polymer can be ascertained by FT-IR and Raman spectroscopy [65,67]. Zhou et al.

reported a hierarchical poly (ionic liquid)-based solid electrolyte (HPILSE) for high-safety Li-ion and Na-ion batteries [68]. This hybrid solid electrolyte is fabricated via in situ polymerizing C1-4TFSI monomers in EMITFSI-based electrolyte which is filled in PDDATFSI porous membrane. FT-IR spectroscopy was employed to verify the polymerization of C1-4TFSI monomers in the presence of EMITFSI-based electrolyte and PDDATFSI porous membrane (Fig. 2b). The FT-IR indicates that C1-4TFSI monomers have been successfully polymerized inside EMITFSI-based electrolyte which is absorbed in the PDDATFSI porous membrane, and therefore giving rise to the formation of HPILSE.

The association of  $\text{Li}^+$ -DEC/DMC complexes with the PEO, PPO chains was confirmed by Lu et al. using a Raman spectrometer (Fig. 2c) [67]. The Raman measurement (HORIBA LabRAM HR800) resolution was  $4\text{ cm}^{-1}$  and the Lorentzian function was used to analyze the  $600\text{--}1000\text{ cm}^{-1}$  bands into constituting peaks.

NMR spectroscopy including  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^7\text{B}$  NMR and  $^{31}\text{P}$  NMR has become the preeminent technique for determining the structures of organic macromolecules. The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule and its individual functional groups. NMR can provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules [69,70]. Shown in Fig. 2d,  $^1\text{H}$  NMR was used by Zhou et al. to analyze the structure of the prepared polymer (PDDATFSI) [68]. The  $^1\text{H}$  NMR spectrum using d-acetone as a solvent with a Bruker DRX-500 NMR spectrometer indicates that the purity of prepared PDDATFSI is  $> 99\%$ .

#### 2.1.2. Morphology

The morphology of surface and cross section of the prepared polymer membrane decides directly the performance of GPE. By observing the morphology of the surface and cross section with scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) or transmission electron microscopy (TEM), non-porous or porous polymer membranes can be confirmed. Furthermore, the shapes, structures and sizes of the pores in the membranes can also be detected [63]. Owing to poor electron conductivity, the polymer membrane should be sputtered with gold prior to the morphology measurements. The membranes are dipped into liquid nitrogen and broken into two parts, subsequently the SEM micrographs of the cross-sections are collected.

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