



Polyvinyl formal based gel polymer electrolyte prepared using initiator free in-situ thermal polymerization method



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HIGHLIGHTS

- A novel polyvinyl formal (PVFM) based gel polymer electrolyte (GPE) was prepared via in-situ thermal polymerization.
- It is the first time to report the PVFM based electrolyte for Li-ion batteries.
- Its conductivity at ambient temperature is $\sim 10^{-3}$ S cm⁻¹.
- Its electrochemical stability window is 1.5–5 V vs. Li/Li⁺.
- The polymerization mechanism is investigated by FTIR analysis.

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ABSTRACT

Novel polyvinyl formal (PVFM) based gel polymer electrolytes (GPEs) are developed using an initiator free thermal polymerization method. The polymerization mechanism during the cross-linking process is investigated by means of Fourier transform infrared (FTIR) spectroscopy measurements. With the prepared GPEs (containing 2 to 5 wt % PVFM), Li polymer batteries with LiFePO₄ as the cathode are assembled, and the electrochemical properties such as interfacial impedance, electrochemical stability window and cycling performance are evaluated. The resulting PVFM based GPEs present a better thermal stability compared with the corresponding conventional liquid electrolyte and an acceptable conductivity of $\sim 10^{-3}$ S cm⁻¹ at ambient temperatures. Cyclic voltammetric (CV) curves reveal that the electrochemical stability window of PVFM based GPE is 1.5–5V vs. Li/Li⁺ and wider than that for the corresponding liquid electrolyte which is 1.8–4.4 V. The discharge capacity of the polymer Li/LiFePO₄ battery is 145 mAh g⁻¹ over a voltage range of 2.5–4.25 V at 1/10 C rate after 80 cycles with a small capacity fade.

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1. Introduction

Safety issues in a lithium-ion battery using a liquid electrolyte, arising from leakage and potential combustion of organic liquids, are of primary concern in their practical applications especially in hybrid electric vehicles (HEVs) and plug-in hybrids (PHEVs) [1,2]. In the past decades, many safer alternatives to liquid electrolytes have been investigated, and gel polymer electrolytes (GPEs), which possess both cohesive properties of a solid electrolyte and diffusive properties of a liquid electrolyte, have been attracting increasing attention [3–9]. The present GPEs for lithium-ion batteries

reported are usually based on the polymer matrix as specified in the following list: poly (ethylene oxide) (PEO), poly (vinylidene fluoride)-hexafluoropropylene (PVdF-HFP), polyacrylonitrile (PAN), poly (methyl methacrylate) (PMMA), and polyvinyl chloride (PVC) [10]. Despite offering safer and flexible packaging alternatives to liquid electrolytes, the present GPEs are plagued with various problems. For example, the PEO based electrolytes offer low ionic conductivity; PAN based electrolytes, although exhibiting a relatively high conductivity and a wide electrochemical stability window, are known to readily passivate upon contact with the lithium metal anode; and the plasticized PMMA based electrolytes show poor mechanical strength [11]. The high dielectric constant of the P (VdF-HFP) polymers and the presence of electron withdrawing fluorine atoms are advantageous factors for dissociating lithium salts to form lithium ions in the redox reactions, however, the formation of stable LiF and >C=CF– unsaturated bonds may not

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only deteriorate the battery performance but also raise safety concerns due to thermal runaway arising from the highly exothermic reactions [12]. In order to overcome these problems, several new kinds of polymer gels are being considered in the field of GPEs.

Polyvinyl acetal based GPEs have been extensively studied for use in nickel-metal hydride batteries [13,14]; the presence of –OH groups are considered as the source of hydrogen bonding which assist in the formation of the polymer gel [15]. Polyvinyl acetal has been used as a suitable polymer matrix in lithium-ion batteries because of high conductivity, unique film-forming properties, and in particular, excellent adhesion on many surfaces [16–18]. In previous studies, polyvinyl acetal based GPEs are usually reported to be formed by a solution casting method, in which polymers are dissolved in a dilute solvent to form a film by volatilization. The low-boiling solvent in the electrolytic solution could volatilize easily from the dilute solvent, leading to difficulty for achieving good ionic conductivity.

Inoue et al. [19] have proposed the use of suitable side groups to build up polymeric networks or molecules with interesting properties. In this study, PVFM with tri-functional groups (vinyl formal, vinyl hydroxyl and vinyl acetate) is chosen as the matrix, as they are expected to form stable polymeric electrolytes with high mechanical strength, good flexibility, and high conductivity. The basic chemical structure of PVFM is shown in Fig. 1. The C=O bond in the side chains of PVFM can interact with the oxygen atoms in plasticizers and thus exhibit good compatibility with the electrolyte solution. As reported by Saito et al. [20], the –OH group is a strong Lewis base thus attracting lithium ions, thereby affecting the cation mobility in a manner similar to that of the oxygen sites in ether in polyethylene oxide (PEO).

According to previous studies [21,22], chemical cross-linking is a dominant method in forming an irreversible gel. The exact details depend upon the use of cross-linking agents and initiators, however, the by-products generated from the initiators, such as oxygen, nitrogen and other reactive radicals may degrade the performance of the lithium polymer batteries. Furthermore, most gel electrolytes show poor wettability for electrodes and poor penetration because of their high viscosity and incomplete formation. In this work, the PVFM based GPE was synthesized by thermal polymerization of a mixed solution of PVFM and a LiPF₆ based liquid electrolyte, without the use of any thermal initiator. The gelling process is shown in Fig. 2. The in-situ thermal polymerization can help improve the interfacial contact between the electrolyte and the electrode through direct transformation from a liquid precursor solution filling the porous electrode to a gel. Thus, gel formation by in-situ cross-linking reaction at a low temperature without using a polymerization initiator should be considered as an important breakthrough for the preparation of GPEs.

2. Experimental

2.1. Preparation of gel polymer electrolytes

Polyvinyl formal (PVFM) with a molecular weight of 70,000 was obtained from Johnson Controls. A weakly polar CO group is rigidly

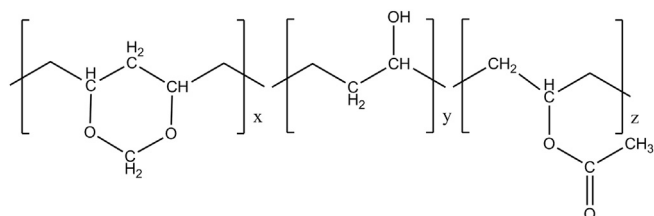


Fig. 1. Molecular structure of polyvinyl formal.

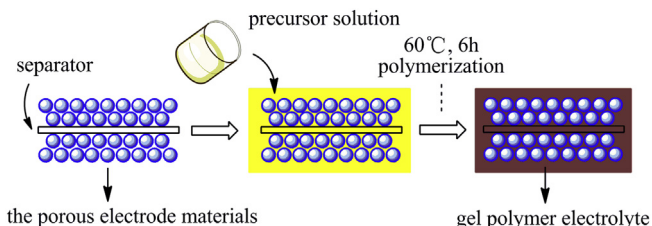


Fig. 2. Schematic diagram depicting transformation from liquid into a gel electrolyte.

attached to the non-polar main chain as shown in Fig. 1. The percentage of ether linkages and hydroxyl groups are both vital parameters for determining the solubility of PVFM in organic solvents on one hand and the extent of polymerization on the other. The molar percentages of vinyl acetal, vinyl hydroxyl and vinyl acetate groups used are 62.3%, 10.5%, and 27.2%, respectively while the degree of acetalization is 92.2%.

For the preparation of the GPEs, PVFM was used without any further purification. Liquid electrolyte consisting of 1M LiPF₆ dissolved in the solvent ethylene carbonate (EC): dimethyl carbonate (DMC) = 3:7 (V/V) was purchased from Beijing Institute of Chemical Reagent. The precursor solution was prepared by dissolving a certain selected amount (2%, 3%, 4% or 5% by weight) of PVFM in the liquid electrolyte. According to the Hansen solubility parameters, PVFM can be dissolved in EC: DMC = 3:7 (V/V) mixture solvent to form a homogenous solution. After stirring in an argon filled glove box for about 30 min, the solution mixture was placed in a sealed container and transferred into a thermostat maintained at 60 °C where it was held for 6 h in order to carry out the cross-linking reaction of polyvinyl formal. Finally, the GPEs were formed which were found to be effective for tethering liquid components and binding the battery parts, such as the separator and the porous electrodes.

2.2. Electrode preparation and battery assembly

For the electrochemical studies, LiFePO₄ based cathode plates were prepared by coating a slurry consisting of LiFePO₄, acetylene black and poly(vinylidene fluoride) (PVdF) in N-methyl pyrrolidone (NMP) as the binder in the ratio of 80:15:5 by weight, on an aluminum foil by the doctor blade process. The thickness of the electrode ranged from 40 to 50 μm after doctor blade coating, followed by mechanical pressing. A number of 2032-type coin cells Li/LiFePO₄ were assembled with tri-layer PP/PE/PP (Ube) as the separator and precursor solutions with different content of PVFM prepared as described in Section 2.1. The batteries were then placed in the thermostat at 60 °C for 6 h to achieve polymerization. For comparison, a liquid electrolyte based coin cell was also assembled. All the batteries were assembled in a glove box filled with Ar, and O₂ and H₂O < 0.5ppm.

2.3. Measurements

The conductivity of GPEs was measured by a conductivity meter (Shanghai Leici, DDSJ-308A, China). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were collected through a NETZSCH STA449F3 analyzer (Germany) from room temperature to 400 °C at a heating rate of 10 °C min⁻¹ in argon atmosphere. FTIR spectra were recorded on NEXUS FT-IR670 spectrometer (USA) in the range of 400–4000 cm⁻¹.

The electrochemical stability windows of the electrolytes were measured by means of cyclic voltammetry (CV) on an electrochemical work station (Chi660a, Shanghai, China) equipped with a

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