The improvement effect of LiF on stability of Li anode in PVDF-HFP gel polymer electrolyte

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Abstract. The porous composite polymer membranes, based on poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) polymer matrix and lithium fluoride (LiF) inorganic additive, were prepared by phase inversion method and gel polymer electrolytes (GPEs) were obtained by immersing membranes into liquid electrolyte. GPEs containing LiF additive exhibited a high ionic conductivity of $1.10 \times 10^{-3}$ S cm$^{-1}$ and a high lithium ion transference number of 0.65 because of the lower crystallinity degree of GPEs. Moreover, we disclosed distinct merits including enhanced migration of Li$^+$ and suppressed Li-ion concentration gradient in GPE near the surface of Li electrode. These merits ameliorated electrochemical performance of Li metal anode by retarding Li dendrite. LiF-GPEs effectively improved the cyclability and rate performance of symmetrical Li cells in a wide current densities rage. Pairing with LiFePO$_4$ cathode, full cells containing LiF-GPEs showed excellent rate performance and cycling stability. This work effectively demonstrates that LiF-GPEs could suppress lithium dendrite by boosting electrochemical characters of mass transfer, and kinetic parameters.

1. Introduction

Lithium-ion batteries (LIBs) have achieved impressive success in market of digital electronics and electric vehicles [1]. However, LIBs lag behind the current practical demands because of the limitation of theoretical energy density [2]. Lithium metal anode is considered as an ideal anode for next-generation batteries due to its ultra-high specific capacity (3860 mAh/g) and the lowest redox potential (-3.04 V vs standard hydrogen electrode) [3]. Despite the impressive advantages, lithium metal anode confronts a troublesome issue of Li dendrites/dead Li formation during the charging/discharging process, which may cause inner short circuit even explosion in battery operation [4].

Although liquid electrolytes were extensively employed in Li metal batteries due to their high ionic conductivity, they are still confronted with flammability and safety hazard [5]. Replacing liquid electrolyte with solid polymer electrolytes (SPEs) is an effective strategy to solve the safety problem [6]. However, the low ionic conductivity and high interfacial resistance of SPEs at room temperature hinder their commercial application. Alternatively, gel polymer electrolytes (GPEs) are equipped with advantages of both liquid electrolyte and SPEs. GPEs are reported with merits of high ionic conductivity, high transference number of Li ion, and low interfacial resistance [7].
conductivity, high mechanical strength, low interfacial resistance and reliable safety [7]. Various polymers have been selected as matrix for GPEs, which include poly(ethylene oxide) PEO [8], poly(methyl methacrylate) PMMA [9] and poly(vinylidene fluoride-hexafluoropropylene) PVDF-HFP [10]. Specifically, PVDF-HFP has absorbed extensive attention because of chemical stability and high ionic conductivity. Until now, amounts of investigations have also employed additives, such as SiO$_2$ [11], Al$_2$O$_3$ [12], to further improve the ionic conductivity and mechanical properties of GPEs. However, the ionic conductivity is not closely related to the formation of Li dendrites in theory. In fact, the Li-ion mass transfer in electrolyte is first step of the whole formation process of Li dendrites. Previous researches have revealed the relationship between formation of Li dendrites and lithium ion transference number in liquid electrolyte [13], but the lithium ion transference number influenced by inorganic additives is rarely investigated in GPEs. The relationship between Li dendrites inhibition effect and lithium ion transference number is also need to be explored.

Recently, lithium fluoride (LiF) has attracted special attention due to the proved benefit for Li dendrites suppression [2]. In addition, LiF, as an essential SEI component, has wide electrochemical stability, good lithium conductivity and high shear modulus [14].

Herein, we introduced LiF into PVDF-HFP polymer matrix to fabricate a free-standing composite membrane by phase inversion method, and GPEs was obtained by soaking membranes with liquid electrolyte, named PF0 GPE and PF2 GPE, respectively. We investigated physical and electrochemical properties of GPEs. On this basis, we discussed the relationship between lithium ion transference number and the formation of Li dendrites in GPEs. Furthermore, LiF was investigated for suppressing Li dendrites. In this work, it was proved possessing high ion conductivity (1.10 $\times$ 10$^{-3}$ S cm$^{-1}$), improved lithium ion transference number (0.65) and wide electrochemical window. Symmetrical cells, Li/PF2 GPE/Li, showed a stable interface and compatibility. LiFePO$_4$/PF2 GPE/Li full cells also exhibited excellent rate performance and cycling stability.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP; $M_w \approx 400,000$) was purchased from Sigma-Aldrich. Lithium fluoride (LiF; 99.99%) was obtained from Shanghai Macklin Biochemical Co., Ltd. Acetone was obtained from Beijing Tongguang Co., Ltd. Li foils were provided by China Energy Lithium Co., Ltd. Cu foils and stainless-steel discs were purchased from Shenzhen Kejing Star Technology Co., Ltd. The liquid electrolyte of 1 M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1, volume ratio) was obtained from Suzhou DoDoChem Technology Co., Ltd. The deionized (DI) water is made by Milli-Q system in our lab. All of reagents were used as received.

2.2. Preparation of gel polymer electrolyte

The phase inversion method was used to prepare different samples in this investigation [15]. Under mechanical stirring, 0.48 g PVDF-HFP was dissolved in 5 mL acetone to form transparent solution. After that, 0.4 mL deionized water and LiF (0 wt.%, 2 wt.%) was added into above solution. The obtained solution was cast on a clean glass plate using a doctor blade. After evaporating 2 h under ambient temperature, two types of membrane samples were transferred in a vacuum oven at 60 °C for 12 h to remove residual water and acetone completely. Finally, the white and opaque membranes were punched into disks. The thickness of obtained membranes are 60 ~ 85 μm. Then these two types of samples were activated by immersing in the liquid electrolyte of 1 M LiPF$_6$ in EC/DEC (1/1, volume ratio) for 12 h to obtain GPEs into glove box.

2.3. Characterization of materials

The surface morphology of polymer membrane was analyzed with scanning electron microscope (JSM-6400, JEOL, Japan). X-ray diffraction (XRD) patterns of polymer membranes were conducted by an X-ray diffractometer (Rigaku Ultima IV, Rigaku, Japan) to characterize the crystalline structure
at a scanning rate of 8° min⁻¹ in the 2θ range of 10-90°. The Young’s modulus was measured by Atomic force microscopy (AFM) (Bruker Multimode 8 with a Nanoscope V controller) to evaluate the mechanical property of membrane. Thermo-gravimetric analysis (TGA) of polymer membranes was carried out by a TGA with the heating rate of 10 °C min⁻¹ from 50 °C to 800 °C in nitrogen atmosphere.

The electrochemical window of GPEs was analyzed via linear sweep voltammetry (LSV) with a potential range from -1 V to 6 V and a scan rate of 1 mV s⁻¹ in a stainless-steel (SS)/GPEs/Li cell. SS was functioned as working electrode, Li metal as reference and counter electrodes.

The ionic conductivities ($\sigma$) of GPEs were calculated by equation (1):

$$\sigma = \frac{d}{S \times R_b}$$

Where $S$ is the area of stainless-steel, $d$ is the thickness of GPEs, and $R_b$ is the bulk resistance of GPEs.

The Li⁺ transference number ($t_{Li^+}$) was measured by equation (2):

$$t_{Li^+} = \frac{I_0(\Delta V - I_0R_0)}{I_0(\Delta V - I_sR_s)}$$

where $I_0$ and $I_s$ are the initial and steady currents, respectively; $R_0$ and $R_s$ are the initial and steady interfacial resistances respectively between GPE and Li electrode, and $\Delta V$ corresponds to polarization potential.

In order to obtain the Li metal plating/stripping cycling performance, the charge and discharge time of Li/Li were 1 h (0.1 mA cm⁻², 0.1 mAh cm⁻²). The charge-discharge and cycle behavior of assembled coin cell LiFePO₄/GPE/Li under different current density conditions (that is C-rate) were tested by battery cycle testing system (Wuhan LAND, China) between 2.5 V to 4.2 V. The cathode was prepared by mixing LiFePO₄ powder, acetylene black, and PVDF in weight ratio of 8:1:1 in N-methyl pyrrolidone (NMP) solvent. The obtained slurry was coated on aluminum (Al) foil and dried in vacuum at 80 °C for 24 h. Then the coated Al foils were punched into electrode disks and mass loading of LiFePO₄ cathode was about 2.5 mg cm⁻². The rate performance of cells was measured from 0.04, 0.2, 0.4, 0.8 to 2 mA cm⁻² and cycling stability at 0.04 mA cm⁻².

3. Results and discussion

3.1. Physical properties of membrane

As shown in Figure 1a and 1b, the surface of PF0 and PF2 membranes were observed by SEM. Both of them have a large amount of large pores with the size between 5 to10 μm and small pores with the size about 1 μm distributed evenly. These pores are beneficial for absorbing and retaining sufficient liquid electrolyte. However, the growth of dendrites can easily penetrate the GPEs through large pores thus cause inner short circuit. Compared with PF0, PF2 could effectively inhibit Li dendrites penetration due to the high mechanical strength with LiF [14]. We tested the Young’s modulus of two membrane samples to characterize mechanical property. As shown in Figure 2c and 2d, the Young’s modulus of pristine PVDF-HFP (PF0) and composite PVDF-HFP films (PF2) are 2.733 GPa and 7.825 GPa, respectively, indicating that composite film with LiF has higher mechanical strength suppressing the penetration of Li dendrites [16].
Figure 1. The SEM images of polymer membrane surface (a) PF0; (b) PF2. Young’s modulus mapping of membranes. (c) PF0; (d) PF2.

Figure 2a shows the X-ray diffraction (XRD) patterns of pristine PVDF-HFP and PVDF-HFP/LiF membranes. Obviously, four characteristic diffraction peaks are found at $2\theta = 18.5^\circ$, $20.2^\circ$, $27.2^\circ$, and $39.1^\circ$, which refer to (020), (110), (021), and (131) planes of PVDF-HFP. After introducing LiF into PVDF-HFP, the similar diffraction peaks become broader and weaker, indicating the crystallinity reducing of PVDF-HFP caused by LiF.

Figure 2. (a) XRD patterns; (b) TGA profiles of PF0 and PF2 membranes.

The thermal stability of polymer membranes was studied by thermo-gravimetric analysis (TGA), which is a crucial factor for application in batteries. As shown in figure 2b, the weight of PF0 and PF2 polymer membranes both retain until 420 ℃. In addition, LiF has little effect on the thermal stability of polymer indicating both polymers are thermal stable enough when working in practical batteries.

3.2. Electrochemical properties of GPE

The electrochemical windows of GPEs were measured by conducting linear sweep voltammetry (LSV) test. According to Figure 3a, PF2 GPE exhibits excellent electrochemical stability up to 5.0 V, while the value of PF0 GPE is about 4.9 V. The addition of LiF has slight effect on the electrochemical stability of GPEs, which should be attributed to the electrochemical stability of LiF [17].
Figure 3. (a) Linear sweep voltammetry of PF0 GPEs and PF2 GPEs between lithium metal and stainless-steel (b) AC impedance spectra of SS/GPEs/SS cells

Ionic conductivity is another key character of GPEs, which describes the speed of ion transport in GPEs. The EIS curves of SS/GPE/SS cells with PF0 and PF2 GPE at room temperature are displayed in Figure 3b. The bulk resistance ($R_b$) values are 3.86 Ω and 4.40 Ω for PF2 and PF0, respectively. Obviously, $R_b$ of PF2 GPE is reduced compared with PF0 GPE. According to equation (1), the ionic conductivity of PF2 GPE was calculated showing $1.10 \times 10^{-3}$ S cm$^{-1}$, which is significantly larger than that of PF0 GPE ($0.59 \times 10^{-3}$ S cm$^{-1}$). This enhancement in ionic conductivity of PF2 GPE could be attributed to the introduction of LiF which reduces the crystalline region of polymer. Therefore, lithium ions migrate faster in the amorphous area compared with moving along the polymer chain segment motion [18].

The lithium ion transference number ($t_{Li^+}$), was determined using chronoamperometry and AC impedance in Li/GPE/Li cells (figure 4). According to equation (2), the calculated lithium ion transference number ($t_{Li^+}$) of PF2 GPE is 0.65, which is obviously higher than that of PF0 GPE (0.42). According to the following equation (3) [19]:

$$i = i_m + i_d$$

Where $i$, $i_m$ and $i_d$ are total mass transfer current, migration current and diffusion current, respectively. Total mass transfer current includes the migration current and the diffusion current. High lithium ion transference number of PF2 GPE indicates that the proportion of the diffusion current in the total mass transfer current decreases. The lower ration of diffusion/migration current in total mass transfer current will decrease the concentration gradient in electrolyte near the surface of lithium electrode because the concentration gradient is micro-geometry related features according to the results of previous reports [20]. In other words, the lower ratio of diffusion/migration current in total mass transfer in electrolyte near the lithium will help to mitigate the adverse effects of surface micro-geometry irregularities. Concentration gradient of lithium ion in electrolyte near the surface of lithium electrode can be described by the following equation (4) [21]:

$$C_s = C_0 - \frac{2j(1-t_{Li^+})}{nF\pi D_{Li^+}} \sqrt{t}$$  

Where $C_s$, $C_0$, $t_{Li^+}$ and $D_{Li^+}$ are the surface concentration, bulk concentration, Li$^+$ transference number and Li$^+$ diffusion coefficient, respectively. $j$ is the employed polarization current density, and $t$ is the polarization time. According to equation (4), the concentration gradient is easier to form in PF0 electrolyte than PF2 electrolyte. Brissot demonstrated that formation of lithium dendrites is induced by the high concentration gradient of lithium ions at the surface of lithium electrode (that or called as, “space charge layer”) [13]. According to the relationship between space charge layer and the formation of dendrites, the microscopic bumps on the surface of lithium metal are the locations where dendrites grow rapidly. It is reasonable that more dendrites formed in PF0 GPE as SEM images shown in Figure 7. Based on above mentioned results, we suggest that improving of lithium ion transference...
number can decrease the effect of concentration gradient of lithium ions in electrolyte near the surface of lithium electrode and inhibit the formation of Li dendrites. The improved performance of PF2 GPE can be ascribed to increased amorphous regions of polymer chains with LiF introducing, which reduce the effect of polymer chains on Li$^+$ and promote the ratio of Li$^+$ migration [22].

3.3. Batteries properties

To investigate the electrochemical compatibility of different kinds of GPEs with Li metal, symmetrical Li/Li cells were assembled and measured by galvanostatic charge and discharge with the capacity of 0.1 mAh cm$^{-2}$. Figure 5a shows the cycling performance at the current density of 0.1 mA cm$^{-2}$. The Li/Li using PF0 GPE shows a higher over-potential and unstable interface, which is attributed to the formation of large amount of Li dendrites [22]. However, the cell with PF2 GPE exhibits a more stable voltage profile, which indicates the PF2 GPE improves interfacial compatibility of Li anode, hence more uniform and smoother deposition layer and stable SEI film are achieved.

In order to observe the micro morphology of deposited Li, the Li metal derived from cells assembled with PF0 GPE and PF2 GPE was analyzed by SEM after 50 cycles and SEM images confirm the difference of lithium deposition. Rod-shaped, branched Li dendrites and lumpy, flat deposited Li are observed from disassembled cell with PF0 and PF2 GPE, respectively (Figure 5b and 5c). It could be illustrated by the presence of LiF that improving lithium ion transference number and mechanical strength ultimately affects the morphology of the deposited Li.
In order to evaluate the properties of PF2 GPE in cycling batteries, two kinds of full batteries, LiFePO4/PF0 GPE/Li and LiFePO4/PF2 GPE/Li were investigated. The batteries were tested at a current density of 0.04 mA cm\(^{-2}\). As shown in Figure 6a, the battery employing PF2 GPE presents higher discharge capacity with steady Coulombic efficiency. After 100 cycles, Coulombic efficiency of PF2 full cell, still maintain above 99.8% while PF0 cell reduces to 88%, which demonstrates that interface of PF2/Li is more stable. In addition, capacity retention is increased from 89% to 98% with the introduction of LiF.

![Figure 6. (a) Cycling performance and CE of LFP/GPEs/Li cells at 0.04 mA cm\(^{-2}\); (b) Rate properties of LFP/GPEs/Li cells employing PF0 and PF2 GPEs at different current densities;](image)

4. Conclusions
In this study, we have prepared a PVDF-HFP-based composite membrane using LiF as inorganic additive by phase inversion method and the gel polymer electrolytes (GPEs) were obtained after activating into liquid electrolyte. The PF2 GPEs show high mechanical strength, high ionic conductivity (1.10 \times 10^{-3} \text{ S cm}^{-1}) and high lithium ion transference number (0.65). On the basis of these advantages, LiFePO4/Li behaves excellent rate performance and cycling stability. This study demonstrates that lithium ion transference number is beneficial to adjust the morphology of lithium deposition and avoid the formation of dendrites.

Acknowledgments
This project was supported by the NSFC project (Grant No. 21872007), National Basic Research Program of China (2015CB251100) and special foundation of Tangyin New Energy Group, JinCheng City, Shanxi Province, China.

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