# Characterization of fibrous gel polymer electrolyte for lithium polymer batteries with enhanced electrochemical properties

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A B S T R A C T

This study highlights physical properties that are associated with the electrochemical properties of lithium batteries. Although the electrochemical properties of electrospun gel polymer electrolytes (GPEs) have been studied and understood in great detail, the physical properties of GPEs, such as ion interaction and phase transformation, have largely been ignored. A nano-fibrous poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) polymer matrix for GPEs was prepared by electrospinning. The ionic conductivity of the GPE was approximately $2.7 \times 10^{-3}$ S cm$^{-1}$ at 30 °C. The phase transition of the PVdF-HFP matrix as well as interaction between solvent or cation and polymer matrix or anion was investigated by Raman spectroscopy. Interaction between PF$_6^-$ anion and PVdF-HFP matrix and phase transformation of the polymer matrix were confirmed. The LiFePO$_4$/GPE/Li cell showed high discharge capacities of 134.6 mAh g$^{-1}$, 131.3 mAh g$^{-1}$, and 113.5 mAh g$^{-1}$ at high current densities of 1 C, 2 C, and 3 C, respectively. Moreover, this cell exhibited excellent cycle stability with high capacity retention. In particular, this nano-fibrous GPE is suitable for application in polymer batteries and is promising as a polymer electrolyte for scaled-up lithium batteries.

## 1. Introduction

The lithium secondary battery is promising for mobile energy storage and is currently utilized in a wide range of devices, from small-sized electronic devices like cell-phones, laptops, and cameras to hybrid electric vehicles (HEVs). In addition, zero-emission, full-electric vehicles (EVs) are expected to be a commercial reality in the near future. This widespread applicability of lithium secondary batteries encourages battery technology breakthroughs aimed at optimizing their performance and consequently, enhancing their market competitiveness and penetration. Accordingly, market shares for lithium secondary batteries have grown exponentially in the last decade [1,2]. However, the full potential of this technology is far from reached; there is still room for improvement and materials research is needed to obtain next-generation lithium secondary batteries.

The electrolyte for lithium secondary batteries must be an ionic conductor capable of solvating and transporting Li$^+$ ions. Ideally, an electrolyte should have the conduction properties of a liquid and the mechanical stability of a solid, along with high chemical stability. The anode, the cathode, and the electrolyte must be compatible with each other to provide a high degree of safety, high cycle ability, and high charge and discharge rates.

To enhance the safety of lithium batteries, a polyethylene oxide (PEO)-based solid polymer electrolyte is widely studied as a promising host polymer because of its good thermal properties, interfacial stability, and its ability to coordinate with a large number of inorganic cations. However, the PEO-based polymer electrolyte shows very low ionic conductivity at temperatures below room temperature due to its high crystallinity [3–6]. Several attempts have been made to increase the ionic conductivity of these polymer electrolytes. Among them, the gel polymer electrolytes (GPEs) have received much attention of late, which can be regarded as an intermediate between typical liquid electrolytes and dry solid-polymer electrolytes. The GPEs possess high ionic conductivities >10$^{-4}$ S cm$^{-1}$ at room temperature and the liquid guest is trapped in the polymer host, thereby preventing the leakage of the liquid electrolyte. However, although the electrochemical properties of electrospun gel GPEs have been studied and understood in great detail, their physical properties, such as ion interaction and phase transformation, have largely been ignored.

Several preparation techniques have been tried for the GPE polymer matrix, such as casting, phase inversion, and electrospinning [2,7–13]. Among these methods, electrospinning provides good mechanical strength and high ionic conductivity to the polymer matrix. Moreover, the polymer matrix should absorb the liquid electrolyte without leakage, be chemically compatible with the electrode materials, and adhere well to the electrode. Among various polymers that meet these requirements, poly(vinylidene fluoride) (PVdF) and its copolymer, poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) are very promising because of their good mechanical and electrochemical

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stabilities and their affinity to electrolyte solutions [14,15]. The fibrous polymer matrix of PVdF-HFP possesses different properties depending on the electrospinning parameters [11], and these properties can enhance the electrochemical performance of the lithium batteries.

In this study, we investigate the physical properties of PVdF-HFP based GPEs, in terms of their optimized synthesis parameters (polymer solution concentration, supply voltage, etc.) and the rate capability of the corresponding LiFePO$_4$ cell. The phase transition of the PVdF-HFP matrix, as well as the interaction between the solvent and cation and the between cation and anion, is investigated. Changes with the incorporation of liquid electrolyte are observed. When PVdF-HFP matrix is incorporated into the LE, the $\alpha$-phase of PVdF-HFP increases and the concentration of Li-coordinated PF$_6^-$ decreases slightly. GPE prepared with optimized synthesis parameters significantly enhances the rate capability of the lithium polymer battery.

## 2. Experimental

A microporous matrix of PVdF-HFP (Kynar 2801) was prepared by electrospinning as per the procedure standardized in our previous studies [11,12]. A 16-wt.% solution of PVdF-HFP in a mixed solvent of acetone and N,N-dimethylacetamide (7/3, w/w) was electrospun by applying a voltage of 18 kV at room temperature. A thin film of ~80 μm thickness was collected on an aluminum foil. The electrospun membrane was vacuum dried at 60 °C for 12 h before further use. The GPE was prepared by immersing the electrospun membrane in a 1 M solution of lithium hexafluorophosphate (LiPF$_6$) in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v). Activation of the membrane to prepare the GPE was performed in an argon-filled glove box under <10 ppm moisture level. The LiFePO$_4$ cathode material having 3 wt.% carbon coating was prepared by mechanical activation under optimized conditions of milling time, heating temperature, heating time, and carbon coating [16–18].

The ionic conductivities of the liquid electrolyte and the GPE were measured from −70 °C to 80 °C in a gold-plated cell, over a frequency range of 10$^{-1}$–10$^6$ Hz using a Novocontrol broadband dielectric spectrometer. Raman spectra of the PVdF-HFP matrix, the liquid electrolyte, and the GPE were recorded on a Bruker IFS 66 Fourier-transform spectrometer, equipped with an FRA 106 Raman module and using the 1064-nm line of a Nd:YAG laser as the excitation source. The laser power was set to 300 mW and the resolution was 2 cm$^{-1}$. Differential scanning calorimetry (DSC) was performed using a Q1000 apparatus (TA Instruments) at a heating rate 10 °C min$^{-1}$ with a 25 mL min$^{-1}$ He flow rate. Typically, the samples were cooled at 20 °C min$^{-1}$ from 40 °C to −120 °C and heated at 10 °C min$^{-1}$ up to 180 °C. The interfacial resistance ($R_f$) of the LiFePO$_4$/GPE/Li cell was measured with an IM6 frequency analyzer by the impedance response over the frequency range 10 mHz to 2 MHz. Lithium ion transference numbers were measured using the DC polarization method with the Bruce and Vincent correction [19]. The frequency range for the electrochemical impedance spectroscopy measurements was 500 kHz–100 mHz, with a 10-mV ac signal. Polarization was performed with a 20-mV dc signal.

For electrochemical measurements, the LiFePO$_4$ powder, carbon black, and the PVdF (Aldrich) binder were mixed in the ratio 87:5:8 by weight in N-methyl pyrrolidone (NMP) and the viscous slurry was cast on an aluminum foil and dried at 95 °C under vacuum for 12 h. The film was cut into circular discs of area 0.95 cm$^2$ and mass ~3.0 mg for use as the cathode. Cyclic voltammetry (CV) measurements of the LiFePO$_4$/GPE/Li cell were performed at a scan rate of 0.1 mV s$^{-1}$ over 2.0–4.5 V. Electrochemical performance was tested using an automatic galvanostatic charge–discharge unit, WBCS3000 battery cycler, between 2.5 and 4.0 V. The experiments were performed at current densities of 0.1 C (0.042 mA cm$^{-1}$), 1 C (0.42 mA cm$^{-1}$), 2 C (0.84 mA cm$^{-1}$), 3 C (1.26 mA cm$^{-1}$), and 5 C (2.1 mA cm$^{-1}$).
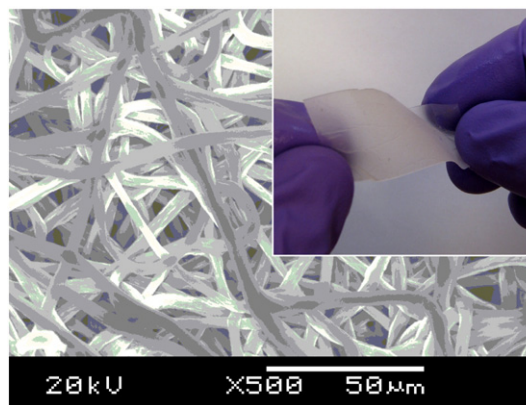


**Fig. 1.** Photo and SEM image of nano-fibrous PVdF-HFP matrix for gel polymer electrolyte.

## 3. Results and discussion

The photograph and the morphology of the prepared PVdF-HFP matrix are presented in Fig. 1. The polymer matrix, with 16 wt.% polymer concentration at 18 kV (Fig. S1), is made up of a network of interlaid fibers with diameters <800 nm. The interlaying of the fibers imparts sufficient mechanical strength to the membrane for safe handling. The presence of fully interconnected micron-sized pores in the membrane structure makes it ideal for application as a host matrix for GPEs. The fibrous PVdF-HFP matrix could theoretically accommodate >250 wt.% liquid electrolyte. However, 60 wt.% liquid electrolyte (LE) was fed into 40 wt.% polymer matrix to prevent the LE leakage and reduction in mechanical strength. The temperature dependence of the ionic conductivity of the GPE and the LE (based on 1 M LiPF$_6$ in EC/DMC) is shown in Fig. 2. The conductivities of both systems increase with increasing temperatures over the investigated temperature range. Although the ionic conductivity of the LE was >2 orders of magnitude higher than that of the GPE over the entire temperature range (−40 to 80 °C), the ion conductivity of the GPE (>10$^{-4}$ S cm$^{-1}$) was high enough for high-power battery applications [20,21]. An ionic conductivity of ~3.0 × 10$^{-4}$ S cm$^{-1}$ was achieved at −10 °C in the GPE, and it increased to ~2.7 × 10$^{-3}$ S cm$^{-1}$ at 30 °C. The latter compares well with the reported values of GPEs with various matrices (Table S1). The ionic conductivity of GPE also depends on the liquid electrolyte uptake. Although the GPE studied here was prepared with low liquid electrolyte uptake (60 wt.%), its ionic conductivity is almost as high as the reported value of GPE with >200 wt.% liquid electrolyte uptake. The ionic
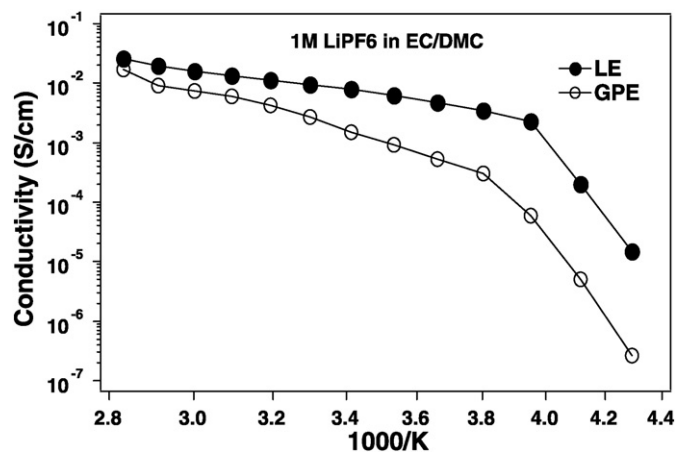


**Fig. 2.** Ionic conductivity as a function of temperature for 1 M LiPF$_6$ in EC/DMC liquid electrolyte (LE) and gel polymer electrolyte (GPE).