



Citrated porous gel copolymer electrolyte composite for lithium ion batteries application: An investigation of ionic conduction in an optimized crystalline and porous structure



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ABSTRACT

Citrated porous PVDF-co-HFP containing LiClO_4 -EC-DEC is prepared with a preferential polymer dissolution process using polyvinyl acetate to create a different porosity ratio of the optimized citrated membrane. All citrated samples (3,5,7,9,11 wt. %) are characterized using X-ray diffraction to show that the sample containing 7 wt. % citric acid has the lowest crystalline structure. The optimized sample is mixed with different PVA concentrations, (4, 8, 12, 16 wt. %), and then all PVA removal copolymer composite samples are immersed in a mixture of a liquid electrolyte containing LiClO_4 , EC, and DEC. The swelling and porosity measurements show that the sample containing 16 wt. % of PVA removal has the highest values, 68% porosity and 115% swelling. Scanning electron microscope is used to show the porous structure of the optimized citrated copolymer electrolyte sample (16 wt. % of PVA removal) compared to the before removing PVA one. DC-electrical conductivity measurement is performed to show the effect of porosity on the conduction process. The sample having 8 wt. % PVA removal shows a high conductivity value of $8 \times 10^{-4} \text{ S cm}^{-1}$ compared to the other samples at room temperature. Complex impedance, electrochemical stability and stress-strain curve are also studied. All results are collected and discussed.

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1. Introduction

In recent years, there has been a growing demand for high-energy density rechargeable lithium batteries for portable electronic products because of their advantages including safety, high-energy density, high single cell voltage, geometry and no memory effect. Polymer electrolytes, new electrolytic materials competing for a place in the future energy generation, storage and distribution markets. Polymer electrolytes offer many advantages over their more conventional liquid counterparts in these developing technologies, such as: flexibility, easy of processing into thin films of a large surface area, good mechanical stability, chemical - electrochemical stability and volumetric stability through charging and discharging processes. However, the ionic conductivity of polymer electrolytes is generally low, often too low for practical application. To improve the basic requirements of the polymer electrolyte, various processes have been used such as electrochemical stability towards lithium battery electrodes, compatibility with the

electrode materials, reasonable ionic conductivity, sufficient thermal stability and good mechanical stability.

Many polymers, such as polyethylene oxide (PEO) [1], polyacrylonitrile (PAN) [2], polymethylmethacrylate (PMMA) [3], and polyvinylidene fluoride (PVDF) [4–6], have been used too as matrices for polymer electrolytes. PVDF-HFP has been attracted as a highly promising material for the polymer electrolyte of rechargeable lithium battery because its high solubility and lower crystallinity and glass transition temperature than PVDF [7–11]. Moreover, it is a semi-crystalline polymer, in which the amorphous domains can trap more liquid electrolyte, and crystalline regions contribute to the improvement mechanical integrity while being processed in free-standing films.

Studies have been made primarily on the enhancement of the ionic conductivity at room temperature via various approaches such as blends, co-polymers, comb shape polymers, cross-linked networks and incorporation of ceramic fillers onto the polymer matrix. Organic acid such as citric acid is one of the important methods used to improve the ionic conductivity [12] in polymer electrolytes due to its strong ligating power to the lithium ion [13]. Also, the porous texture has proved an effective approach to

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improve the overall performances of polymer electrolyte, which usually showed good mechanical performances with enhanced ionic conductivity at room temperature besides the activation process requires a critical moisture control only during the last activation step because of high water sensitivity of lithium salt [14–18].

In the present work, we try to prepare citrated gel copolymer electrolyte composites (citric acid + PVDF-co-HFP–LiClO₄-EC-DEC) with a porous structure to enhance the ionic motion within the copolymer matrix. The ionic motion in general will depend on the crystallinity and porosity ratios of the matrix. But the question is still what the optimum ratios of crystallinity and porosity are in a composite system to show an optimized structure with an optimum ionic motion, to get finally a good polymer electrolyte. Here, we used polyvinyl acetate to prepare different porosity ratios of PVDF-co-HFP electrolyte composites containing citric acid to study the porosity dependence of the conduction process.

2. Experimental

2.1. Materials

PVDF-co-HFP (M.wt = 550,000, Sigma–Aldrich), PVA (Sigma–Aldrich), Citric acid (Merck), LiClO₄ (Sigma–Aldrich), Ethylene carbonate (EC) and diethyl carbonate (DEC) (Sigma–Aldrich) were used as starting materials to prepare citric co-polymer composites and porous citric gel co-polymer electrolyte composites.

2.2. Preparation of citric co-polymer composites films

First, the co-polymer (PVDF-co-HFP) was dissolved in acetone. Different wt. % of citric acid (0, 3, 5, 7, 9 and 11 wt. %) were added. The resultant homogeneous viscous solutions were spread as films on a glass substrate. Then, the polymer composites films were dried at 50 °C in a vacuum oven for 6 h to remove any further traces of acetone. The thickness of the films was obtained in the range of 2–4 mm. Finally, the resultant citric polymer composites films were characterized using X-ray diffraction to optimize the citric acid content within PVDF-co-HFP matrix.

2.3. Preparation of porous citric gel co-polymer composites electrolytes films

The optimized sample of citric co-polymer composite was taken and dissolved in DMF. Polyvinyl acetate with different amounts (0, 4, 8, 12 and 16 wt. %) was also added. The resultant viscous solutions were spread as films on a glass substrate. These films were dried at 80 °C in a vacuum oven for 6 h to remove any further traces of DMF. The thickness of the films was determined to be in a range of 2–4 mm. The films were immersed in a pool of excess of deionized water at 60 °C to remove PVA from PVDF-co-HFP matrix to form a porous structure with different distribution ratios. These porous citric co - polymer composites membranes were dried under vacuum at 80 °C for 6 h. Finally, the samples were activated by soaking in 1 M LiClO₄ electrolyte solution containing 1:1 (v/v) ratio of EC and DEC (the electrolyte solution has a conductivity value of $8.5 \times 10^{-3} \text{ S cm}^{-1}$) for 18 h to get porous citric gel co-polymer composites electrolytes.

2.4. Characterization of samples

X-ray diffraction analysis was performed on a Diano (made by Diano Corporation, U.S.A.) with Cu-filtered CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) energized at 45 kV, and 10 mA. The samples were measured at room temperature in the range from $2\theta = 10^\circ$ to 70° .

Scanning electron microscope was carried out with JOEL-scanning electron microscope (JSM-35CF) to show the ability of PVA to create a porous structure within the matrix of the citric co-polymer composites.

The porosity (P) was determined using the following equation [9]:

$$P = [(m_a/\rho_a) \div (m_a/\rho_a + m_p/\rho_p)] \times 100 \quad (1)$$

Where m_a is the weight of citric co-polymer composites after impregnation with 1-butanol and m_p is the weight of citric co-polymer composites before impregnation with 1-butanol. Similarly, ρ_a and ρ_p are density of 1-butanol and the citric co-polymer composites, respectively. Swelling behavior of the citric co-polymer composites was also studied. The extent of swelling (S_w) of citric co-polymer composites was determined to investigate its dependence on the porous structure. The percentage of swelling was determined using Eq. (2) [19]:

$$S_w = [(W - W_0) \div (W_0)] \times 100 \quad (2)$$

Where W_0 is the weight of dried films and W is the weight of swelled films.

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were performed in Argon atmosphere with a constant heating rate of 10 K/min. in a temperature range of 298–473 K using Shimadzu DT-50.

The stress–strain characteristic was recorded at room temperature by using Bruker–Digital force gauge (1000 N). The sample was cast in a dimension of 60 mm \times 20 mm. The thickness of cast sample is 2 mm.

2.5. Electrochemical characterization

The ionic conductivity measurements were performed by sandwiching the citric co-polymer electrolyte composites between two stainless steel electrodes using a programmable automatic LCR bridge (Model RM 6306 Phillips Bridge) in various temperatures ranging from 303 to 353 K. The electrochemical stability of citric co - polymer electrolyte composite having the highest ionic conductivity was evaluated with cell featuring a stainless steel (SS) as a working electrode and lithium as counter and reference electrodes by linear sweep voltammetry at 25 °C using an EG&G Electrochemical analyzer (Model-6310) in the scan rate of 1 mV/s. The cell was assembled in a glove box under argon atmosphere.

3. Results and discussion

3.1. Optimization of citric co-polymer composites

X-ray diffraction patterns of co-polymer with different wt. % of citric acid (0, 3, 5, 7, 9 and 11 wt. %) are displayed in Fig. 1. The figure showed an absence of citric acid crystalline peaks with the co-polymer at all concentrations and this may be attributed to the interaction of the polymer backbone and citric acid. Also, the figure showed that the sample containing 7 wt. % citric acid has low relative intensity peaks (low crystalline structure) and more broadening ones. This shows that the optimized concentration of citric acid within the PVDF-co-HFP matrix can be achieved when 7 wt. % is added. The values of crystallinity percent (X_c) were calculated from the intensity ratio of the peaks and tabulated in Table 1. The composite containing 7 wt. % citric acid showed lower X_c value (75%) than the other ones.

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