

Preparation and proton conductivity of poly(vinylidene fluoride)/layered double hydroxide nanocomposite gel electrolytes

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Abstract Layered double hydroxide (LDH) was synthesized in the presence of sodium dodecyl sulfate. X-ray diffraction (XRD) and infrared spectrum revealed that dodecyl sulfate (DS) anions were successfully intercalated into the interlayers of LDH. Poly(vinylidene fluoride)/LDH nanocomposite membranes were prepared by mixing the DS intercalated LDH with poly(vinylidene fluoride) (PVDF) in *N,N'*-dimethylformamide solution followed by the solvent evaporation. The nanocomposite membranes were further swollen with a H_3PO_4 solution in ethylene carbonate-propylene carbonate to obtain the proton conducting nanocomposite gel electrolytes. XRD and transmission electron microscope results showed that LDH particles were well-dispersed in the polymer matrix and partially intercalated by polymer chains. The proton conductivity was highly enhanced in the nanocomposite gel electrolyte systems. In the case of the nanocomposite gel electrolyte containing 7.40 wt.% LDH, the proton conductivity increased by about 2.5 times compared to pure PVDF gel electrolyte.

Introduction

In recent years, proton conducting polymer gel electrolytes have become an area of widespread interest due to their possible applications in a variety of electrochemical devices, such as fuel cells, chemical sensors, and electrochromic displays [1–4]. Polymer gel electrolytes using

poly(vinylidene fluoride) (PVDF) and its copolymers as the host matrixes have received much attentions, as the polymer electrolytes fulfill most of the properties required for the battery application [5–8]. Zukowska et al. [9] prepared a novel proton conducting gel electrolyte from PVDF-dimethylformamide- H_3PO_4 system, and high conductivity (5×10^{-2} S/m at 20 °C) was achieved in a relatively narrow component concentration range. Singh et al. [10–12] prepared a new family of non-aqueous proton conducting polymer gel electrolytes containing different weak acids namely, aromatic carboxylic acids by using PVDF and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) as the gelling polymers. The obtained gel electrolytes possessed high value of conductivity in the range of 10^{-1} – 10^{-2} S/m at room temperature. Choi et al. [13] prepared polymer gel electrolytes consisted of a PVDF-HFP matrix and entrapped solvents such as propylene carbonate (PC), ethylene carbonate (EC), dimethylformamide, and dimethyl sulfoxide with a dissolved H_3PO_4 .

In order to improve the performance of polymer electrolytes, many attentions have also been paid to the modification of polymer electrolytes by incorporating nanometer inorganic materials. It is widely known from the literature that the addition of non-conductive ceramics (Al_2O_3 , SiO_2 etc.) and various clay nanoparticles, to the lithium polymer electrolytes enhances the ionic conductivity [14–17]. While for proton conducting polymer electrolytes, such as Nafion film, the conductivity always decreases, as ceramics or clay nanoparticles are added [18–20].

Layered double hydroxides (LDHs) are a class of new inorganic materials, which were very recently used for the modification of lithium conducting polymer electrolytes. Liao et al. [21–23] prepared all solid-state poly(ethylene oxide)/LDH nanocomposite electrolytes by using two kinds

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of oligo(ethyl oxide) modified LDHs. The well-dispersed LDH layers in PEO/LiClO₄/LDH nanocomposite electrolytes rendering the formation of amorphous phase, resulted in an enhancement of ionic conductivity by three orders of magnitude compared to the pure PEO/LiClO₄ electrolyte. Cho et al. [24, 25] prepared nanocomposite electrolyte films composed of poly(ethylene glycol diacrylate)/LiCF₃SO₃ with various weight percent of Mg–Al LDH, and found that the ionic conductivity and tensile modulus were highly enhanced in the nanocomposite system.

In this work, Mg–Al LDH intercalated with dodecyl sulfate anion was prepared and incorporated into PVDF-based proton conducting polymer gel electrolytes. The morphology and conductivity of the resulting composite polymer gel electrolytes will be investigated.

Experimental

Materials

The materials used in the synthesis of the LDHs, were Mg(NO₃)₂·6H₂O (Shanghai Chemical Reagents Co., China), Al(NO₃)₃·9H₂O (Shanghai Chemical Reagents Co., China), NaOH (Hangzhou Chemical Reagents Co. China), and sodium dodecyl sulfate (Shanghai Chemical Reagents Co., China) in analytical reagent grade and used without further purification. LDH with the formula of Mg_{0.67}Al_{0.33}(OH)₂(CO₃)_{0.17}·2H₂O (LDH-CO₃) was supplied by Fumeida New Materials Co., Dalian, China.

PVDF was purchased from Atofina Co. *N,N'*-dimethylformamide (DMF) with analytical purity was purchased from Gaojing Fine Chemical Co., Hangzhou, China, and distilled under reduced pressure before use. Ethylene carbonate (Johnson Matthey), propylene carbonate (Johnson Matthey), and H₃PO₄ (Aldrich, crystal 98%) in analytical reagent grade and used without further purification.

Preparation of MgAl–NO₃ LDH and LDH intercalated with dodecyl sulfate anion

MgAl–NO₃ LDH (LDH-NO₃) and LDH intercalated with dodecyl sulfate anion (LDH-DS) were prepared by co-precipitation method. In order to exclude carbonate from the LDH, doubly deionized water was used in the preparation, and the preparation was carried out in the protection of N₂ atmosphere.

To synthesize LDH-NO₃, the aqueous solution of Mg(NO₃)₂·6H₂O (0.2 mol) and Al(NO₃)₃·9H₂O (0.1 mol), and the aqueous solution of NaOH (1.2 mol), were spontaneously added to a three-necked round-bottle flask. The pH value was adjusted to about 10 by controlling

the adding rate of NaOH solution. The mixture was aged at 80 °C for 12 h. The resultant precipitate was filtered, thoroughly washed with doubly deionized water, and vacuum dried at 50 °C overnight.

To synthesize the LDH-DS, Mg(NO₃)₂·6H₂O (0.2 mol) and Al(NO₃)₃·9H₂O (0.1 mol) were dissolved in 5 × 10⁻⁴ m³ deionized water. The nitrate solution was then slowly dropped into vigorously stirred 5 × 10⁻⁴ m³ water solution of sodium dodecyl sulfate (0.2 mol). The pH value of the solution was maintained at 10 by adding 1 M NaOH solution. After the addition of nitrate solution, the mixture was aged at 80 °C for 12 h. The resultant precipitate was filtered, washed several times with doubly deionized water, and vacuum dried at 50 °C for 24 h.

Preparation of PVDF/LDH nanocomposite gel electrolyte

PVDF/LDH nanocomposite gel electrolytes with various amounts of LDH-DS (1.91, 3.85, 7.40, 9.10 wt.% based on the weight of PVDF) were prepared by using LDH-DS obtained from the aforementioned process. A typical procedure for the preparation of the nanocomposite gel electrolyte was as follows: Initially, an appropriate quantity of LDH-DS was introduced into DMF with stirring for 24 h at 70 °C. PVDF resin was added to the above DMF dispersion, and the dispersion was stirred until it was homogeneous. Then the resulting viscous dispersion was cast onto a glass plate and dried in a dry box to obtain a membrane having thickness of 120–200 μm. Finally, the membrane was allowed to swell with a H₃PO₄ solution in EC/PC (1:1, v/v) with the concentration of 1 × 10³ mol/m³ for 5 h, to obtain PVDF/LDH nanocomposite gel electrolyte membrane.

Characterization

The X-ray diffraction (XRD) patterns were determined by using a XRD-6000 X-ray diffractometer (Shimadzu Co., Japan), using CuKα radiation (λ = 0.1542 nm), at a scanning rate of 4° min⁻¹ over 2θ intervals from 2 to 70°. The generator tension and current were 40 kV and 30 mA, respectively. The FT-IR spectra were recorded on a Perkin-Elmer System 2000 Fourier-transformed infrared spectrophotometer with a spectral resolution of 4 cm⁻¹.

The particle size distribution of LDH-DS in DMF was measured by using a Malvern particle size analyzer (Malvern Instrument Co.). PVDF/LDH nanocomposite was cryogenically ultra-thin sectioned, and the morphology was observed by using a JEM-1230 transmission electron microscope (JEOL Co., Japan).

The electrical conductivity was measured using ac impedance techniques with a Solartron1250 frequency response analyzer, where the given electrolyte membranes were placed sandwiched between two stainless-steel electrodes with a contact area of $1.0 \times 10^{-4} \text{ m}^2$. The applied frequency ranged from 1 Hz to 1 MHz.

Results and discussion

Characterization of LDH-DS

XRD patterns of LDH- CO_3 , LDH- NO_3 , and LDH-DS are shown in Fig. 1. The strong Bragg reflection peaks appeared at $2\theta = 11.4^\circ$ and 9.96° for LDH- CO_3 and LDH- NO_3 , respectively, were attributed to the reflections of (00 *l*) series plane diffractions. The basal spacing calculated from Bragg's equation was 0.78 nm for LDH- CO_3 and 0.89 nm for LDH- NO_3 . The XRD pattern of the LDH-DS demonstrates that the diffraction peaks of (003) shown in the patterns of the LDH- CO_3 and LDH- NO_3 disappear, and a strongest diffraction peak appears at $2\theta = 3.24^\circ$. The calculated basal spacing was 2.73 nm, corresponding to the interlayer spacing of 2.25 nm. The increase of basal spacing of the LDH-DS demonstrated that the dodecyl sulfate anions, which have a large volume, were effectively intercalated into the interlayer of LDH to replace NO_3^- and CO_3^{2-} . Additionally, the existence of diffraction peaks of (006) and (009) indicates that the layer characteristic of the LDH-DS is extremely pronounced.

Figure 2 shows the FT-IR spectra of LDH- CO_3 , LDH- NO_3 , and LDH-DS. The fingerprint bands at 610 and 430 cm^{-1} for all samples are associated with O–M–O stretching modes in the LDH sheets [26]. The strong and

broad absorption bands at about $3,500 \text{ cm}^{-1}$ and $1,640 \text{ cm}^{-1}$ appeared in the spectra of three samples are associated with the hydroxyl stretching mode (ν_{OH}) and the bending mode of interlayer water ($\delta_{\text{H}_2\text{O}}$), respectively [27]. The strong band at $1,365 \text{ cm}^{-1}$ appeared in Curve *a* is associated with the asymmetric stretching vibration of CO_3^{2-} anions, and that at $1,375 \text{ cm}^{-1}$ appeared in Curve *b* is associated with the stretching vibration of the NO_3^- anions. The absorption bands at $1,220 \text{ cm}^{-1}$ and $1,050 \text{ cm}^{-1}$ that shown in FT-IR spectrum of the LDH-DS are assigned to the stretching vibrations of RSO_4^- . The characteristic bands associated with the vibration of $-\text{CH}_3$ and $-\text{CH}_2$ groups occur at $2,845$ – $2,960 \text{ cm}^{-1}$. These FT-IR assignments further confirm that dodecyl sulfate anion is successfully intercalated into the gallery of the LDH.

Dispersion of LDH-DS in DMF and PVDF nanocomposite

The intercalation of dodecyl sulfate anions into LDH would increase the compatibility of LDH with DMF, and thus improve the dispersion ability of LDH in DMF. The typical particle size distribution of LDH-DS in DMF is shown in Fig. 3. It can be seen that the sizes of most LDH-DS particles are lower than 100 nm, the volume (weight) fraction of LDH-DS particles with size greater than 100 nm is about 6.8%, while the number fraction of these LDH-DS particles would be even lower.

The dispersion state of LDH-DS particles in the PVDF nanocomposites was even more important, since it would directly affect the conductive and mechanical properties of gel electrolytes. The typical TEM image of PVDF/LDH-DS nanocomposite is shown in Fig. 4. The dark strips in

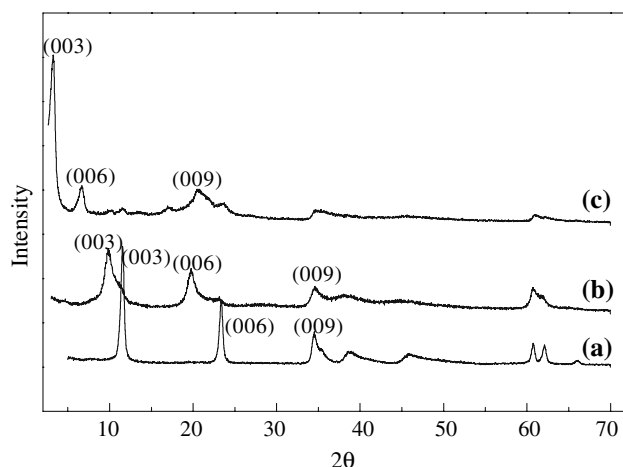


Fig. 1 XRD diffraction patterns of LDH- CO_3 (a), LDH- NO_3 (b), and LDH-DS (c)

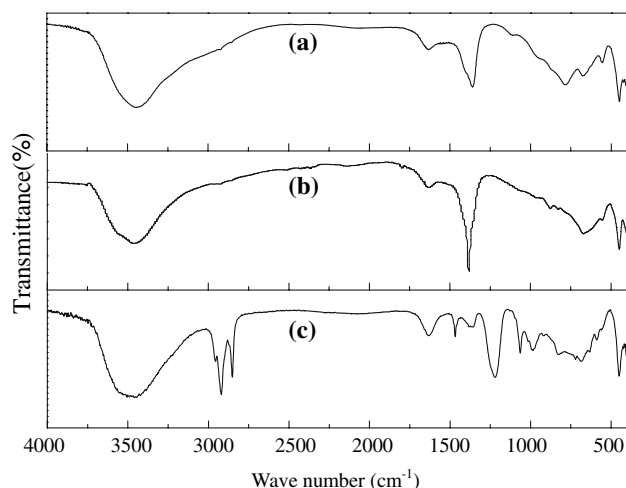


Fig. 2 FT-IR spectra of LDH- CO_3 (a), LDH- NO_3 (b), and LDH-DS (c)

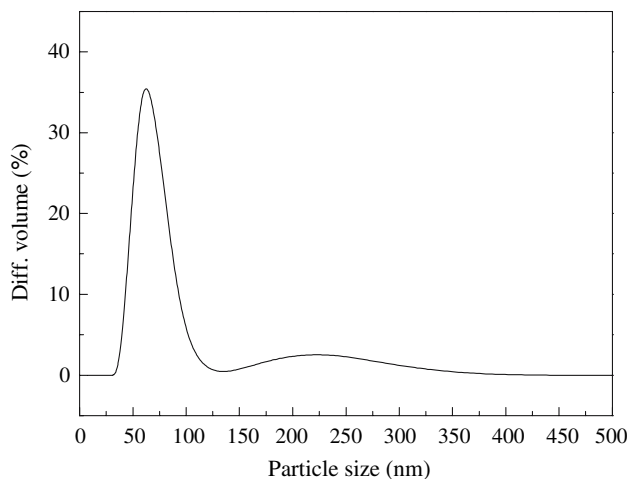


Fig. 3 Particle size distribution of LDH-DS in DMF



Fig. 4 TEM micrograph of PVDF nanocomposite having 3.85 wt.% LDH-DS (scale bar 200 nm)

the figure correspond to LDH-DS layers. The TEM image shows that the LDH-DS layers are well dispersed in PVDF matrix and much less strongly oriented. The length of LDH layers ranges from 50 to 200 nm and the thickness of LDH layers is about 20 nm, indicating the partially intercalated structure of LDH-DS in the nanocomposite.

Figure 5 shows the XRD patterns of pure PVDF membrane and PVDF membrane containing 3.85wt LDH-DS. It can be seen that two patterns are almost same. The (003) diffraction peak of LDH-DS does not appear in the pattern of PVDF/LDH-DS nanocomposite, indicating the increase of basal spacing and intercalation of LDH-DS.

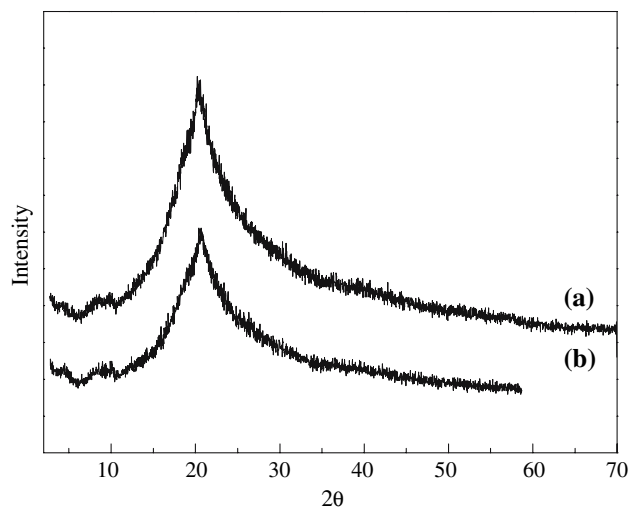


Fig. 5 XRD patterns of pure PVDF membrane (a) and PVDF membrane containing 3.85 wt.% LDH-DS (b)

Effect of LDH-DS content on the proton conductivity of PVDF gel electrolytes

The effect of LDH-DS weight fraction on the electrochemical properties of nanocomposite gel electrolytes was investigated. Figure 6 shows the *ac* impedance spectra in Nyquist form for PVDF and PVDF/LDH-DS nanocomposite gel electrolytes. All profiles show semicircles starting from the origin of the plot in the high-frequency range followed by straight lines inclined to the real axis in the low-frequency range.

With the help of Z-Plot/Z-View system software, the bulk resistance (R_b) of electrolyte film can be estimated. The ionic conductivity (σ) of the gel electrolytes is calculated as follows:

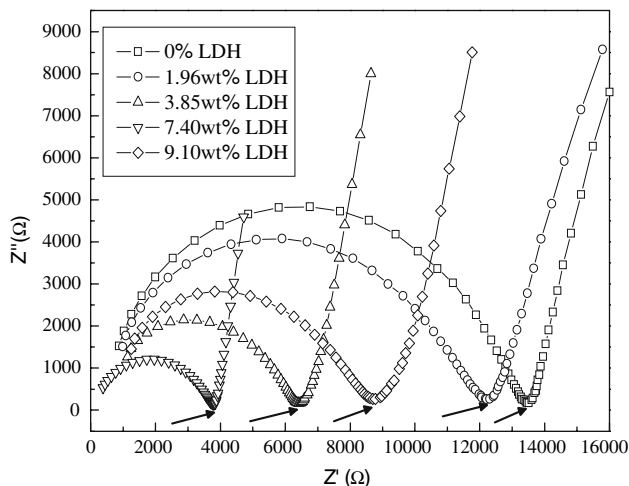


Fig. 6 Experimental data of impedance spectra for PVDF and PVDF/LDS-DS nanocomposite gel electrolytes

Table 1 Bulk resistance, thickness, and ionic conductivity of PVDF and PVDF/LDH-DS nanocomposite gel electrolyte films

Sample Number	Weight percent of LDH-DS (%)	R_b (Ω)	D (μm)	σ (10^{-4} S/m)
1	0	13,456	179	1.33
2	1.96	12,207	199	1.63
3	3.85	6,431	172	2.67
4	7.40	3,797	120	3.16
5	9.10	8,775	201	2.29

The contact area between the electrodes and film (A) is $1.0 \times 10^{-4} \text{ m}^2$

$$\sigma = \frac{1}{R_b} \cdot \frac{d}{A}$$

where d is the thickness of the electrolyte membrane and A is the contact area between the electrodes and the electrolyte membrane.

The bulk resistance, thickness, and the calculated ionic conductivity of PVDF and PVDF/LDH-DS nanocomposite gel electrolyte films are listed in Table 1. It can be seen that the ionic conductivity increases with LDH-DS content initially, and the maximum conductivity is observed in the sample having an optimum content of 7.40 wt.%. The ionic conductivity decreases for the sample containing 9.10 wt.% LDH-DS. The enhancement of the ionic conductivity might be related with the existence of special interaction, so-called Lewis acid-base interaction, between the surface of LDH nanosheets and the PO_4^{3-} . This might further allow the enhanced mobility of H^+ in the polymer matrix. In case of the electrolyte membrane containing greater LDH-DS contents, LDH-DS acts as a mere insulator to impede ionic movement.

Conclusions

LDH intercalated with dodecyl sulfate anions was prepared by co-precipitation method, and incorporated into PVDF by solution mixing followed by solvent evaporation. XRD and IR spectrum revealed that dodecyl sulfate anions were successfully intercalated into the layers of LDH. XRD and TEM results showed that LDH particles were well-dispersed in PVDF matrix and partially intercalated by polymer chains. PVDF/LDH nanocomposite membranes swollen with a H_3PO_4 solution in ethylene carbonate-propylene carbonate, exhibited the enhanced proton conductivity compared to pure PVDF gel electrolyte

membrane. The maximum proton conductivity was achieved when 7.40 wt.% LDH was incorporated into PVDF gel electrolyte.

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