



Short communication

Preparation and performances of LiFePO₄ cathode in aqueous solvent with polyacrylic acid as a binderZ.P. Cai^{a,b}, Y. Liang^{a,b}, W.S. Li^{a,b,*}, L.D. Xing^{a,b}, Y.H. Liao^{a,b}^a School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China^b Key Lab of Electrochemical Technology on Energy Storage and Power Generation in Guangdong Universities, South China Normal University, Guangzhou 510631, China

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ABSTRACT

Here we report the preparation of LiFePO₄ cathode for lithium ion battery in the aqueous solvent with polyacrylic acid (PAA) as a binder. Its performances were studied by cyclic voltammetry (CV), charge–discharge cycle test, electrochemical impedance spectroscopy (EIS), X-ray diffraction (XRD), and scanning electron microscopy (SEM), and compared with the cathode prepared in N-methyl-2-pyrrolidone (NMP) solvent by using polyvinylidene fluoride (PVDF) as a binder. It is found that the cathode prepared in the aqueous solvent shows better performances than that in NMP solvent, including the better reversibility, the smaller resistances of solid electrolyte interphase and charge exchange, the less polarization, higher capacity and cyclic stability for lithium ion intercalation in or de-intercalation from LiFePO₄. The aqueous solvent is also more environmental friendly and cheaper than NMP. In addition, PAA is less costly than PVDF. Consequently, the preparation of LiFePO₄ cathode in the aqueous solvent by using a PAA binder provides lithium ion battery with improved performances at a less cost and in a more environmental friendly way.

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1. Introduction

One of the most important problems lithium ion battery faces is safety, partly because unstable cathode materials such as LiCoO₂ and Li₂MnO₄ are used [1–3]. Due to its low cost, the high theoretical capacity density (170 mAh g⁻¹), the excellent reversibility and thermal stability, LiFePO₄ has been considered to be a promising cathode material for lithium ion battery [4–9]. However, the application of LiFePO₄ is always accompanied with the large cathodical polarization, particularly in the case of high rate demands, which is ascribed to the low electronic conductivity of LiFePO₄ [10]. Therefore, many efforts have been made to improve the electronic conductivity of LiFePO₄, including coating conductive carbon or metals on LiFePO₄ surface [11–15] or doping ions in the crystalline lattice of LiFePO₄ [16–18]. However, no satisfactory results have been reported. The reason may be that the cathodical polarization is related to not only the electronic conductivity of the cathodical material but also the charge transfer kinetics of the cathode as well as lithium ion transportation in cathode.

The conventional method to prepare LiFePO₄ cathode is similar to that for LiCoO₂ cathode, in which polyvinylidene fluoride (PVDF)

is used as a binder in the organic solvent N-methyl-2-pyrrolidone (NMP). NMP was found to be effective for the dispersion of cathode materials. However, NMP is a volatile and combustible solvent, which creates severe pollution and safety problems in lithium ion battery industry. In addition, PVDF is a good binder for cathode preparations, but it is an electronic as well as ionic insulator. As a result, the application of PVDF will increase the resistance of LiFePO₄ cathode. Finally, both NMP and PVDF are expensive.

Aiming to reduce the cathodical polarization as well as the pollution from NMP and the cost for the cathode preparation, we propose a new method for the preparation of LiFePO₄ cathode, in which the aqueous solvent and polyacrylic acid (PAA) binder are introduced. Aqueous solvent, or water, is far cheaper than NMP and environmental friendly. PAA is cheaper than PVDF, and it has been used as an additive in anode and cathode preparation [19–21] and found to be beneficial to lithium ion battery.

2. Experimental

The LiFePO₄ electrode was prepared in aqueous solution as follows: Carbon-coated LiFePO₄ (2 wt% carbon, STL energy Co., Ltd., Tianjin, China) and PAA (average molecular weight: 1,000,000, Wako Pure Chemical Industries, Ltd.) were first mixed at a ratio of 90:10 (by mass) in distilled water. The slurry was then coated on an aluminum foil and dried under the vacuum at 80 °C for 12 h. The LiFePO₄ electrode, prepared in NMP (Sinopharm Chemical Reagent

* Corresponding author at: School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China. Tel.: +86 20 39310256; fax: +86 20 39310256.

E-mail address: liwsh@scnu.edu.cn (W.S. Li).

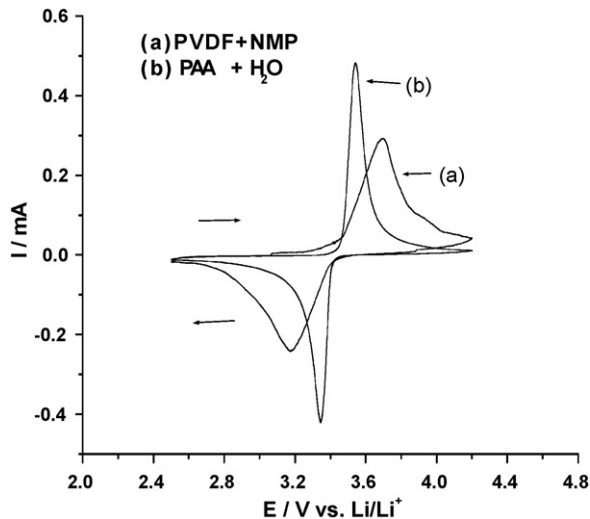
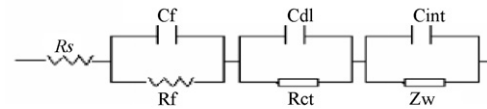


Fig. 1. Cyclic voltammograms of LiFePO_4 electrodes in 1-M $\text{LiPF}_6/\text{EC}:\text{DMC}:\text{EMC}$ (volume ratio 1:1:1), scan rate: 0.1 mV s^{-1} . (a) The electrode was prepared in NMP by using PVDF as a binder and (b) the electrode was prepared in the aqueous solvent by using PAA as a binder.

Co., Ltd.) under the same conditions by using the same LiFePO_4 and using PVDF (Kureha Co., Ltd.) as a binder and carbon black with a ratio of 82:12:6 (by mass), was used for comparison. Before use, the electrode prepared in aqueous solvent was dried for 12 h at 100°C under the vacuum to remove the residual water in the electrode. Both electrodes were cut into the shape with an area of 0.785 cm^2 for coin cell use and had a load of about 1.27 mg cm^{-2} LiFePO_4 .

The electrochemical performances of the LiFePO_4 electrodes were evaluated in a 2016 coin-type $\text{LiFePO}_4/\text{Li}$ cell, in which the lithium electrode was used as the counter electrode as well as the reference electrode. The electrolyte was 1 M LiPF_6 in ethylene carbonate (EC)–dimethyl carbonate (DMC)–ethyl and methyl carbonate (EMC) with a volume ratio EC:DMC:EMC = 1:1:1. All the cells were assembled in an argon-filled glove box (MIKROUNA).

All electrochemical measurements were conducted on Autolab (PGSTAT-30, Eco Chemie B.V. Company). The potential scan rate in cyclic voltammetry was 0.1 mV s^{-1} . The impedance measurement was performed at the fully charged state of the LiFePO_4 electrodes. Prior to the impedance measurements, LiFePO_4 electrodes were cycled 3 times between 2.5 and 4.2 V and then held at the open circuit potential for 30 min. The frequencies were from 10^5 to 10^{-2} Hz and the potential amplitude was 5 mV. The impedance was analyzed with the software provided by Eco Chemie B.V. Com-



R_s : solution resistance ;

R_f and C_f : resistance and capacitance of SEI;

R_{ct} and C_{dl} : charge transfer resistance and double layer capacitance at the interface of SEI/ LiFePO_4 ;

Z_W and C_{int} : Warburg impedance and intercalation capacitance of lithium ion in LiFePO_4 .

Fig. 3. The equivalent circuit for the fitting of the experimental electrochemical impedance spectra of lithium ion intercalation or de-intercalation.

pany. The charge–discharge cycle tests were performed using A BS-9300R type battery charger (Guangzhou Qingtian Industrial Co., Ltd., China) at a current density of 0.2 mA g^{-1} between 2.5 and 4.2 V (vs. Li/Li^+).

X-ray diffraction (XRD) was performed on an X-ray diffractometer (Rigaku D/MAX-RC, Japan) equipped with a Cu target X-ray tube (30 kV, 30 mA, step size = 0.02° , scan rate: $12^\circ \text{ min}^{-1}$, $10^\circ < 2\theta < 90^\circ$). The morphology of the electrodes was examined by an S-520 SEM (Hitachi) (Oxford, INCA), accelerative voltage 20 kV.

3. Results and discussion

3.1. Cyclic voltammogram

Fig. 1 presents the voltammograms of LiFePO_4 electrodes prepared in aqueous solvent as well as NMP. It can be seen from **Fig. 1** that both electrodes show the oxidation current peaks for lithium ion de-intercalation during the forward potential scanning and the reduction current peaks for lithium ion intercalation during the backward potential scanning. However, the peak potentials, peak currents and the current change were different for both electrodes. Specifically, the electrode prepared in aqueous solvent showed a smaller difference between the oxidation peak and reduction peak potential, i.e., 0.19 V , than that in NMP, in which the peak potential difference is 0.53 V . However, the current before the peak appearing in the electrode prepared in aqueous solvent increases more quickly than that in NMP during the forward or backward potential scanning, indicating that the electrode prepared in

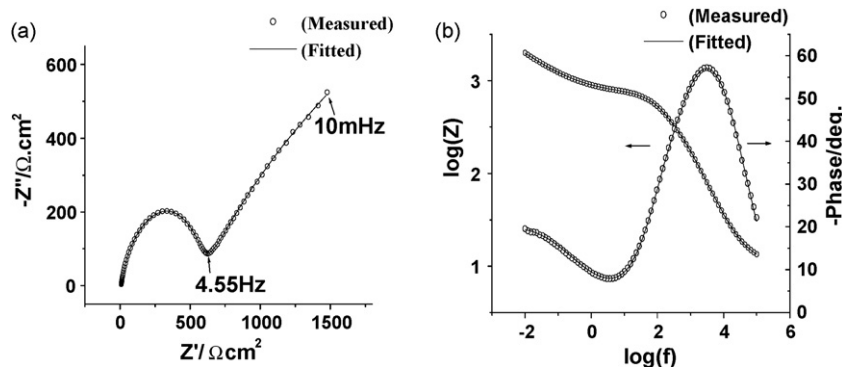


Fig. 2. Electrochemical impedance spectra of the LiFePO_4 electrode prepared in NMP. (a) Nyquist plot and (b) Bode plot.

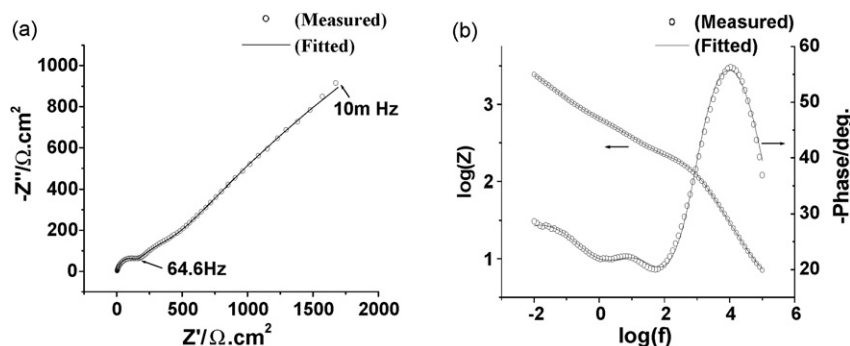


Fig. 4. Electrochemical impedance spectra of LiFePO₄ electrode prepared in the aqueous solvent. (a) Nyquist plot and (b) Bode plot.

aqueous solvent by using a PAA binder has the better reversibility, which can be ascribed to the lower resistances of solid electrolyte interphase (SEI) on LiFePO₄ and charge transfer for lithium ion intercalation and de-intercalation than those of the electrode prepared in NMP and with a PVDF binder.

3.2. Electrochemical impedance spectrum

Fig. 2 showed the experimental electrochemical impedance spectra (the dot lines) of the fully charged LiFePO₄ electrode prepared in NMP. The Nyquist plot of Fig. 2 showed a large semicircle from the high to medium frequencies and a nearly straight line at low frequencies. It has been reported that the impedance spectra of lithium ion intercalation as well as its de-intercalation in a cathode of lithium ion battery usually show three characteristic time constants, corresponding to the high, medium and low frequency range of impedance spectra, respectively, and can be fitted by an equivalent circuit as shown in Fig. 3 [22,23]. They characterized the lithium ion transport in the SEI, the charge transfer at the interface between SEI and LiFePO₄, and the intercalation or de-intercalation reaction of lithium ions in LiFePO₄ electrode, respectively. The solid lines in Fig. 2 represented the fitted results by the equivalent circuit of Fig. 3. It can be seen that the experimental impedance data can be well fitted by the equivalent circuit, indicating that the whole

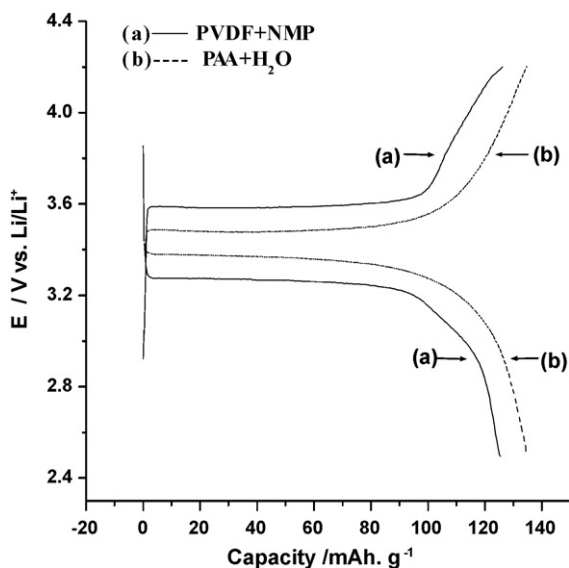


Fig. 5. Charge-discharge curves of LiFePO₄ electrodes in 1-M LiPF₆/EC:DMC:EMC (volume ratio = 1:1:1) in the first cycle. (a) The electrode was prepared in NMP with PVDF as a binder and (b) the electrode was prepared in the aqueous solvent with PAA as a binder.

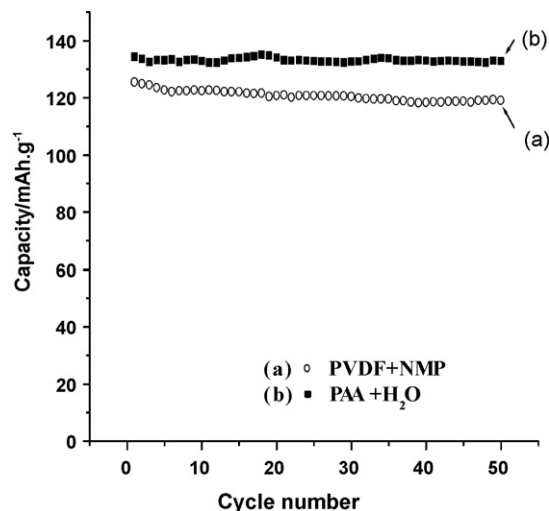


Fig. 6. Cyclic stability of LiFePO₄ electrodes in 1-M LiPF₆/EC:DMC:EMC (volume ratio = 1:1:1). (a) The electrode was prepared in NMP with PVDF as a binder and (b) the electrode was prepared in the aqueous solvent with PAA as a binder.

dynamic process of lithium ions follows the three-time constants model. Particularly, based on the fitting, the resistances of the SEI and the charge transfer of lithium ion intercalation/de-intercalation for the electrode prepared in NMP were found to be 180.2 and 385.4 Ω cm², respectively.

In Fig. 4, the electrochemical impedance spectra of both experiments (dot lines) and model fittings (solid lines) were shown for full charged LiFePO₄ electrode prepared in aqueous solvent. It can

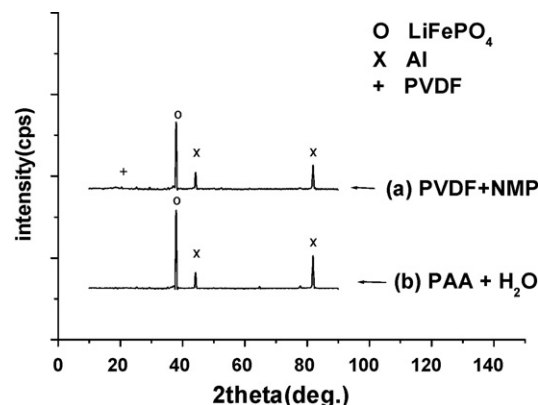


Fig. 7. XRD patterns of LiFePO₄ electrodes. (a) The electrode was prepared in NMP with PVDF as a binder and (b) the electrode was prepared in the aqueous solvent with PAA as a binder.

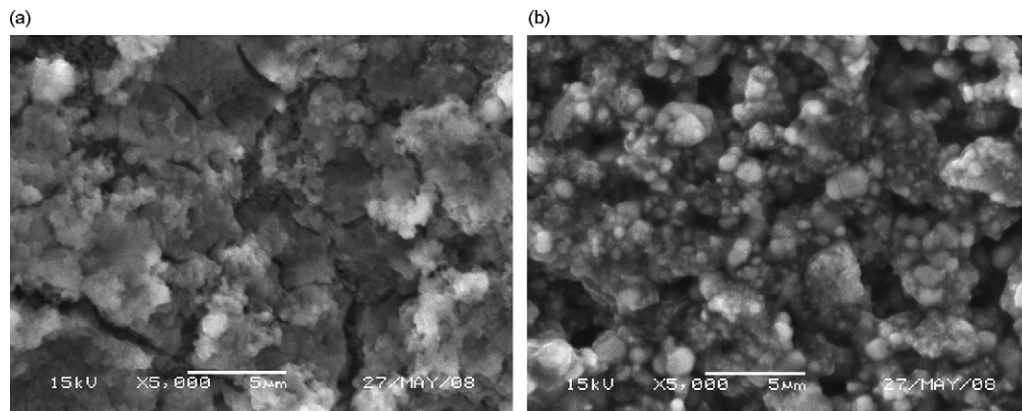


Fig. 8. SEM images of LiFePO₄ electrodes. (a) The electrode was prepared in NMP with PVDF as a binder and (b) the electrode was prepared in the aqueous solvent with PAA as a binder.

be seen that the experimental spectra can be well fitted with the equivalent circuit in Fig. 3. The Bode plot of Fig. 4 shows the frequency ranges for the three time constants, 10^{-2} to 0 Hz, 0 to 10^2 Hz and 10^2 to 10^5 Hz, respectively. It implied that the kinetic process of lithium ion intercalation or de-intercalation may not be influenced by the preparation solvent, i.e., H₂O or NMP. However, the value of kinetic parameters changed with the solvent. Specifically, based on the model fitting, the resistances of both the SEI and the charge transfer of lithium ion intercalation/de-intercalation for the electrode prepared in aqueous solvent were found to be 131.0 and 210.5 $\Omega \text{ cm}^2$, respectively, which were significantly different from those in NMP.

It is interesting to note that, for the electrode prepared in aqueous solvent, the resistances of both the SEI and the charge transfer of lithium ion intercalation/de-intercalation were smaller than those for the electrode prepared in NMP. It indicates that the electrode prepared in the aqueous solvent may have a less resistance SEI film and a faster charge transfer step than that prepared in NMP. However, because the solvents did not remain in the prepared electrode, the observed difference between the electrodes prepared in aqueous solvent and NMP may be ascribed to the binder, i.e. PAA and PVDF. Particularly, PAA may have some effects on the improvement of the charge transfer step of lithium ion in the intercalation/de-intercalation in LiFePO₄ electrode. These effects can be ascribed to the carbonyl group in PAA, which is similar to those in the solvent molecules, EC, DMC and EMC, and helps to set up a compatible interface between LiFePO₄ and electrolyte.

3.3. Charge–discharge performance

Fig. 5 showed the charge–discharge curves of the LiFePO₄ electrode prepared in both the aqueous solvent and NMP. It was clear that the electrode prepared in aqueous solvent showed better charge and discharge performances than that prepared in NMP, including a lower charge plateau potential, a higher discharge plateau potential, and a larger discharge capacity. Specifically, the discharge plateau potential is 3.37 V for the electrode prepared in aqueous solvent, while it is only 3.27 V for that prepared in NMP. Similarly, the charge plateau potential is 3.48 V for the electrode prepared in aqueous solvent, which is about 0.10 V lower than 3.58 V for that prepared in NMP. At the same time, the discharge capacity for the electrode prepared in aqueous solvent is 134.4 mAh g⁻¹, higher than 125.6 mAh g⁻¹ observed in the electrode prepared in NMP. Moreover, as shown in Fig. 5, both charge and discharge curves of two electrodes are almost in parallel with each other. These results indicate that, for the electrode prepared

in aqueous solvent, the increase in the capacity may come from the decrease in the polarization.

In addition, the electrode prepared in the aqueous solvent has a better cyclic stability than the electrode prepared in NMP, as shown in Fig. 6. Particularly, after 50 cycles, the capacity for the electrode prepared in aqueous solvent was 132.9 mAh g⁻¹, about 98.8% of its initial capacity, whereas for the electrode prepared in NMP, the capacity was 119.2 mAh g⁻¹, only about 94.9% of its initial capacity.

3.4. X-ray diffraction pattern

In Fig. 7, the XRD patterns for the electrode prepared in both aqueous solvent and NMP were shown. Both electrodes showed strong diffraction peaks at 38°, 44° and 82°, respectively. The peak at 38° can be ascribed to LiFePO₄ while the peaks at 44° and 82° can be ascribed to the current collector Al. There were weak diffraction peaks around 20.5° for the electrode prepared in NMP with PVDF as the binder, which can be ascribed to PVDF. However, there were no such diffraction peaks appearing in the electrode prepared in aqueous solvent, indicating that there is difference between two electrodes.

3.5. Surface morphology

The morphology of electrodes prepared in both aqueous solvent and NMP has been examined by SEM. The results were shown in Fig. 8. Before the SEM examination, both electrodes have been charged and discharged for 3 cycles. As shown in Fig. 8, there were cracks appeared in the electrode prepared in NMP with PVDF as a binder, but none have been found in the electrode prepared in the aqueous solvent with PAA as a binder. It is clear that PAA helps to form more compact electrode than PVDF, which can improve the cyclic stability of the electrode.

4. Conclusion

In this work, we report the preparation of LiFePO₄ cathode for lithium ion battery by using water as solvent and PAA as a binder, which is different from the conventional preparation method using NMP as the solvent and PVDF as a binder. The new preparation method has many advantages, comparing with the conventional method. The new method has a lower cost and more environmental friendly. It can enhance the stability of LiFePO₄ electrode, and in particular, reduce the polarization thereafter improve the battery performances. The improvement in performance can be ascribed to the binder PAA, which can reduce the resistances of the SEI and

the charge transfer of lithium ion intercalation or de-intercalation and help to form a more compact electrode.

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