



# Preparation and Electrochemical Properties of $\text{LiFePO}_4$ -PSS Composite Cathode for Lithium-ion Batteries

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In this study, we prepared  $\text{LiFePO}_4$ -poly (sodium 4-styrenesulfonate) (PSS) composite by the hydrothermal method and ball-milling process. Different wt% PSS were added to  $\text{LiFePO}_4$ . The cathode electrodes were made from mixtures of  $\text{LiFePO}_4$ -PSS: SP-270: PVDF in a weighting ratio of 70%: 25%: 5%.  $\text{LiFePO}_4$ -PSS powders were characterized by X-ray diffraction (XRD), and scanning electron microscopy (SEM). The electrochemical properties of  $\text{LiFePO}_4$ -PSS/Li batteries were analyzed by cyclic voltammetry, charge/discharge tests, and AC impedance spectroscopy. A Li/ $\text{LiFePO}_4$ -PSS battery with 4.75 wt% PSS shows the best electrochemical properties, with a discharge capacity of 128 mAh/g.

**Keywords:**  $\text{LiFePO}_4$ , PSS, Hydrothermal method, Poly (sodium 4-styrenesulfonate)

## 1. INTRODUCTION

In order to provide renewable green energy sources, many methods have been tried. Among these, the rechargeable Li ion battery has attracted a great amount of interest. A Li ion battery has the ability to store and reversibility release electric energy with high density. It is used in many fields, such as powered portable devices like mobile-phones or laptops, and power sources for electrical vehicles and hybrid electrical vehicles. The Lithium ion battery is one type of lithium transition metal oxide that can release oxygen from the crystal or irreversibility transfer phase, at elevated temperature [1,2]. In this respect, numerous studies have been carried out, in order to find a safe and stable cathode material, and also to try to improve the battery safety, and reduce its cost.

Among the known cathode materials, the  $\text{LiFePO}_4$  ordered olivine-type structure has been attractive, mainly due to its high theoretical specific capacity (~170 mAh/g) [3-5], high stability, low cost, and high compatibility with the environment [6,7]. But its low electronic conductivity ( $\sim 10^{-9}$  S/cm) [8] effect on initial

capacity loss, poor rate capacity, and very slow diffusion of  $\text{Li}^+$ , lead to limitations in its practical application. Many researchers have tried to solve these problems as follows: (1) coating with a conductive layer around the particles [9], (2) substituting the ionic in the materials [10], and (3) changing the particle properties, such as shape, size, texture and phase distribution [11].  $\text{LiFePO}_4$  can be synthesized by various methods, such as the sol-gel method [12], mechanical alloying [13], microwave processing [14], solid-state reaction method [3], emulsion-drying method [9], co-precipitation method [15], and hydrothermal method [16]. Compared with other methods, the hydrothermal synthesis has some advantages, such as simple synthesis process and low energy consumption. Ball-milling (using a planetary mono mill) is also a useful method for synthesizing cathode materials. Due to the very fine nature of the nanoparticles and their large specific surface area that is obtained by this method, the electronic conductivity of  $\text{LiFePO}_4$ -PSS composites can be improved.

Conducting polymers (e.g. polythiophene [17], polypyrrole (PPy) [18], polyaniline (PANI) [20], etc.) have been deeply researched, in order to improve the electronic conductivity of  $\text{LiFePO}_4$ , due to important properties of its: (1) high conductivity in the doped state, and (2) fast charge/discharge electron-transfer kinetics. In this work, we used PSS. PSS is an ionomer (a type of polymer) of polystyrene. Ionomers have unique physical properties, including electrical conductivity and isoviscosity - specifically, increase in ionomer solution viscosity with increasing temperature [19].

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In this study, LiFePO<sub>4</sub>-PSS composites were prepared by a hydrothermal method, and followed by ball-milling. Different PSS were added to improve the electronic conductivity of LiFePO<sub>4</sub> nanoparticles. LiFePO<sub>4</sub>-PSS/Li batteries were fabricated in an argon-filled glove box, and their electrochemical properties were analysed by scanning electron microscopy (SEM), X-ray diffraction (XRD), cyclic voltammetry (CV), and charge/discharge experiments.

## 2. MATERIALS AND METHODS

LiFePO<sub>4</sub>-PSS composites were prepared from starting materials of LiOH.H<sub>2</sub>O, FeSO<sub>4</sub>.7H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub>, and C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>. After LiOH.H<sub>2</sub>O was dissolved in 30 ml distilled water, H<sub>3</sub>PO<sub>4</sub> and FeSO<sub>4</sub> powder were added to LiOH solution in a molar ratio of Li: Fe: P= 3:1:1. Addition of C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> as a reducing agent was useful in preventing the conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup> and generation of α-Fe<sub>2</sub>O<sub>3</sub> during the heat treatment process. The mixture solution was filled in a Teflon obturation vessel (TAF-SR-50, TAIATSU TECHNO), and was sealed in a stainless steel autoclave, then heated at 170 °C for 12 h. After cooling down to ambient temperature, the solutions were filtered, to separate the precipitate powders. The obtained powders were dried at 110 °C for 1h under vacuum. Then, different wt% PSS (0%, 2.91%, 4.75%, 7.36%) were added to LiFePO<sub>4</sub>, and milled at 300 rpm for 10 h. The obtained powders were pelleted, and further heated at 500 °C for 1h in a tubular oven, under dry argon flow. After cooling down to room temperature, the LiFePO<sub>4</sub>-PSS composites were ball-milled again for 10h. Finally, the mixture was dried at 90 °C for 12 h.

The X-ray diffraction (XRD) measurement was carried out on a high resolution X-ray Diffractometer using a Cu Kα radiation source (λ=1.5406 Å), with a step size of 4° min<sup>-1</sup> from 10° to 50°. The morphology of LiFePO<sub>4</sub>-PSS cathode was characterized by Cold Field Emission scanning electron microscope (FE-SEM).

The composite electrodes were made from mixtures of as-prepared LiFePO<sub>4</sub>-PSS with SP-270, polyvinylidene fluoride (PVDF) in a weighting ratio of 70%: 25%: 5%. After being ball-milled, the slurry was coated onto aluminum foil, and dried at 90 °C for 1 h before roll-pressing. Then the electrodes were cut into 2×2 cm<sup>2</sup> sections and dried again at 110 °C for 24 h under vacuum. The beaker-type batteries were assembled in an argon-filled glove box, using lithium as the anode, and 1 M LiPF<sub>6</sub>-EC/DMC (1:1) as the electrolyte. The electrochemical properties of LiFePO<sub>4</sub>-PSS/Li batteries were analyzed by charge/discharge tests (WBCS3000, WonATech) in the potential range of 2.0-4.5 V at room temperature and cyclic voltammetry, with scan rate of 0.1 mV s<sup>-1</sup> from 2.3 to 4.5 V. To investigate the interface properties and resistance of cell when charging/discharging, the electrochemical impedance was measured, with frequencies ranging from 10 mHz to 2 MHz.

## 3. RESULTS AND DISCUSSIONS

The XRD patterns of LiFePO<sub>4</sub>-PSS nanoparticles with different wt% PSS conductive additives are shown in Fig. 1. All the patterns can be indexed to a single-phase material, having an orthorhombic olivine-type structure with a space group of Pnma. This is the same as the X-ray powder diffraction data file (JCPDS card number 81-1173) by the American Society for Testing Materials that we call standard. The unit cell parameters for the LiFePO<sub>4</sub> sample are: a = 10.3494 Å, b = 6.0359 Å, c = 4.6999 Å and V = 293.5949 Å<sup>3</sup>. The unit cell parameters of the other samples can be seen in Table 1 below, with the best value of LiFePO<sub>4</sub> being 4.75 wt% PSS. Its unit cell parameter is a = 10.375 Å, b = 5.9730 Å, c = 4.6921 Å, and the unit cell V = 290.7677 Å<sup>3</sup>. The XRD results dem-

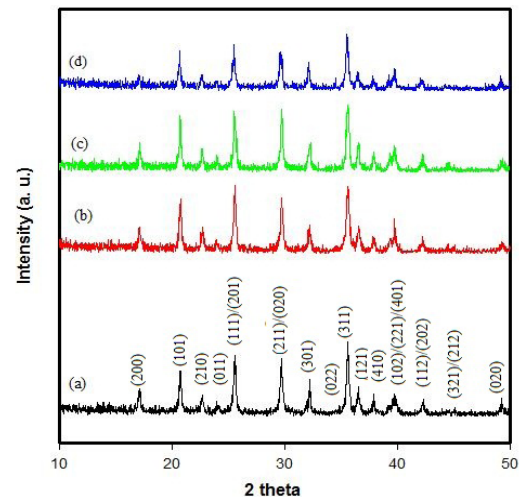


Fig. 1. XRD patterns for LiFePO<sub>4</sub>-PSS composites with: (a) 0%, (b) 2.91%, (c) 4.75%, (d) 7.36% wt. PSS.

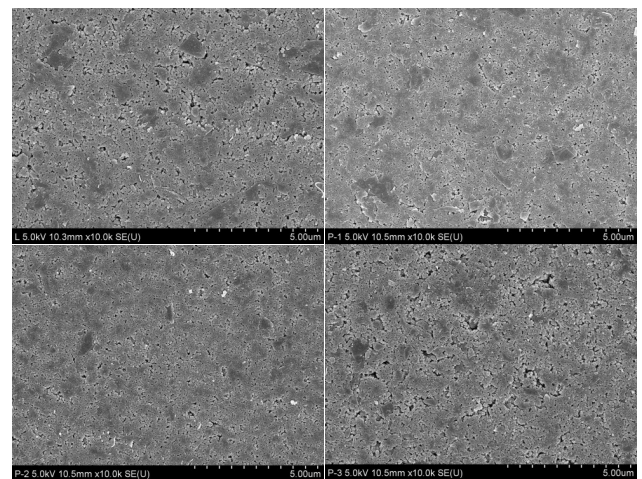


Fig. 2. FE-SEM images of LiFePO<sub>4</sub>-PSS cathode with: (a) 0%, (b) 2.91%, (c) 4.75%, (d) 7.36% wt. PSS.

Table 1. The unit cell parameters of LiFePO<sub>4</sub>-PSS composites.

Specimen	a (Å)	b (Å)	c (Å)	V(Å <sup>3</sup> )
0%	10.3494	6.0359	4.6999	293.4959
2.91%	10.3504	6.0268	4.7054	293.5215
4.75%	10.375	5.9730	4.6921	290.7677
7.36%	10.4202	5.9985	4.7051	294.0915

onstrate that the only phase observed is LiFePO<sub>4</sub>. No impurity was found in the LiFePO<sub>4</sub>-PSS powders. This demonstrates that the PSS-added samples do not change the crystal structure of LiFePO<sub>4</sub> nanoparticles.

The images of LiFePO<sub>4</sub>-PSS electrodes are shown in Fig. 2. LiFePO<sub>4</sub>-PSS electrodes consist of LiFePO<sub>4</sub>-PSS powders, PVdF, and SP-270. In Fig. 2(a), we can recognize the existence of LiFePO<sub>4</sub>, with conductive material SP-270, and binder PVDF. When making film with conductive material PVdF and binder SP-270, many pores appear. As more pores appear, the movement of electrons is resisted; and as the pore size increases, the charge-discharge efficiency decreases. Since PSS is added, the pore appearance is smaller, and they get clogged. This means that PSS is stuck on the surface of LiFePO<sub>4</sub>, and forms a layer around the

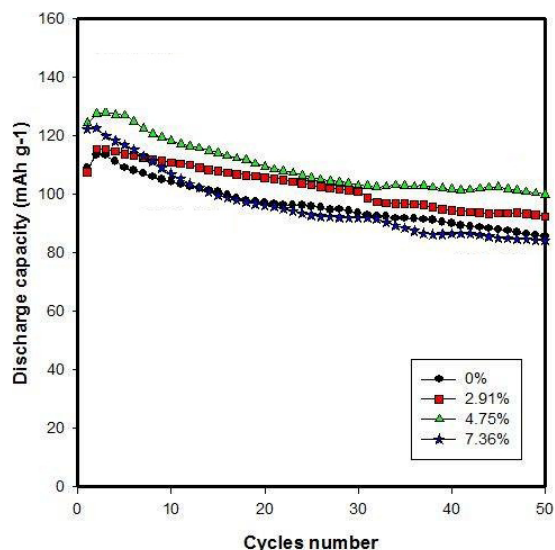


Fig. 3. Cycling performances of Li/LiFePO<sub>4</sub>-PSS batteries.

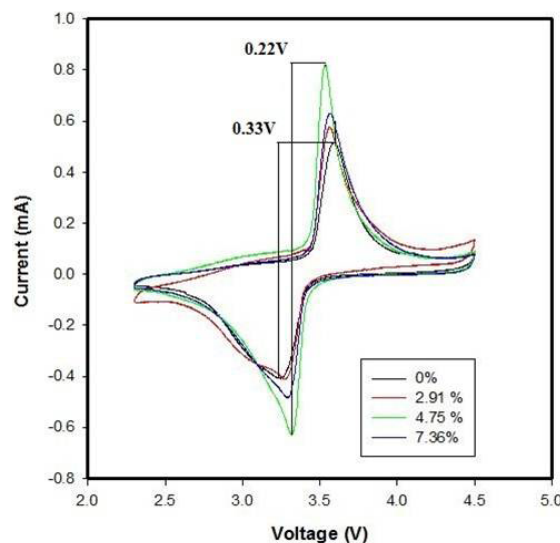


Fig. 4. Cyclic voltammograms of Li/LiFePO<sub>4</sub>-PSS batteries with different wt% PSS additives at 3<sup>rd</sup> cycle.

surface of the LiFePO<sub>4</sub> particles. This is helpful to increase reversibility and electronic conductivity of LiFePO<sub>4</sub>. To prove these assumptions, the electronic conductivities of LiFePO<sub>4</sub>-PSS electrodes are measured. The results confirm that the electronic conductivity of LiFePO<sub>4</sub>-PSS electrodes are improved from  $1.09 \times 10^{-9}$  S/cm of pure LiFePO<sub>4</sub> to  $2.75 \times 10^{-4}$  S/cm,  $2.47 \times 10^{-3}$  S/cm,  $4.32 \times 10^{-3}$  S/cm of LiFePO<sub>4</sub> with 2.91 wt%, 4.75 wt%, 7.36 wt% PSS, respectively.

Figure 3 shows the cycling performances of Li/LiFePO<sub>4</sub>-PSS batteries. As shown in Fig. 3, the Li/LiFePO<sub>4</sub>-PSS batteries with 2.91 wt%, 4.75 wt%, 7.36 wt% PSS show cycling performance at 2<sup>nd</sup> cycle with discharge capacities of 115.4 mAh/g, 128 mAh/g, 122.5 mAh/g; and discharge capacities of 92.4 mAh/g, 100.39 mAh/g, 84.4 mAh/g, respectively, after 50 cycles. In the meantime, the discharge capacity of pure Li /LiFePO<sub>4</sub> battery at 2<sup>nd</sup> cycle is 113.48 mAh/g, and at 50<sup>th</sup> cycle is 86 mAh/g. The discharge capacity of LiFePO<sub>4</sub> with 4.75 wt% PSS showed the best discharge capacity. This was considerably increased, due to the increase in electronic conductivity and specific surface area, and decrease in average crystal size when adding different PSS contents.

The cyclic voltammograms of LiFePO<sub>4</sub>-PSS/Li batteries with different PSS conductive additives at 3<sup>rd</sup> cycle are shown in Fig. 4. As for CV, the voltage difference between oxidation peak and reduction peak is an important parameter in valuing the electrochemical reaction reversibility [20].

As shown in Fig. 4, the oxidation and reduction peaks in the 3<sup>rd</sup> cycle appear at around 3.59 and 3.24 V, respectively. The voltage difference between the two peaks is 0.35 V. However, in the case of Li/LiFePO<sub>4</sub>-PSS with 4.75 wt% PSS, the oxidation and reduction peaks in the 3<sup>rd</sup> cycle appear at around 3.54 and 3.32 V, respectively. The voltage difference between the two peaks is 0.22 V. Meanwhile, the redox peak profiles of Li/LiFePO<sub>4</sub>-PSS batteries with 4.75 wt% PSS are more symmetric than that of the LiFePO<sub>4</sub>/Li battery. This demonstrates that the reversibility and reactivity of Li/LiFePO<sub>4</sub>-PSS batteries are better than that of LiFePO<sub>4</sub>/Li batteries.

The impedance spectra of Li/LiFePO<sub>4</sub>-PSS batteries with different wt% PSS after 3 cycles are shown in Fig. 5. As can be seen from Fig. 5, the resistance of Li/LiFePO<sub>4</sub>-PSS batteries with 0 wt%, 2.91wt%, 4.75 wt%, and 7.36 wt% is 283 Ω, 155 Ω, 150 Ω, 175 Ω, respectively. This is consistent with the results of Fig. 4. This phenomenon can be explained in terms of the electric polarization due to an increase in the IR drop, where I is the current

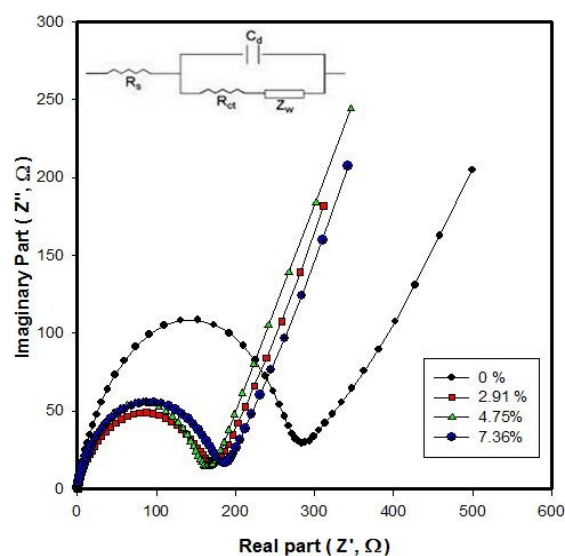


Fig. 5. Impedance spectra of Li/LiFePO<sub>4</sub>-PSS batteries with different wt% PSS after 3 cycles.

passing the battery and R is the battery impedance.

## 4. CONCLUSIONS

LiFePO<sub>4</sub>-PSS composites have been synthesized successfully, by a hydrothermal method, and subsequent ball-milling. To improve the low electronic conductivity of LiFePO<sub>4</sub>, different PSS additives were added. The XRD results demonstrate that LiFePO<sub>4</sub>-PSS composites have an orthorhombic olivine-type structure, with a space group of Pnma. A Li/LiFePO<sub>4</sub>-PSS battery with 4.75 wt% PSS shows the best electrochemical properties, with the highest discharge capacity of 128 mAh/g, and the smallest voltage between the reduction peak and oxidation peak of 0.22 V, the smallest resistance of 150 Ω, and high electronic conductivity of  $2.47 \times 10^{-3}$  S/cm.

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