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Highly oriented LiFePO₄ thin-film electrodes were fabricated via chemical solution deposition combined with spin coating. The effects of the precursor concentrations and types of substrates on microstructures and electrochemical performances were studied. Single-phase LiFePO₄ with orientations perpendicular to the (211)/(020) and (311) planes prepared using stainless steel as substrate presents the capacity of 4.9 $\mu\text{Ah}\cdot\text{cm}^{-2}$ and the apparent activation energy of 59.2 $\text{kJ}\cdot\text{mol}^{-1}$, indicating its great potential to be used as cathode material for lithium thin film batteries.

Keywords

chemical, via, electrodes, deposition, film, solution, thin, lifepo₄, oriented, highly

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Li, Q., Chou, S., Wang, J., Shi, D. & Liu, H. (2014). Highly oriented LiFePO₄ thin film electrodes via chemical solution deposition. *Solid State Ionics*, 268 (Part A), 117-124.

Highly oriented LiFePO₄ thin film electrodes via chemical solution deposition

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Abstract

Highly oriented LiFePO₄ thin-film electrodes were fabricated via chemical solution deposition combined with spin coating. The effects of the precursor concentrations and types of substrates on microstructures and electrochemical performances were studied. Field-emission scanning electron microscopy, X-ray diffraction, Raman spectroscopy, and X-ray photoelectron spectroscopy were employed to characterize the morphology, the crystal structure, the chemical composition, and the element valence states. The electrochemical behaviour was studied by means of cyclic voltammetry, charge/discharge cycling, and electrochemical impedance spectroscopy. Single-phase LiFePO₄ with orientations perpendicular to the (211)/(020) and (311) planes prepared using stainless steel as substrate presents the capacity of 4.9 $\mu\text{Ah}\cdot\text{cm}^{-2}$ and the apparent activation energy of 59.2 $\text{kJ}\cdot\text{mol}^{-1}$, indicating its great potential to be used as cathode material for lithium thin film batteries.

Keywords: LiFePO₄; thin film; chemical solution deposition; Li-ion battery; cathode materials

1. Introduction

Olivine-type LiFePO_4 is one of the most promising cathode materials for Li-ion batteries due to its flat voltage plateau, moderate theoretical specific capacity, good thermal stability, long cycling life, environmental friendliness, cost effectiveness, and safety in operation [1-5]. In spite of these advantages, however, olivine LiFePO_4 has the intrinsic drawbacks of low electronic conductivity and low Li^+ diffusion mobility, which limit its high-rate performance [6, 7]. Several innovative approaches have been reported to enhance the rate capability in LiFePO_4 bulk electrodes, such as carbon coating [8-10], reducing the particle size [11-13], and doping [14-16].

Fabrication of LiFePO_4 thin film has attracted great interest for both fundamental research and applications. First, thin film electrodes can be employed as a simplified model for understanding the electrochemical activities of deposited active materials, because they are binder and conductive additive free, and they have good contact with the current collector as well as a controllable geometry [4, 17]. Second, LiFePO_4 thin film is an ideal positive electrode utilized in all-solid-state thin film batteries, which have a range of prospective applications, such as non-volatile memories, remote sensors, smart cards, and implantable medical devices [18, 19]. Moreover, for both objectives, thin film electrodes can naturally suppress the intrinsic drawbacks of LiFePO_4 because the thickness has been reduced to a value at which the transport and diffusion of electrons and ions can take place instantly through the very thin electrodes [20, 21].

Recently, there have been a few reports on the growth of LiFePO_4 thin films via pulsed laser deposition (PLD) [4, 17, 19, 21-27], radio-frequency magnetron sputtering (RFMS) [5, 18, 28,

29], and electrostatic spray deposition (ESD) [30]. To the best of our knowledge, however, chemical solution deposition (CSD) combined with the spin-coating technique has never been employed to produce LiFePO_4 thin film. The challenge is due to the critical requirements on the coating solution, which must be a homogeneous solution or sol without any visible suspension, but have appropriate surface tension, polarity, and viscosity corresponding to the relevant substrate.

In the present work, we first developed a cost-effective approach involving CSD combined with spin coating to simply fabricate LiFePO_4 thin films without using any high-cost equipment, such as PLD or RFMS systems. The appropriate coating solution was achieved by the solvent-in-gel (SIG) processing route [31], which successfully resolved the issue of the insolubility of metal phosphates in methanol. The morphology, the crystal structure, and the electrochemical behaviour of the LiFePO_4 thin films prepared on two different substrates and with various precursor concentrations were studied.

2. Experiment

The fabrication process consists of 3 steps: preparing the precursor solution, coating the substrate to form the wet film, and the heat-treatment. Firstly, lithium phosphate monobasic (LiH_2PO_4 , 99%, Aldrich) and iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 98\%$, Sigma-Aldrich) were dissolved in deionized water with an element ratio of $\text{Li}:\text{Fe}:\text{P} = 1:1:1$, followed by stirring for 1 h at ambient temperature. The brown solution was then transferred to an evaporator to remove the water with gentle distilling. For refinement, the resultant brown gel was washed with methanol (CH_3OH , anhydrous 99.8%, Sigma-Aldrich) and vacuum distilled 3 times. The final coating solution was achieved by adding methanol to obtain the desired concentrations of LiFePO_4 (0.5, 0.75, and 1.0 M). Figure 1 shows the process of preparing

the LiFePO_4 precursor solution by the SIG method. Metal phosphates, such as LiH_2PO_4 , cannot thoroughly dissociate in methanol, resulting in insolubility; however, they are easily ionized in water, leading to a soluble state, which remains stable even if the solution is distilled to become a gel, because residual H_2O molecules still separate the ions to prevent precipitation. Then, methanol molecules substitute for the H_2O during refinement to form a usable solution for spin coating.

Figure 1. Process for preparing coating solution for LiFePO_4 thin films.

To improve the wetting performance between the coating solution and the substrates, the nickel-tungsten (Ni-W, 5% tungsten in nickel, THEVA) substrates were pre-treated in argon/hydrogen (5%) atmosphere at 800 °C for 1 h, and single crystal LaAlO_3 (LAO, MTI) substrates were pre-treated by ultrasonic washing in ethanol for 5 min, while stainless steel (SS, common spacer of coin cell) substrates can be soaked well by the precursor without any pre-treatment. Thin film deposition was carried out by spin coating on these substrates at the rate of 4,000 rpm for 1 min. The wet films were baked on a hot-plate at 80 °C. The thin film

grown on LAO substrate was only employed for thickness measurements. Finally, the precursor films were slowly pyrolyzed up to 400 °C with a ramp rate of 2 °C·min⁻¹ in an argon atmosphere to form the amorphous films, which then were annealed at 600 °C in a flowing argon/hydrogen (5%) gas mixture with a 60 min dwell time to achieve LiFePO₄ thin-film electrodes. The chemical reaction is as follows:

The surface morphology was characterized by field-emission scanning electron microscopy (FESEM, JEOL JSM-7500FA). The crystal structure and phase of the thin films were identified by X-ray diffraction (XRD, GBC MMA diffractometer) with a Cu K_α source. Raman spectra were collected by a Jobin Yvon HR800 Raman spectrometer with a 10 mW helium/neon laser at 632.8 nm excitation. The film thickness was estimated by using FESEM as well, through observing the cross-sections of thin-film samples deposited on LAO substrate with precursor concentrations of 0.5 and 0.75 M. The element valence of Fe on the surface of LiFePO₄ thin films was verified by X-ray photoelectron spectroscopy (XPS). The XPS was conducted using a SPECS PHOIBOS 100 Analyser installed in a high-vacuum chamber with base pressure below 10⁻⁸ mbar. X-ray excitation was provided by Al K_α radiation with photon energy $h\nu = 1486.6$ eV at the high voltage of 12 kV and power of 120 W. XPS binding energy spectra were collected with the pass energy of 20 eV in the fixed analyser transmission mode.

For the electrochemical measurements, 2032-type coin cells were constructed using LiFePO₄ thin films as the working electrodes and pieces of lithium foil as the counter and reference electrodes. The electrolyte was 1 M LiPF₆ in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1, and the separator was porous

polypropylene film. The cells were assembled in an argon-filled glove box. Cyclic voltammograms (CVs) were collected on a Biologic VMP3 electrochemical workstation at a sweep rate of $0.05 \text{ mV}\cdot\text{s}^{-1}$ over the voltage range of 3.0 to 3.8 V. The cycling performance was tested under galvanostatic conditions by a Land Battery Test System in a voltage window from 3.0 to 3.8 V (vs. Li/Li^+). The electrochemical impedance spectroscopy (EIS) measurements were carried out on a PARSTAT 2273 advanced electrochemical system over a frequency range of 0.01 Hz to 1 MHz at the 50% discharge stage.

3. Results and Discussion

FESEM images of the surfaces of LiFePO_4 thin films fabricated on different substrates are shown in Figure 2. It can be seen that no more continuously smooth films were formed on either substrate when the concentration of coating solution reached 1.0 M, as shown in Fig. 2(e) and (f). Therefore, only the thin films fabricated from the precursor concentrations of 0.5 and 0.75 M can be candidates for thin-film electrodes. Fig. 2(a)-(d) shows the surface morphology of the films grown with 0.5 and 0.75 M precursor. The surface-grain size distribution runs from less than one hundred to several hundred nanometres on these samples. In contrast to the formation of granular pellets on SS substrate, many particles have irregular shapes on Ni-W substrate. Furthermore, from the enlarged FESEM images, as shown in the corresponding insets, the particles observed at low magnification are actually aggregated from smaller grains ($\sim 10 \text{ nm}$) on Ni-W substrate, while the same microstructure cannot be found on SS substrate. The results indicate that the LiFePO_4 films on Ni-W substrates may have larger specific surface area than those on SS substrates. Therefore, the surface morphologies of the LiFePO_4 films were altered very little by changing the concentration of the coating solution (below 0.75 M), but varied considerably if the films were deposited on different substrates.

Figure 2. SEM images of LiFePO_4 thin films deposited from 0.5 M (a, b), 0.75 M (c, d), and 1.0 M (e, f) precursor solutions on Ni-W (a, c, and e) and SS (b, d, and f) substrates, respectively. The insets are high magnification images showing the microstructure of the particles on the film surfaces.

Figure 3 shows the X-ray diffraction patterns of LiFePO_4 thin films on different substrates. The reference blank substrates experienced the same heat-treatment as the thin-film samples.

The samples deposited from 0.5 and 0.75 M coating solutions show highly preferred orientations, resulting in much fewer diffraction peaks compared with LiFePO_4 powder (JCPDS 83-2092). The samples follow a trend of random orientations when the precursor concentration reaches 1.0 M. When the precursor concentration is increased from 0.5 to 0.75 M, the sole peak indexed to the [420] direction becomes two peaks assigned to the [420] and [321] directions on Ni-W substrate; however, the two peaks corresponding to the [211]/[020] and [311] directions remain almost invariable on SS substrate. This difference is probably attributable to the substrate contributions, since the other preparation conditions were the same. The direction along the b -axis, namely, the [010] orientation, has been considered to have the lowest activation energy for lithium ion migration in the model of either one- or two-dimensional (1D or 2D) ion diffusion in orthorhombic olivine-type LiFePO_4 with the following lattice parameters: $a = 10.334 \text{ \AA}$, $b = 6.01 \text{ \AA}$, and $c = 4.693 \text{ \AA}$ [23, 32-34]. Although our samples are not purely [010] oriented, they can be used as thin film electrodes, to investigate electrochemical activities depending on the crystal orientation of the thin-films.

Figure 3. XRD patterns of the LiFePO_4 thin films deposited from 0.5, 0.75, and 1.0 M precursor solutions on Ni-W substrate (a) and SS substrate (b), and the XRD patterns of their corresponding substrates, respectively. The substrates were processed under the same heating sequence as the thin-film samples.

Raman spectra of the substrates and the films are shown in Figure 4. The peaks at 680, 950, 1330, and 1600 cm^{-1} can be attributed to magnetic Fe_3O_4 , symmetric PO_4 in LiFePO_4 , and the D and G bands of carbon, respectively [17, 35]. For the films on Ni-W substrate, the Fe_3O_4 peak rises with increased concentration of the coating solution, indicating that a thicker film has more possibility of forming substoichiometric $[(1-x)\text{LiFePO}_4 + x\text{FePO}_4]$ phase [36, 37]. The sharp PO_4 peaks demonstrate the existence of high-quality LiFePO_4 phase, while the absence of the two peaks belonging to the D and G bands of carbon implies that the coating solution produces carbon-free thin films, which can be used to investigate the intrinsic electrochemical properties of LiFePO_4 . In the case of the SS substrates, however, the strong background of Fe_3O_4 and carbon from the stainless steel has obscured most information on the LiFePO_4 thin films prepared on them. It can be inferred that carbon-free LiFePO_4 thin films were also formed on SS substrate due to the detection of small PO_4 peaks, and the reduction in the carbon peaks with greater film thickness.

Figure 4. Raman spectra of the LiFePO_4 thin films deposited from 0.5 and 0.75 M precursor solutions on Ni-W substrate (a) and SS substrate (b), and the Raman spectra of their

corresponding substrates, respectively. The substrates were subjected to the same heating sequence as the thin-film samples.

Figure 5 shows the Fe 2p XPS spectra for the LiFePO₄ films deposited from 0.5 M precursor solution on Ni-W and SS substrates. The Fe 2p spectra are split into two peaks because of spin orbit coupling, namely, Fe 2p_{3/2} and Fe 2p_{1/2}, with a theoretical area ratio of 2 [38]. For the Fe²⁺ and Fe³⁺ ions, the 2p_{3/2} peak position corresponds to the binding energy of ~710 and ~712 eV, and the 2p_{1/2} peak position corresponds to ~724 and ~726 eV, respectively [38]. Thus, both LiFePO₄ films contain some Fe³⁺ impurities, which could exist in Fe₃O₄ and/or FePO₄ phase according to the Raman spectra. Moreover, the Fe 2p peaks are shifted more to the left on Ni-W substrate than on SS substrate, implying higher Fe³⁺ content in the sample, which could be attributed to the larger specific surface area, as shown in Figure 2.

Figure 5. High-resolution Fe 2p XPS spectra of LiFePO₄ films deposited from 0.5 M precursor solution on Ni-W and SS substrates.

Since it is hard to obtain a sharp, straight, and undamaged edge on the metal substrates, thin-film samples deposited on LAO substrate were utilized to measure the film thickness via

cross-sectional views. Cross-sectional SEM images of the LiFePO_4 films prepared from the 0.5 and 0.75 M coating solutions on LAO substrate are shown in Figure 6. Both films are dense with a few pores. The thicknesses of these films are about 155 and 225 nm, corresponding to the films prepared from the 0.5 and 0.75 M precursor solutions, respectively. The results demonstrate that the thickness is almost proportional to the precursor concentration. It should be noted, however, that the measured result only can be an estimated value for the film thickness on other substrates, because this can vary depending on the surface roughness and the surface energy of different substrates.

Figure 6. SEM images of the cross-sections of LiFePO_4 films deposited from 0.5 M (a) and 0.75 M (b) precursor solutions on LAO substrate.

Cyclic voltammograms (CVs) of the thin-film electrodes prepared from the 0.5 and 0.75 M precursor solutions on Ni-W and SS substrates are shown in Figure 7. The CVs were collected in the voltage range from 3.0 to 3.8 V at a scan rate of $0.05 \text{ mV} \cdot \text{s}^{-1}$, using Li metal as both counter and reference electrode in the coin cells. All of the curves exhibit a unique and explicit pair of anodic (lithium ions extracted from the film) and cathodic (lithium ions inserted into the film) peaks at 3.4 and 3.5 V, implying the characteristic redox reaction belonging to single-phase LiFePO_4 [1, 39]. The ratio of the anodic to the cathodic peak current density is close to 1 for every sample, indicating good reversibility and high

coulombic efficiency. The higher concentration of coating solution results in a comparable enhancement of the redox peak current density on both substrates, probably due to more concentrated precursor leading to thicker films, as shown in Figure 6.

Figure 7. Cyclic voltammograms of LiFePO_4 thin-film electrodes prepared from 0.5 M (solid line) and 0.75 M (dashed line) precursor solutions on Ni-W substrate (a) and SS substrate (b) at a scan rate of $0.05 \text{ mV} \cdot \text{s}^{-1}$.

The charge/discharge profiles of the LiFePO_4 thin-film electrodes prepared from 0.75 M precursor solution on Ni-W and SS substrates are shown in Figure 8(a) and (b). The galvanostatic measurements were conducted at a current density of $2 \text{ } \mu\text{A} \cdot \text{cm}^{-2}$. Both electrodes display the typical electrochemical features of olivine-type LiFePO_4 with straightforward and flat charge and discharge plateaus at around 3.45 and 3.40 V. The highest discharge capacities are 5.0 and $4.9 \text{ } \mu\text{Ah} \cdot \text{cm}^{-2}$ on Ni-W and SS substrates, respectively. For both electrodes, the coulombic efficiency for the initial cycle and for the second cycle is about 55% and more than 85%, respectively. The low initial coulombic efficiency was also reported for the thin-film LiFePO_4 samples prepared by either pulsed laser deposition or electrostatic spray deposition [4, 19, 30]. The irreversible capacity loss in the first cycle is mainly attributed to the impurities that have been described in the Raman and XPS sections. Compared with the electrode on Ni-W substrate, the electrode on SS substrate shows more

stable cycling capacity and smaller polarization. Figure 8(c) and (d) shows the rate capabilities of the electrodes. The retention of capacities remains 76% and 80% for the electrodes on Ni-W and SS substrates, respectively, after a 5-fold enhancement of current density from 2 to 10 $\mu\text{A}\cdot\text{cm}^{-2}$.

Figure 8. Charge/discharge profiles of the LiFePO₄ thin-film electrodes prepared from 0.75 M precursor solution on Ni-W (a) and SS (b) substrates. The charge/discharge current density was fixed at 2 $\mu\text{A}\cdot\text{cm}^{-2}$. Rate capabilities of the LiFePO₄ thin-film electrodes prepared from 0.75 M precursor solution on Ni-W (c) and SS (d) substrates. The current density range is from 2 to 10 $\mu\text{A}\cdot\text{cm}^{-2}$.

To investigate the electrode kinetics, the apparent activation energies of LiFePO₄ thin-film electrodes were calculated from electrochemical impedance spectra (EIS) using a previously

reported method [40, 41]. Figure 9 shows the Nyquist plots of the thin-film electrodes prepared from 0.5 and 0.75 M precursor solutions on Ni-W and SS substrates at various temperatures. The plots were collected at frequencies from 1 MHz to 10 mHz at a cathodic potential of 3.4 V versus Li/Li⁺ for different temperatures after charge-discharge for 10 cycles. The impedance curves show one compressed semicircle in the medium-frequency region, which could be assigned to charge-transfer resistance (R_{ct}), and an inclined line in the low-frequency region, which could be considered as Warburg impedance. The R_{ct} can be calculated using the equivalent circuit shown in the insets of Figure 9. The exchange current (i_0) and the apparent activation energy (E_a) for the lithium insertion into the LiFePO₄ films can be calculated from Equations (2) and (3), respectively.

$$i_0 = RT / nFR_{ct} \dots\dots(2)$$

$$i_0 = A \exp(-E_a / RT) \dots\dots(3)$$

where R is the gas constant, T is the absolute temperature, n is the number of transferred electrons corresponding to one ion migration, F is the Faraday constant, and A is a temperature independent coefficient. Figure 10 shows the Arrhenius plots of $\log i_0$ as a function of $1/T$. The activation energies ($E_a = -Rk \cdot \ln 10$, where k = the slope of the fitting line in Figure 10) of the LiFePO₄ thin-film electrodes are calculated to be 75.2 kJ·mol⁻¹ (0.5 M precursor, on Ni-W), 86.3 kJ·mol⁻¹ (0.75 M precursor, on Ni-W), 61.3 kJ·mol⁻¹ (0.5 M precursor, on SS), and 59.2 kJ·mol⁻¹ (0.75 M precursor, on SS), respectively. The activation energy is comparable to the previously reported value in the data for single crystal LiFePO₄, in which the activation energies reported for ionic conductivities were in the range of 59.6 - 71.2 kJ·mol⁻¹ (0.62 - 0.74 eV) [42]. For our data, the large difference in E_a between electrodes on different substrates can be attributed to the combined effect from the films' surface morphologies and crystal orientations; whereas, differences in E_a on the same substrate are possibly due to the films' texture, namely, the lattice orientation. As shown in

Figure 3, with a greater concentration of coating solution, a film that has a single orientation with respect to the [420] direction becomes a doubly oriented film with respect to the [420] and [321] directions, resulting in an E_a gap as large as $\sim 11 \text{ kJ}\cdot\text{mol}^{-1}$ on Ni-W substrate; however, the films with stable out-of-plane orientation along the [211]/[020] and [311] directions exhibit an E_a gap as small as $\sim 2 \text{ kJ}\cdot\text{mol}^{-1}$ on SS substrate. Single-phase LiFePO_4 with orientations perpendicular to the (211)/(020) and (311) planes on stainless steel substrate shows the lowest apparent activation energy of $59.2 \text{ kJ}\cdot\text{mol}^{-1}$, indicating its great potential to be used as cathode material for lithium thin film batteries.

Figure 9. Nyquist plots of the LiFePO_4 thin-film electrodes prepared from 0.5 M (a, b) and 0.75 M (c, d) precursor solutions on Ni-W substrate (a, c) and SS substrate (b, d) at a cathodic

potential of 3.4 V (vs. Li/Li^+) for different temperatures at frequencies from 1 MHz to 10 mHz.

Figure 10. Arrhenius plots of $\log i_0$ versus $1/T$ for the LiFePO_4 thin-film electrodes deposited from 0.5 and 0.75 M precursor solutions on Ni-W (a) and SS (b) substrates at a cathodic potential of 3.4 V (vs. Li/Li^+). The solid lines are the linear fitting results.

4. Conclusions

Single-phase LiFePO_4 thin-film electrodes were successfully fabricated by a simple and cost-effective CSD method. The breakthrough was in preparing an appropriate spin-coating solution by the SIG process. On different substrates, LiFePO_4 thin films showed different surface morphologies and lattice orientations, both of which had an impact on the kinetic behaviour of the electrodes. When the concentration of the coating solution varied within a certain range, the microstructure did not change to any significant extent, whereas the film's texture could change, depending on the substrate. If the orientation showed an obvious difference, the apparent activation energy could also be considerably altered, implying anisotropic Li^+ diffusion in olivine LiFePO_4 .

Acknowledgements

This work is supported by the Australian Research Council through a Linkage Project (LP120200432) and a Discovery Project (100103909). The authors would like to also thank Dr Tania Silver for critical reading of the manuscript.

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