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ELECTROCHEMICAL STUDIES OF THE LiFePO₄ THIN FILMS PREPARED WITH PULSED LASER DEPOSITION

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ABSTRACT

Thin films of LiFePO₄ have been prepared on stainless steel substrates with pulsed laser deposition utilizing an Ar atmosphere. Films were characterized with XRD, SEM, Raman spectroscopy and electrochemistry in liquid electrolyte. Raman spectral analysis revealed the presence of carbon in the films, even though the targets contained less than a few percent residual carbon. The Raman spectra also suggest the presence of various iron oxide species on the surface of the film. The 75nm film showed reversible cycling of more than 90 mAh/g for 60 cycles and a coulombic efficiency close to 1. Variable sweep rate cyclic voltammetry showed a diffusion-controlled reaction with an effective diffusivity of about 10^{-12} cm²/s. The performance of the thicker film was poor with a coulombic efficiency much less than 1.

INTRODUCTION

There has been considerable interest in LiFePO₄ as a cathode active material in Li-ion cells because of its superior cost, safety, stability and low toxicity. The major drawback has been the low capacities achievable at even moderate discharge rates. The poor performance is due to 1) limited electronic conductivity, 2) slow Li⁺ transport and/or 3) slow interface movement of the LiFePO₄-FePO₄ two-phase interface (1). LiFePO₄ cathodes showing good high-rate performance have been developed by using very small particles of LiFePO₄ together with large quantities of conductive carbon in the matrix (2-6). The role of the carbon in the two-phase reaction is extremely important and not well understood. As with most cathode-active materials, it is nearly impossible to prepare and study porous electrodes without the influence of the conductive carbon, since electrochemical cycling is very slow without it. We have been preparing battery-active materials in thin film form on conductive substrates for electrochemical characterization in the absence of conductive diluents or binders (7). Electrochemical studies on geometrically well-designed thin films may help clarify reaction mechanism and failure mode of porous electrodes. In this paper, we report our initial results with thin LiFePO₄ films, prepared with pulsed laser deposition (PLD).

EXPERIMENTAL

LiFePO₄ films were prepared on stainless steel substrates (SS) with PLD at 700 °C in 50 mtorr of Ar backpressure. Deposition utilized an XeCl excimer laser with 3-4 mJ/cm² at 10 Hz impinging on two different targets (dark gray-colored and green-colored) pressed from pure LiFePO₄ powders prepared by hydrothermal techniques. Deposition times were 6 - 20 minutes to obtain films with different thickness. The distance between the target and the substrate was approximately 5 cm. Reasonable crystallinity was obtained for films as deposited on the substrates heated at 700 °C. Thin films deposited for 6 minutes with the dark gray-colored target, were light blue-brown and shiny. The thicker films deposited for 20 minutes with the green-colored target, were brown-colored and shiny. From the color and the preparation conditions of the targets we believe that the greenish target, used to deposit the thicker films, was lower in residual carbon than the darker target used for the thinner films. Film thickness and morphology were measured with a FESEM (Jeol 6340 FESEM). The crystal structure of the film was identified by X-ray diffraction using an X-ray diffractometer (Siemens D5000) with Ni filtered Cu K α radiation at 40 kV and 30 mA, and a scan rate of 1.5°/min with 0.05° steps. Film structure was also characterized by Raman spectroscopy. Raman spectra were recorded using a Labram Raman microscope, ISA Group Horiba at ambient conditions, using the 632nm line of a He-Ne laser at 1mW. Backscattering optics geometry with double notch filter and a standard CCD detector were used to collect, process and analyze the Raman signal.

The electrochemical cell used to study the electrochemistry of the LiFePO₄ films on SS contained Li reference (RE) and counter electrodes (CE) and has been described previously (7). Cyclic voltammetry was carried out at sweep rates from 0.1 to 100mV/s from 3.0-4.1V with an EG&G 273 potentiostat. Films were cycled between 2.5 and 4.0V vs. Li/Li⁺ at a current density of 1 μ A/cm² for a 75nm thick film, using an Arbin Battery Cycler (College Station, TX). All electrodes were tested in 1M LiPF₆/EC+DMC (1:1) electrolyte (EM Industries).

RESULTS AND DISCUSSION

Film Characterization

Surface and cross-section SEM images of the as deposited films are shown in Figure 1. Image clarity is poor due to charging of these low-conductivity films. However, we were able to estimate film thickness and particle size. Figure 1(a) shows a film with an average thickness of 75nm and particle sizes of 35-45nm with some 80nm aggregated particles. The SEM of the thicker film, shown in Figure 1(b), shows an average thickness of about 335nm with significantly larger particles (150-220nm), possibly due to aggregation during the longer high-temperature deposition. It should be noted that the target was pressed from battery-active powders with a mean particle size of 600nm. The weight of the films were estimated from this measured thickness and the crystallographic density of 3.6 g/cm³ for LiFePO₄.

The crystallinity of the films was assessed from the XRD patterns shown in Figure 2. Comparison with the powder pattern for LiFePO₄ shows that the 335nm thick film on stainless steel substrate is reasonably well-crystallized in the orthorhombic (*Pmnb*) structure of LiFePO₄. The thinner film shows only a few of the major reflections, mostly due to the low amount of material in the film.

Raman spectra from the two films are shown in Figure 3. The main peak due to the LiFePO₄ is at 941 cm⁻¹. The large peak at 672 cm⁻¹ is attributable to a magnetite (Fe₃O₄) layer formed at the surface of a substoichiometric Li_{1-x}FePO₄[2,8]. The peak near 2250cm⁻¹ in the thin film was thought to be due to an interfacial layer of oxidized stainless steel substrate. However, the spectrum of a highly oxidized substrate (700°C in air for 2 hours) showed no peaks in this frequency range (also shown in Fig. 3). In addition to the peaks discussed above, significant peaks attributable to carbon are clearly seen. Both the so-called G-band, associated with the graphene layers in graphite and the D-band for disordered carbon are observed near 1586 and 1315cm⁻¹, respectively. This carbon is probably due to the transfer of C from the targets during PLD. The relatively weaker carbon bands are observed for the thick film deposited from the target with the lower carbon content. These small amounts of carbon are difficult to quantify.

Variable Rate Cyclic Voltammetry of LiFePO₄ films

The cyclic voltammograms (CV), recorded at sweep rates from 0.1 to 100 mV/s, are shown in Figure 4 as pseudocapacitance (i.e. normalized to the sweep rate). Peaks are observed at 3.35 and 3.5V, characteristic of the insertion and removal of Li from the FePO₄ structure [1,6]. The initial sweeps for all samples tested showed additional anodic currents at high voltages on the as-deposited films. These anodic currents tended to disappear within a few cycles. The potential difference between the anodic and cathodic peaks (ΔE_p) increased and the pseudocapacitance peaks decreased with increasing sweep rate. These changes may be correlated to the kinetics of lithium reaction at the electrode/electrolyte interface and/or the rate of lithium diffusion in the film. Integration of the cathodic curves for the 75nm film (Figure 4) show capacities of 41 mAh/g and 22 mAh/g at 0.5 and 100 mV/s, respectively, and ΔE_p , increased from 146 to 246 mV for this change in sweep rate. The thicker film showed slightly higher capacity at slow sweep rate (63 mAh/g at 0.5mV/s) and the same high sweep rate capacity. This would be expected for a semi-infinite diffusion process. However, ΔE_p for the thicker film increased from 152 to 402 mV, possible due to the lower carbon content in the film. Results from a wider range of film thickness are clearly necessary for further quantification.

The anodic peak currents (I_p) are plotted in Figure 5 versus both sweep rate, v , and $v^{1/2}$, as expected for kinetic and diffusion-controlled processes, respectively. The dependence of I_p on sweep rate is linear with $v^{1/2}$ for 335nm film, consistent with semi-infinite diffusion control for the range of sweep rates used. For the 75nm film, I_p showed half-order dependence on sweep rate only for $v > 5$ mV/s. From the slope of I_p vs. $v^{1/2}$, we have calculated lithium diffusivities assuming semi-infinite lithium diffusion and the molar volume of LiFePO₄. The calculated diffusivities for both films are in the order of 10⁻¹² cm²/s.

Constant Current Cycling of LiFePO₄ films

After CV, constant-current cycling of a 75nm thick film was carried out at $1\mu\text{A}/\text{cm}^2$ between 2.5 and 4.0V. This film showed an excellent cycling stability. The voltage profile in Figure 6(a) shows a plateau at around 3.45V on charge and 3.40V on discharge corresponding to the two-phase reaction between LiFePO_4 and FePO_4 . The plot of specific capacity for this moderate rate (about C/3) is shown in Figure 6(b). The first discharge capacity was about 119 mAh/g dropping to 93mAh/g at 30th cycle. Thereafter, the capacity was stable till the end of testing (about 100 cycles total), with a coulombic efficiency close to 1. On the other hand, the thicker film showed extremely low coulombic efficiency ($< 60\%$) throughout 200 cycles, regardless of cycling rate. It appears that at 335nm we have exceeded a practical thickness for this low conductivity material. Future work will focus on the identification of the surface species present on the as-deposited film and the preparation of intermediate thickness films of varying carbon content.

SUMMARY

The preparation of LiFePO_4 films of variable thickness using pulsed laser deposition in an Ar atmosphere has been achieved. A 75 nm thick film of LiFePO_4 cycled reversibly delivering $>90\text{mAh/g}$ at low rate of $1\mu\text{A}/\text{cm}^2$. However, Raman spectroscopy indicated that the films prepared from targets containing residual carbon also contained carbon on the surface. A thick “low-carbon” film (335nm) cycled stably but with a low capacity and a low coulombic efficiency. Both films showed diffusion-limited performance at high-rate with characteristic diffusivities on the order of $10^{-12}\text{ cm}^2/\text{s}$. Optimization of film thickness for electrochemical measurements and the identification of the surface species are presently under investigation. This model system should be very useful for interfacial studies as well as the effects of added carbon on the performance of this promising cathode material.

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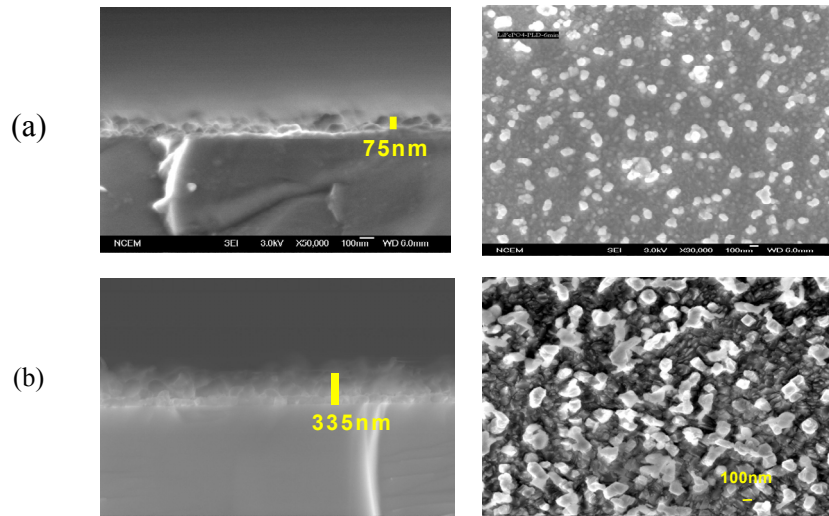


Figure 1. SEM image of cross-section and surface morphology for (a) 75nm thick film and (b) 335nm thick film.

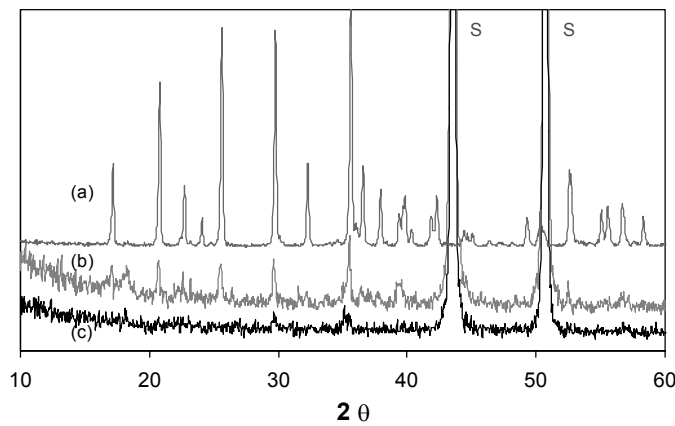


Figure 2. XRD patterns of (a) LiFePO₄ powder used as a target (dark grey-colored), (b) 335nm thick film and (c) 75nm thick film; S denotes the reflections from stainless steel susbtrate.

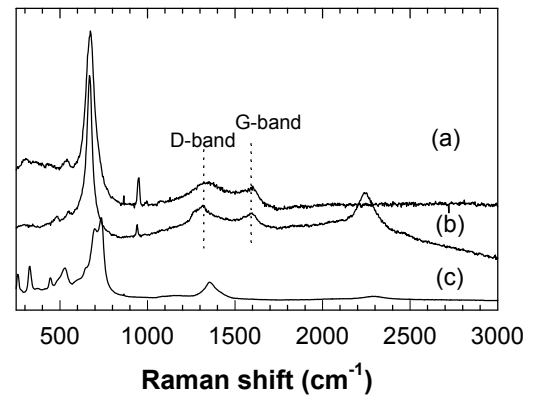


Figure 3. Raman spectra of (a) 335nm thick film, (b) 75 nm thick film and (c) SS substrate heated to 700°C in air.

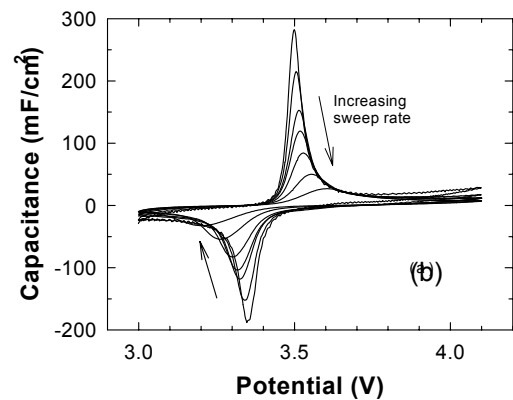
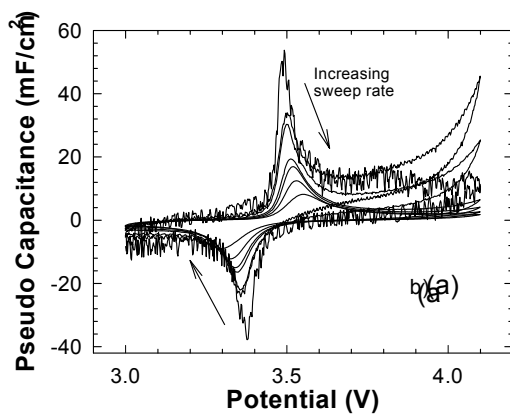


Figure 4. Variable sweep rate cyclic voltammetry for (a) 75nm thick film and (b) 335nm thick

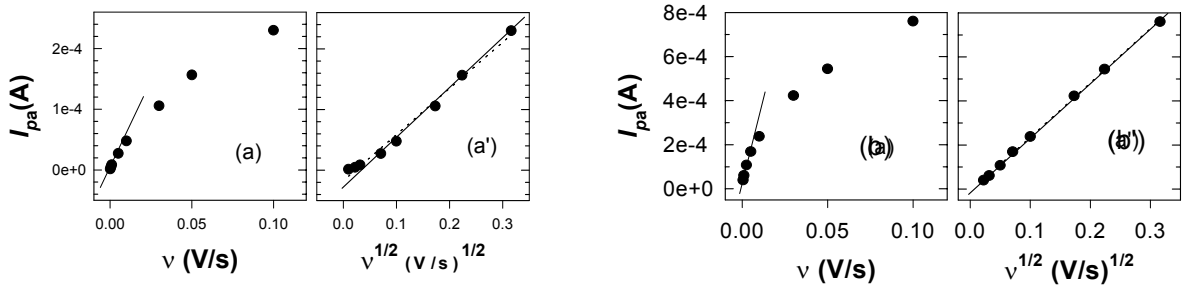


Figure 5. Plots of I_p vs. v and I_p vs. $v^{1/2}$ for (a) and (a') 75nm thick film, and (b) and (b') 335nm thick film, respectively, where I_p were obtained from the variable sweep rate CV in [1].

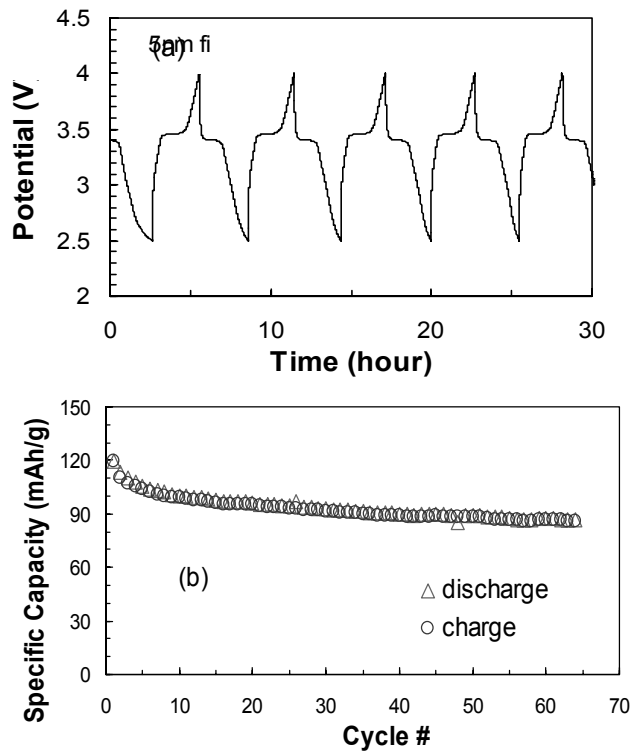


Figure 6. Voltage profiles of the Li/LiFePO₄ cells for 75nm (a) and its capacity plot with cycle number (b).