Characterization and Performance of LiFePO₄ Thin-Film Cathodes Prepared with Radio-Frequency Magnetron-Sputter Deposition

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LiFePO₄ films with a thickness of 1 μm were deposited on a stainless steel substrate by radio-frequency magnetron sputtering of a LiFePO₄/carbon composite target. Raman spectra revealed the presence of carbon in the film, which increased the electronic conductivity of the film relative to reports of the carbon-free material. X-ray diffraction revealed that the films were well crystallized, free of second phases, and may have a texture with a (011) orientation. The LiFePO₄ plus carbon film showed a good capacity and rate capability at 25° and −20°C when cycled as the cathode of a lithium battery, although the film was still inferior to the carbon-coated LiFePO₄ powder electrodes with 0.5 μm particle size.
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The olivine-type LiFePO₄ phase, proposed by Padhi et al.[1] and modified by Chiang,[2] has been shown to be a promising material for the cathode of rechargeable lithium-ion batteries. In fact, it has been commercialized recently by A123 Systems[3] due to its superiority in cost, safety, stability, low toxicity and high-rate performance. The rate capability of LiFePO₄ strongly depends on (*i*) the electronic conductivity,[2] (*ii*) Li⁺ diffusion coefficient,[4] and (*iii*) kinetics of phase transformation between LiFePO₄ and FePO₄.[5] There have been considerable efforts to increase the rate performance of LiFePO₄ by doping,[2] carbon coating,[6] and using nanoscale particles.[7] However, the mechanism of doping and role of carbon are still not completely understood in spite of their importance in the rate capability and cycle stability of LiFePO₄ electrodes. This is because the use of composite electrodes (consisting of active materials, organic binders, and conductive additives) often leads to difficulties in detailed analysis of their electrochemical lithium insertion/extraction behavior because the complex structure of the composite results in nonuniform potential distributions and unknown electrode surface areas.

Thin-film electrodes are useful for investigating the intrinsic properties of active materials because they do not need polymer binder and carbonaceous powder. With a good thin film, all-solid thin-film batteries can be fabricated using the technologies developed by Bates and Dudney.[8,9] LiFePO₄ thin-film electrodes have been successfully fabricated by electrostatic deposition (ESD) combined with sol-gel methods[10] and pulsed laser deposition (PLD).[11-15] Although the ESD method offers a low cost setup, high deposition efficiency, and easy control of composition of the deposited film, it is difficult to synthesize a dense LiFePO₄ film using this method.[10] For PLD LiFePO₄ thin film, the performance is very sensitive to carbon content (electronic conductivity)[12] and film thickness (Li-ion diffusion).[10-13] The cycling capacity and coulombic efficiency of PLD LiFePO₄ film decreased from 100 to 40 mAh/g when the film thickness increased from 75 to 335 nm[12] due to the limitation in the ionic and electronic conductivity of PLD LiFePO₄ film. Interestingly, LiCoO₂ thin films synthesized using radio-frequency magnetron sputter deposition (RF-MSD) show a superior electrochemical performance and faster relaxation characteristics than LiCoO₂ PLD films. This is believed to be due to large and badly oriented grains of the PLD films where the CoO₂ layers are parallel to the substrate

(*c*-axis orientation), whereas RF-MSD films have finer grains with a preferred *a*-axis texture.[16] Because RF-MSD avoided unfavorable orientation of large grains for LiCoO₂ films, and because LiFePO₄ also has a preferred conduction direction, it seems likely that RF-MSD LiFePO₄ thin films may have a much better performance than the PLD LiFePO₄ thin films. Therefore, the radio-frequency magnetron-sputtering was used to deposit LiCoPO₄[17] and LiFePO₄ thin films.[18-20] The sputter-deposited LiFePO₄ films prepared by Eftekhari[18] showed only a poor performance compared with a powder electrode. Due to the lack of structural, carbon content, and morphology information in the Eftekhari investigation,[18] the exact reason for the poor electrochemical performance is unclear. Recently, Chiu[19,20] deposited 0.5 μm LiFePO₄ thin films on Ti-coated Si, Si, and stainless-steel substrates using RF-MSD. A high specific capacity was observed at low discharge currents, although the annealed films were less crystallized than the parent LiFePO₄ powder target and contained small amounts of impurity phases (LiFeP₂O₇, Li₃Fe₂(PO₄)₃, and Fe₂O₃).

In this paper, we successfully synthesized for the first time a 1 μm pure LiFePO₄ plus carbon thin-film electrode using the RF-MSD method. This radio-frequency sputter-deposited LiFePO₄ film exhibited a similar crystallization with LiFePO₄ powders. The electrochemical performance of RF-MSD LiFePO₄ films were linked with their crystalline orientation, carbon content, and electronic/ionic conductivity which were tested using XRD, Raman spectroscopy, and electrochemical impedance spectroscopy.

Experimental

Six LiFePO₄ films were deposited on six 304 L stainless steel (SS) plates with a 1.3 cm² surface by planar radio-frequency magnetron sputtering of LiFePO₄/C targets. Each SS substrate was polished on successively finer grades of silicon carbide paper with intermediate ultrasonic cleaning in twice-distilled water before being carefully dried. The LiFePO₄ targets, 2 in. diam and 0.125 in. thick, were prepared by isostatic pressing of a mixture of 95% LiFePO₄ powder containing 2.5 wt % carbon (Hydro-Quebec, Canada) with 5% PEG binder (Mw 400, Aldrich), and then sintering to a density of about 64% at 973 K for 2 h under a reduced Ar/5%H₂ atmosphere. The LiFePO₄ targets were sputtered using a 2 in. magnetron (Kurt Lesker) in flowing Ar (flow rate 30 standard cm³/min), at a pressure of 2.7 Pa (20 m Torr). With the radio-frequency power density of 70 W, assuming a density of 3.6 g/cm³ for the films,[21] the deposition was 20 Å/min as measured by a quartz-crystal monitor positioned at the substrate plane 5 cm from the target. The film thickness estimated by the product of the deposition rate and the

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deposition time was within 5 to 10% of the value measured with a Dektek stylus profilometer.[22] The thicknesses of six RF-MSD LiFePO$_4$ films were 0.9–1 μm. As-deposited amorphous LiFePO$_4$ films were crystallized at 923 K for 2 h in a dilute H$_2$ gas mixture (95% Ar, 5% H$_2$). The surface morphology of the film was observed by a JEOL 840 (FEI Company, Hillsboro, Oregon) scanning electron microscope (SEM), and the composition of the film was measured by an EDAX (Mahwah, NJ) energy-dispersive X-ray analysis system (EDX). The crystallinity of the film was characterized by X-ray diffraction (XRD, Rigaku ARC5, Tokyo, Japan) using Cu Kα radiation. The Raman spectra were collected using a Dilor XY800 Raman Microprobe (JY, Inc., Edison, NJ) at ambient conditions, using an Innova 308c Ar$^+$ laser (Coherent, Inc., Santa Clara, CA) at the wavelength of 5145 Å with 5 mW output power. A 10x objective lens was used to collect Raman spectra from a ∼10 μm spot on the sample surface. The ionic and electronic conductivity of RF-MSD LiFePO$_4$ films in perpendicular directions to the SS substrate was measured after coating an Ag layer on the top surface of the LiFePO$_4$ film. The impedance was measured with a potentiostatic sine wave signal with an amplitude of 5 mV using a Solartron FRA 1260 frequency response analyzer, and the ionic and electronic conductivities were obtained by fitting the impedance data with the equivalent circuit proposed by Jamnik, which included grain, grain boundary, and particle-to-particles impedances.[23] The total (grain + grain boundary) impedance was used to calculate the ionic and electronic conductivities. For comparison, the ionic/electronic conductivity of the LiFePO$_4$ powder used for targets was also measured using a LiFePO$_4$ pellet. The pellet was prepared by die-pressing LiFePO$_4$ plus carbon powder (Hydro-Quebec, Canada, without carbon black and binder additions) at a pressure of 1.5 ton/cm^2, and then coating them with an Ag conductor paste on both sides to form the blocking electrodes. The size of the pellets was around 1.3 cm in diameter and 0.1 cm thick with a density of 2.3 g/cm^3.

Electrochemical properties of the film electrodes and powder electrodes were measured using a coin cell (2032) with a lithium foil disk as a counter electrode. The LiFePO$_4$ powder electrodes were prepared using the following procedures. An 80:10:10 mixture by weight of active material, carbon black and polyvinylidene fluoride (PVDF, Kynar, Elf-Atochem) was added to 1-methyl-2-pyrrolidinone solvent to form a viscous paste. The paste was homogenized in an ultrasonic bath for 30 min and stirred thoroughly before use. The paste was then coated uniformly on a sheet of carbon-coated Al foil using a doctor blade. The film was then dried in a vacuum oven at 120°C. The loading of active material was about 5.0 mg/cm^2. All testing cells were assembled in an argon-filled glove box, which consisted of the cathode (working electrode), lithium foil as the anode, a composition of 1.0 M LiPF$_6$ in EC-DEC-DMC-EMC (1:1:1:3 by volume) (Ferro Corporation, Cleveland, Ohio) as the liquid electrolyte, and a polypropylene (PP) microporous film as the separator. Before testing the electrochemical performance, the cells were activated through several charge/discharge cycles with a small current (0.1C, 1C = 160 mA/g) using an Arbin Corporation (College Station, TX) automatic battery cycler.

Results and Discussion

Film characterization.— EDX analysis revealed that P:Fe:O ratio in the LiFePO$_4$ thin film is within ±3% of 1:1:4, which showed a nearly stoichiometric composition. The XRD patterns of the stainless steel plate, the LiFePO$_4$ target, and an annealed film (923 K for 2 h) are shown in Fig. 1. The stainless steel plate showed three peaks at 2θ = 43.5, 44.5, 50.5°. Reflections due to the austenite phase γ are clearly identified as the (111) and (200) planes. The polishing procedures with sandpaper also generate the strain-induced martensite phase (α′) and it is revealed through the (110) reflections as labeled in Fig. 1. Figure 1 shows that the martensite (α′) phase becomes undetectable in the XRD of annealed LiFePO$_4$ film on a SS substrate because the strain-induced martensite (α′)
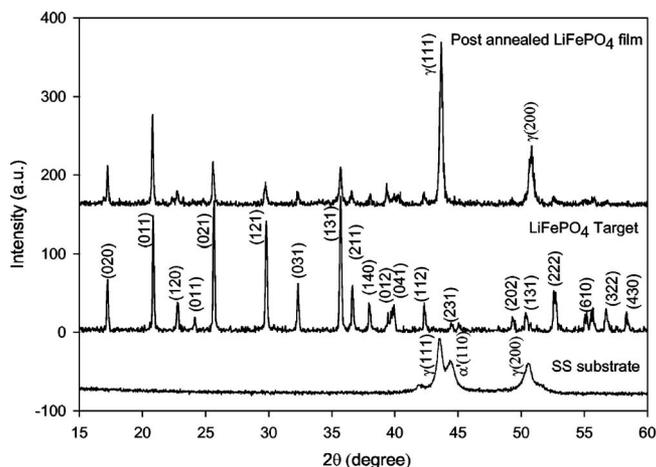

Figure 1. XRD patterns of stainless steal substrate, LiFePO$_4$ target, and heat-treated RF-MSD LiFePO$_4$ film deposited on stainless steal substrate.

phase transformed into austenite phase γ during heat-treatment. The as-prepared thin film gave no visible diffraction peaks (not shown), which indicated that the as-deposited film is in an amorphous state. After heat-treating at 923K for 2 h in Ar/H$_2$, the film showed similar diffraction peaks to the LiFePO$_4$ target, which is a typical diffraction pattern of single-phase LiFePO$_4$ with a polycrystalline structure and is in perfect agreement with triphylite LiFePO$_4$.[24] However, the intensity ratios of the film X-ray peaks were slightly different from those of the powder target. The high relative intensities of the (011) plane reflections for RF-MSD LiFePO$_4$ film indicate that the film may be textured. Because Li ions in LiFePO$_4$ are aligned along the *b*-axis, a preferred orientation with (011) plane parallel to the substrate can provide easier lithium transport along the *b*-axis. Textured LiFePO$_4$ films have been previously synthesized using the PLD method.[12,14] The RF-MSD LiFePO$_4$ film with (011) texture and a fine polycrystalline structure should have performance similar to a powder electrode, but a higher rate-capacity than that of the (120) oriented PLD LiFePO$_4$ film.[14]

The surface morphology image of RF-MSD LiFePO$_4$ film after annealing at 650°C for 2 h is shown in Fig. 2. The film shows aggregated particles or columns giving a rough surface. A similar surface morphology image was also observed on a sputter deposited
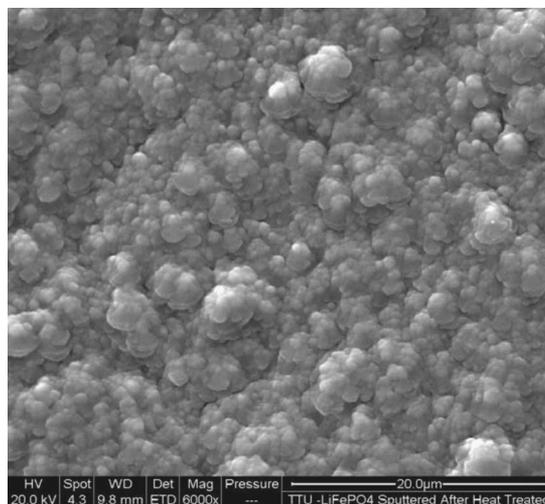

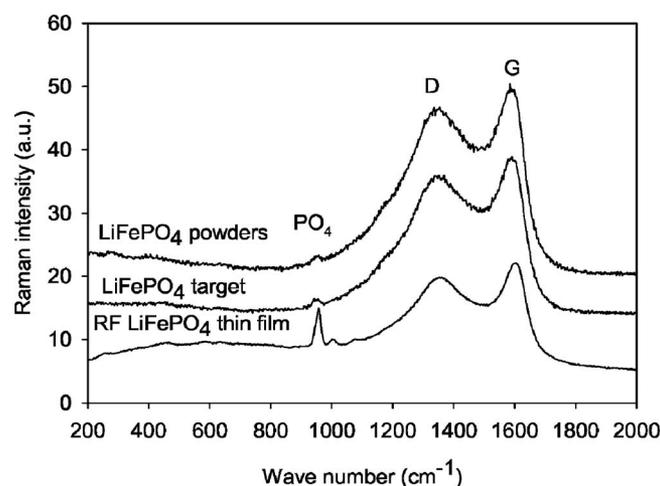**Figure 2.** SEM micrographs of RF-MSD LiFePO$_4$ film after heat-treatment.

Figure 3. Raman spectra of carbon-coated LiFePO$_4$ powder, LiFePO$_4$ target, and LiFePO$_4$ thin film deposited using RF-MSD method.

Figure 4. Impedance spectroscopy of RF-MSD LiFePO$_4$ thin film measured at room temperature.

LiCoPO$_4$ film after annealing at 500°C for 1 h[17] and LiFePO$_4$ deposited on a Si substrate at 600°C using pulsed laser deposition.[15]

Because the electrochemical performance of LiFePO$_4$ is very sensitive to the distribution and structure of the coated carbon, the surface structure of RF-MSD LiFePO$_4$ film was investigated using Raman spectroscopy, and compared with the Raman spectra from the carbon-coated LiFePO$_4$ powder and target (Fig. 3). All Raman spectra showed a relatively small band at 950 cm^{-1} and two broad two broad lines at 1345 and 1583 cm^{-1}. The Raman spectra of RF-MSD LiFePO$_4$ is similar to the Raman spectra of PLD LiFePO$_4$ film reported by Song et al.[12] The band at 950 cm^{-1} corresponds to the symmetric PO$_4$ stretching vibration in LiFePO$_4$ olivine, and two broad lines at 1345 and 1583 cm^{-1} are a fingerprint of carbon. The band at 1583 cm^{-1} mainly corresponds to the G line associated with the optically allowed E$_{2g}$ zone center mode of crystalline graphite, while the band at 1345 cm^{-1} mainly corresponds to the D line associated with disorder-allowed zone-edge modes of graphite. A very weak PO$_4$ peak in the Raman spectra of the LiFePO$_4$ powders and target indicated that LiFePO$_4$ particles in the powder and target were covered by the carbon with the thickness less than 30 nm because the penetration depth for carbon with Raman spectroscopy is approximately 30 nm.[25] The D/G intensity ratio (disordered/graphite[26]) is related to the carbon disorder, i.e., decreasing D/G intensity correlates with increasing the amount of graphitic bonding in amorphous carbon.[27] The D/G intensity slightly decreased in order of carbon-coated LiFePO$_4$ powders (1.19) > LiFePO$_4$ target (1.17) > RF-MSD LiFePO$_4$ film (0.95), indicating that the sintering process at 973 K for 2 h in forming a target and the annealing process at 923 K for 2 h help the graphitization of the carbon coating. The low D/G ratios will increase the electronic and ionic conductivity, and thus improve the electrode utilization.[27] The intensity ratio of PO$_4$ to carbon bands at 953 cm^{-1} in Raman spectra is a good indicator of the surface coating of the deposited carbon over LiFePO$_4$ olivine compound, a small ratio indicating more uniform coating of carbon.[28] The PO$_4$/(G + D) values increased in the following trend: Powders (0.01) < Target (0.02) < Thin film (0.21), which indicates that some carbon was lost during radio-frequency sputtering of the LiFePO$_4$ target. However, there is still some amount of carbon left in the RF-MSD LiFePO$_4$ film as indicated by 0.21 of the PO$_4$/(G + D), resulting in an increase in the electronic conductivity of the sputter deposited LiFePO$_4$ film.

Because the LiFePO$_4$ film has less carbon, and the film thickness (1 μm) is larger than the particle size (∼0.5 μm) of carbon-coated LiFePO$_4$ parent po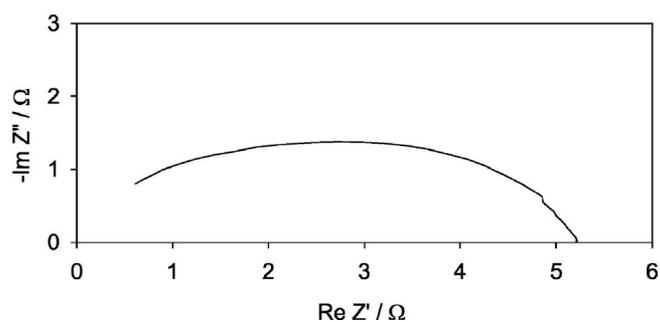wders, the ionic/electronic conductivities of the LiFePO$_4$ film should be different from that of the LiFePO$_4$ parent powders. Electrochemical impedances of the LiFePO$_4$ thin film (Fig. 4) and LiFePO$_4$ parent powders[29] were measured using a blocking electrode.[4] The results from the fitting showed that the ionic conductivity (5 × 10^{-6} S/cm) of the RF-MSD LiFePO$_4$ was three times lower than that (1.5 × 10^{-5} S/cm[29]) of the parent LiFePO$_4$ powders and the electronic conductivity (6 × 10^{-7} S/cm) of the RF-MSD LiFePO$_4$ film was three orders of magnitude poorer than that (5 × 10^{-4} S/cm[29]) of the parent LiFePO$_4$ powders. The much lower electronic conductivity of RF-MSD LiFePO$_4$ film comparing with LiFePO$_4$ parent powders is mainly due to the lower carbon content, as evidenced by the higher intensity ratio of PO$_4$/(G + D) in Raman spectroscopy of the LiFePO$_4$ film. However, the electronic conductivity of this RF-MSD LiFePO$_4$ is still much higher than that (10^{-9} S/cm) of carbon-free PLD LiFePO$_4$.[15] The low ionic conductivity of RF-MSD LiFePO$_4$ film is not understood at this time.

Electrochemical performance.— The electrochemical performances of two RF-MSD LiFePO$_4$ films with the (0.9 and 1 μm thick) were tested. The discharge rate performances of the 1 μm thick RF-MSD LiFePO$_4$ film and its parent LiFePO$_4$ powder electrode are shown in Fig. 5. The flat potential profiles at 3.4 V correspond to the redox couple of Fe^{2+}/Fe^{3+}. The C-rates of the thin film were calculated by estimating the weight of LiFePO$_4$ in the film from the film thickness and crystallographic density of 3.6 g/cm^3. The 1 μm RF-MSD LiFePO$_4$ showed a similar capacity (around 150 mAh/g) as the LiFePO$_4$ powder electrode at a low discharge current (0.1 C), but the rate capacity of the RF-MSD film is still lower than that of the parent powder electrode. The low rate capacity of RF-MSD LiFePO$_4$ film comparing with LiFePO$_4$ powder is attributed to low Li-ion and electronic conductivity, low electrochemical reaction area due to small interface between LiFePO$_4$ film and electrolyte, and long Li-ion diffusion path due to the larger RF-MSD LiFePO$_4$ film thickness (1 μm) than that (around 0.5 μm) of the particle size of LiFePO$_4$ powders,

Despite the low rate performance compared to a powder cathode, the RF-MSD films are superior to earlier reports of PLD films. It is reported that the capacity of PLD LiFePO$_4$ quickly decreased from 90 to 40 mAh/g when the thickness of the film increased from 75 to 335 nm due to the diffusion limit of lithium ions through the diminishing LiFePO$_4$/FePO$_4$ interface.[12] However, the discharge capacity (100 mAh/g) of the 1 μm RF-MSD LiFePO$_4$ film at 0.5C-rate is still two times higher than that (40 mAh/g) of PLD LiFePO$_4$ electrodes at the same discharge current[12] even when the thickness of PLD film is only one-third that of the RF-MSD film. The superior electrochemical performance of RF-MSD films over PLD films was also observed in the LiCoO$_2$ cathode.[16] The RF-MSD LiCoO$_2$ film showed 100% electrochemical activity compared to only 6% for PLD LiCoO$_2$ film.[16] Similar to PLD LiCoO$_2$, the carbon-free PLD LiFePO$_4$ only exhibits 5% of the expected capacity.[15]

(a)

(b)

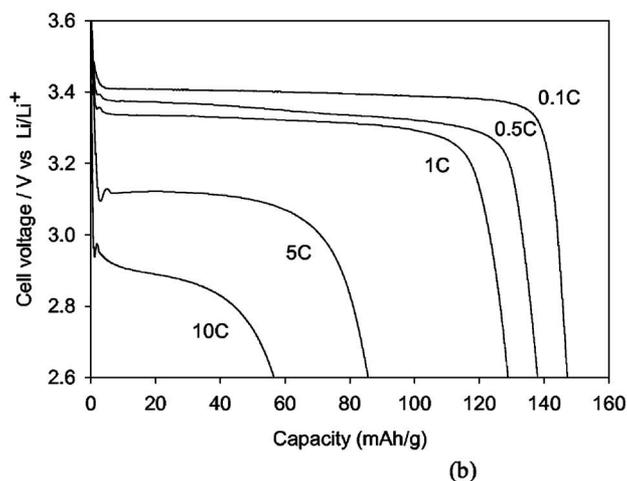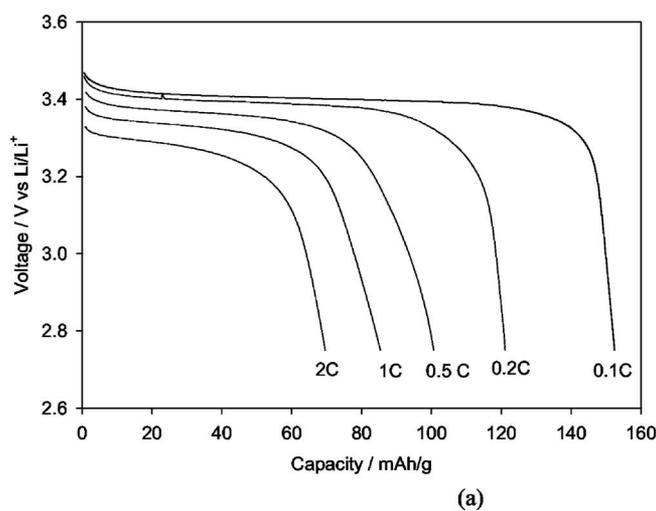**Figure 5.** The discharge profiles of (a) RF-MSD LiFePO$_4$ thin film with thickness of 1 µm and (b) the LiFePO$_4$ parent powders with an average particle size of 0.5 µm at the different discharge rates.

The low-temperature performances of the 1 µm RF-MSD LiFePO$_4$ film and the 0.5 µm parent LiFePO$_4$ powder electrode at different discharge currents were also examined at −20°C using the Li/LiFePO$_4$ coin cell and the results are shown in Fig. 6.

The 1 µm LiFePO$_4$ can still be discharged at −20°C, even at 1C, although its rate capacity is only 50% of the 0.5 µm parent LiFePO$_4$ powder electrode at the same currents. The low ionic conductivities of the electrolyte and LiFePO$_4$ film, the slow reaction kinetics of the phase transformation between LiFePO$_4$ and FePO$_4$, and the charge-transfer reaction at low-temperatures explain the low capacity of this film.

Conclusions

An olivine structured LiFePO$_4$ thin film with a thickness of 1 µm was prepared by radio-frequency magnetron sputtering deposition. The as-deposited thin films with amorphous structure were crystallized during annealing treatment at 923 K for 2 h in dilute H$_2$ atmosphere to give a polycrystalline and phase-pure film. A weak (011) texture provides a favorable orientation for Li$^+$ diffusion in film. The residual carbon in the RF-MSD LiFePO$_4$ film obtained from the carbon-containing target enhances the electronic conductivity to 6×10^{-7} S/cm (compared to 10^{-9} S/cm for carbon-free PLD LiFePO$_4$[13]), which results in a high rate capability. The 1 µm thick film of LiFePO$_4$ can deliver over 150 mAh/g at a discharge
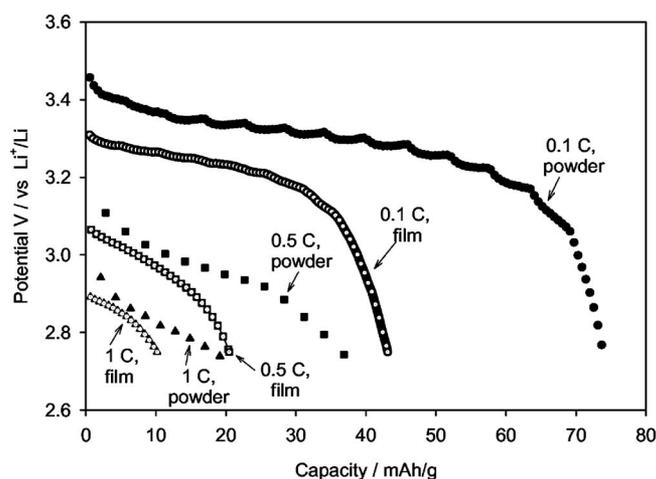

Figure 6. The rate performances of 1 µm LiFePO$_4$ film and 0.5 µm powder electrode at −20°C.

current of 0.1 C and retain almost 50% of the capacity even at 2 C. This 1 µm LiFePO$_4$ film can also provide capacity of 45 mAh/g at 0.1 C and 10 mAh/g at 1 C at −25°C. Studies of LiFePO$_4$ films are very useful to investigate the effects of ionic/electronic conductivity, to study kinetics of phase transformation on the rate performance of LiFePO$_4$ materials, and to make a great all-solid thin-film battery with a thin-film solid electrolyte such as Lipon.

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