

Electrochemical Studies of LiFePO₄ Thin Films Prepared with Pulsed Laser Deposition

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There has been considerable interest in LiFePO₄ as a cathode active material in Li-ion cells because of its superior cost, safety and stability attributes. The major drawback has been the low capacities achievable at even moderate discharge rates. The rate behavior is improved by the preparation of small particles and the incorporation of conductive carbon¹. A dramatic improvement in electronic conductivity has been demonstrated with small atom percentages of metals such as Zr, Nb or Mg into the Li sites². As with most cathode-active materials, it is nearly impossible to subtract out 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 binders³. In this paper, we report our initial results with thin LiFePO₄ films, prepared with pulsed laser deposition (PLD), that are cycleable without any added carbon.

LiFePO₄ films were prepared on stainless steel substrates with PLD at 700°C in 50 mtorr of Ar. Deposition utilized an XeCl excimer laser at 10 Hz impinging on a target pressed from pure LiFePO₄ powder, received courtesy of S. Whittingham, prepared by hydrothermal techniques. Deposition times were kept short to obtain a uniform film morphology. Reasonable crystallinity was obtained for films as-deposited on the 700°C substrates. Film structure was characterized with XRD. Films were light blue-brown and shiny, as prepared from the pure LiFePO₄. Film thickness and morphology were measured with a FE-SEM. The films electrochemical properties were studied in LiPF₆/EC/DMC electrolyte, with Li foil CE and RE³.

Cyclic voltammetry (CV) for a 75 nm film was carried out at 1 and then 10 mV/s between 3 and 4.1 V. CV data are shown in Fig. 1 as a pseudocapacitance (i.e. normalized to the sweep rate). The initial sweeps for all samples tested showed unexpected anodic currents on the as-prepared films. These anodic currents disappeared with continued cycling. Integration of these curves shows that at 1 mV/s, 46 mAh/g is being cycled and 76% of that is cycled at the higher rate. This is considerable higher than the 32% that would be expected for a diffusion-controlled reaction. Further rate measurements on these and thicker films will be discussed.

Constant-current cycling was carried out at 1 μA/cm² between 2.5 and 4.0 V. The specific capacity for this moderate rate (about C/3) is shown in Fig. 2. After the first cycle, the coulombic efficiency was very close to 1.

It is clear that LiFePO₄ can cycle reversibly in the absence of added carbon. This model system will be very useful for studies of the effects of the added carbon, metal dopants as well as stability of the interface for the promising cathode material.

Acknowledgments

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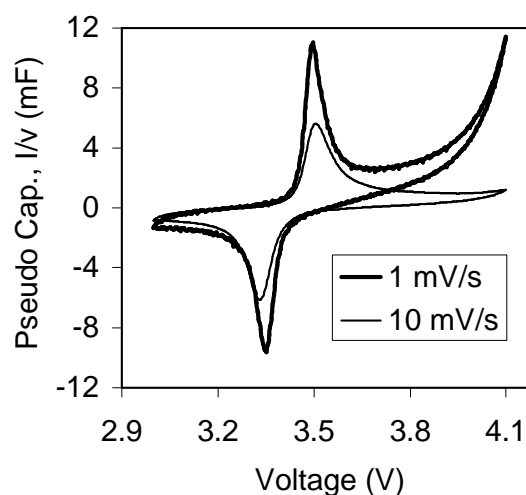


Figure 1. Cyclic voltammetry of 75 nm PLD-LiFePO₄ film in 1M LiPF₆/EC/DMC, at room temperature.

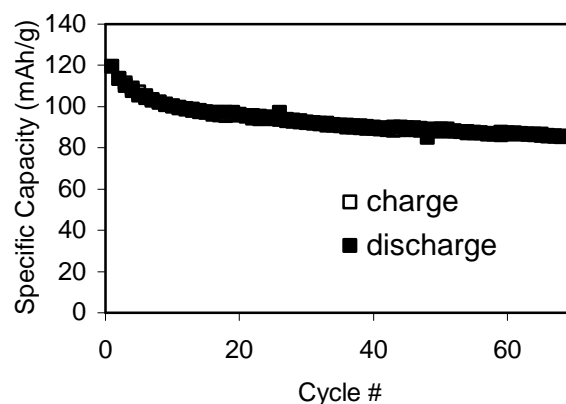


Figure 2 Constant-current cycling (1 μA/cm²) of 75 nm PLD LiFePO₄ film between 2.5 and 4.0 V vs. Li/Li⁺ in 1M LiPF₆/EC/DMC, at room temperature.