



Short communication

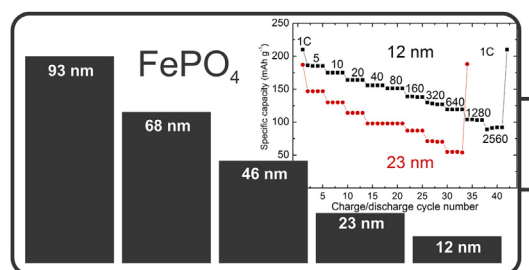
Ultra-high power capabilities in amorphous FePO₄ thin filmsKnut B. Gandrud^{*}, Ola Nilsen, Helmer Fjellvåg

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HIGHLIGHTS

- Rapid Li⁺ pseudocapacitance observed for the first time in an amorphous material.
- Amorphous FePO₄ thin film electrodes behave as pseudocapacitors.
- Specific power of 1 MW kg^{−1} obtained in addition to excellent cycling performance.
- Self-enhancing kinetics resulted in 50% increased specific capacity during cycling.

GRAPHICAL ABSTRACT



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ABSTRACT

Record breaking electrochemical properties of FePO₄ have been found through investigation of the thickness dependent electrochemical properties of amorphous thin film electrodes. Atomic layer deposition was used for production of thin films of amorphous FePO₄ with highly accurate thickness and topography. Electrochemical characterization of these thin film electrodes revealed that the thinner electrodes behave in a pseudocapacitive manner even at high rates of Li⁺ de/intercalation, which enabled specific powers above 1 MW kg^{−1} FePO₄ to be obtained with minimal capacity loss. In addition, a self-enhancing kinetic effect was observed during cycling enabling more than 10,000 cycles at current rates approaching that of a supercapacitor (11s charge/discharge). The current findings may open for construction of ultra-high power battery electrodes that combines the energy density of batteries with the power capabilities of supercapacitors.

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1. Introduction

Today, lithium ion batteries suffer from dramatic reductions in energy capacity at rapid charge/discharge rates [1,2]. Supercapacitors do not suffer from this effect, however, they provide a much lower energy density than batteries [3]. An energy storage device that would combine the rate performance of supercapacitors with the energy density of batteries would significantly

improve portable power technology. Recently, an effect termed rapid Li⁺ intercalation pseudocapacitance was discovered in crystalline mesoporous Nb₂O₅ [4–6], which allows charge to be stored and accessed in the bulk of a material without being kinetically limited by solid-state diffusion. This observation suggest that crystalline mesoporous Nb₂O₅ exhibits superior Li⁺ charge storage kinetics compared to other transition metal oxides [4], and the rapid intercalation pseudocapacitance effect found in this material may enable electrodes with energy densities of batteries combined with the power densities of supercapacitors [1,6]. However, such rapid Li⁺ intercalation pseudocapacitance is rarely observed because most Li⁺ intercalation materials, even as thin films, are limited by solid-state diffusion [7–9]. Furthermore, the previous

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obtained results suggest the importance of having a crystalline material for the rapid intercalation pseudocapacitance effect to occur, as it was only observed in crystalline Nb_2O_5 , while no such effect was found for the amorphous Nb_2O_5 [4,5]. Currently, there is little fundamental understanding of the requirements for good Li^+ intercalation pseudocapacitive properties [5,10]. Among suggested key-features is the presence of a crystalline network that offers two-dimensional facile transport pathways with minimum structural change [6], as well as no first order phase transformation during intercalation [6,10].

Crystalline olivine-type LiFePO_4 is a well investigated Li-ion battery cathode material with more than 2000 research publications since the initial work by Padhi et al. [11] in 1997 [12]. However, the amorphous counterparts, both the lithiated LiFePO_4 and the unlithiated FePO_4 have received much less attention as cathode materials for Li-ion batteries [13]. Through the use of precise model systems we have studied the true-rate performance of amorphous FePO_4 electrodes, as a function of the electrode thickness in the nm-range, and we currently report on the first observations of rapid Li^+ intercalation pseudocapacitance in an amorphous material. This surprising observation challenges the previous beliefs of the importance of having a crystalline material for this exotic effect to occur. Furthermore, the amorphous FePO_4 electrodes also possesses a higher voltage vs. Li/Li^+ (~ 3 V) than the previous reported Nb_2O_5 material (~ 2 V), resulting in an increased specific energy.

2. Experimental

Fabrication of the amorphous FePO_4 thin film electrodes was reported previously [14]. Briefly, the films were deposited on 316 stainless steel disks (CR20) by atomic layer deposition at 246°C using $\text{Fe}(\text{thd})_3$ ($\text{Hthd} = 2,2,6,6\text{-tetramethyl-3,5-heptanedionate}$), Me_3PO_4 (trimethyl phosphate), H_2O (water) and O_3 (ozone) as precursors. Prior to the deposition the stainless steel disks were washed with ethanol, in addition to an ozone treatment at 246°C .

The electrochemical properties of the as-deposited amorphous thin film electrodes were investigated in CR2032 coin cells. The cells were assembled in an argon-filled glove box with water and oxygen levels below 0.1 ppm. Metallic lithium (99.9%, Sigma–Aldrich) was used as the anode with a liquid electrolyte mixtures of 1 M LiClO_4 in ethylene carbonate (EC) (99%, Sigma–Aldrich):dimethyl carbonate (DMC) ($\geq 99\%$, Sigma–Aldrich) (EC:DMC) = 1:1 in weight ratio. A voltage range of 2.0–4.0 V was used for the galvanostatic measurements. All electrochemical measurements were carried out at room temperature using a MPG2 potentiostat/galvanostat (Biologic). For the lifetime test at high rate both the charge and discharge current was fixed at 320C (57 A g^{-1}) where each charge and discharge cycle was followed by a 2 min rest. Rates are reported in C-rate convention, where nC is the rate (current per gram) corresponding to complete charging or discharging to the theoretical capacity of the materials in 1/n hours. Here, 1C corresponds to 178 mA g^{-1} .

3. Results and discussion

Initially, a selection of amorphous FePO_4 (a- FePO_4) electrodes with thicknesses of 12, 23, 46, 68 and 93 nm was analyzed by slow-scan cyclic voltammetry (CV) and galvanostatic cycling at C-rates from C/10 to 40C (see Fig. S1–S3). A clear influence of the electrode thicknesses on the electrochemical properties was observed, most notably that the theoretical capacity could not be obtained for the two thickest investigated electrodes (68 and 93 nm). In fact, the amount of charge that could be reversible stored in the 68 and 93 nm thick electrodes was similar to the 46 nm thick electrode, suggesting that for the a- FePO_4 thin film electrodes the thickness of

the active material is limited to ~ 50 nm. This observation shows the importance of having precise thickness control of the active electrode material when dealing with poorly conductive materials.

In order to further explore how the charge storage kinetics of these amorphous electrodes are affected by the electrode thickness, CV-measurements were carried out with increasing sweep rates from 0.1 to 1000 mV s^{-1} in the voltage range 2.0–4.0 V. A cyclic voltammogram obtained from sweep rates in the range 40– 1000 mV s^{-1} for a 12 nm thick a- FePO_4 electrode is given in Fig. S4. The first feature indicating facile kinetics for the 12 and 23 nm thick amorphous electrodes is shown in Fig. 1a as they both displays a more or less constant peak separation versus sweep rates below 20 mV s^{-1} (charge/discharge in 100 s), see Fig. 1a. This observation is similar to what was observed for the previous material exhibiting rapid Li^+ intercalation pseudocapacitance [6]. Furthermore, these CV-measurements also reveal that the measured peak currents for the 12 and 23 nm thick electrodes are linearly proportional to the sweep rate over a wide range of sweep rates, which is a strong indication for pseudocapacitive behavior [6]. Fig. 1b presents $\log(i)$ versus $\log(v)$ for sweep rates from 0.1 to 1000 mV s^{-1} for all the studied electrode thicknesses. The current can be described by a power-law with respect to the sweep rate [8]:

$$i = av^b \quad (1)$$

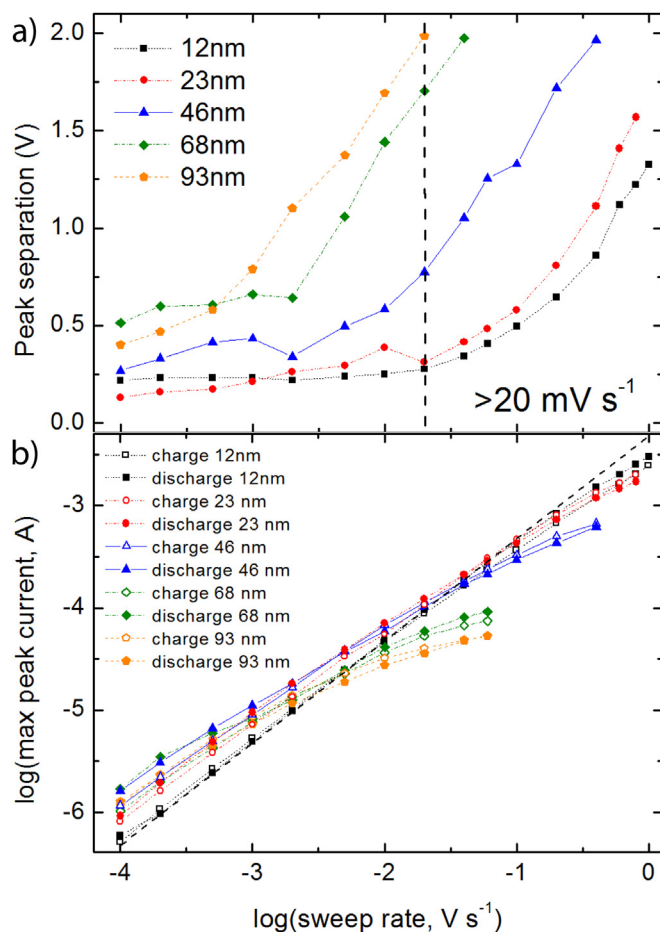


Fig. 1. Kinetic analysis of the electrochemical behavior of thin amorphous FePO_4 electrodes measured by CV in the voltage range of 2.0–4.0 V. **a)** Cathodic and anodic peak separation and **b)** b-value determination of the anodic and cathodic peak currents for electrodes with increasing thickness from 12 nm to 93 nm as a function of sweep rate. The stippled line corresponds to a b-value of 1.

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