



Electrochemical Synthesis of Iron Phosphides as Anode Materials for Lithium Secondary Batteries



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ABSTRACT

We report the electrochemical synthesis of iron phosphide films used as anodes of lithium secondary batteries. The phosphorus content in the film was increased to a level almost equal to that of Fe (corresponding to a FeP_y composition with $0.85 < y < 0.91$) through the selective electrochemical dissolution of Fe and Fe-rich phase from the electroplated film. The as-deposited film exhibited a dense structure characterised by numerous submicron-sized nodules in contact with each other, and maintained its overall mechanical integrity even after the selective dissolution. The as-deposited and the selectively etched films with high P content were tested as anodes of lithium secondary batteries. The performance of the selectively etched films far exceeded that of the as-prepared films. In particular, a 500-nm-thick film maintained a reversible discharge capacity greater than 420 mA h g^{-1} after 30 cycles. No specific physical damage was observed in the film after the cycling tests.

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1. Introduction

Lithium secondary batteries are widely used as power sources for portable electronic devices; they are also being increasingly used in energy storage systems (ESSs) and electric vehicles. In addition, the rise in electric power consumption resulting from the increasing complexity of electronic devices, as well as from the strong demand for extended device operation, is stimulating the development of energy storage devices with high energy density. The development of high-energy-density lithium secondary batteries has advanced beyond conventional methods of performance improvement via the increase in the packing density of existing batteries, and current studies are extensively focusing on the search and application of cathode and anode materials with superior lithium storing abilities [1–7].

When phosphorus reacts with lithium, it forms Li_3P by three-electron transfer. Hence, P exhibits a high theoretical capacity of 2596 mA h g^{-1} , which is seven times higher than that of graphite [8]; however, its low electronic conductivity and the large change in volume ($\sim 300\%$) during alloying with lithium [9] represent serious drawbacks. Current attempts to overcome these problems include formation of composites with carbon [8,10–13] and of metal-phosphorus compounds [9,14–35]. In particular, a variety of

metal phosphides (MP_x , where $\text{M} = \text{Fe}$ [9,14–20], Co [21–23], Ni [24–28], Cu [29], Zn [30], Ge [31], Mo [32], Sn [33], Sn-Fe [34,35], etc.) have been proposed as promising high-performance anodes, as extensively reviewed in the recent literature [2,5].

Among such compounds, iron phosphide has attracted particular attention for its superior thermodynamic stability, corrosion resistance, environmental friendliness, and economic efficiency [19]. Iron phosphide can form various compounds: Fe_3P and Fe_2P , which comprise Fe-rich phases, have been reported to exhibit no reactivity with lithium [2], while FeP , FeP_2 , and FeP_4 reversibly react with lithium, exhibiting theoretical capacities of 926, 1350, and 1790 mA h g^{-1} , respectively [9].

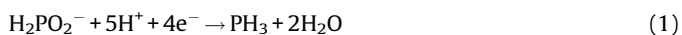
Electroplating is one of the common methods used for preparing a film. No complex equipment is required for deposition and a film with the desired composition and morphology can generally be obtained by the application of a low voltage or current at room temperature. This approach is thus frequently utilized as an inexpensive alternative to dry methods such as sputtering, chemical vapour deposition, and atomic laser deposition for film preparation. The amorphous character of electrodeposited iron phosphides [36] and the correspondingly lower atomic packing density compared to their crystalline forms are expected to be more effective at reducing the mechanical stress induced during

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alloying with lithium, leading to improved cycling stability [37]. These considerations highlight the potential of electro-deposited iron phosphides as key materials for the on-chip microbattery of miniature electronic devices. In addition, the strong adhesion to the substrate and the tuneable thickness and morphology of these materials might allow their application as the anode of flexible lithium batteries [38].

The electroplating of iron phosphides involves the following reactions [17,39]:



Based on Eq. (2), the maximum content of P in a film electroplated with iron phosphide is 40 at.% (corresponding to $\text{FeP}_{0.67}$). In order to increase the PH_3 amount and minimize single plating of iron (Eq. (3)), the pH of the electrolyte should be kept as low as possible. However, lowering the pH results in the active generation of hydrogen gas during plating, which causes loss of uniformity and degradation of the adhesive properties of the film.

Our previous study [17] showed that pH 2 is the minimum value that enables the formation of a film uniformly electroplated with iron phosphide, with a maximum P content of 31 at.% (corresponding to a $\text{FeP}_{0.45}$ composition). Even when NH_4^+ was added to provide an additional plating path for P [40], the maximum content of P in a uniform film did not exceed 38 at.% (i.e., $\text{FeP}_{0.60}$). As a result, when the electrolytic iron phosphide was used as the anode of a lithium secondary battery, its capacity per weight was inferior to that of graphite, even though its capacity per volume was higher.

This work represents a continuation of our previous efforts to increase the P content in a film electroplated with iron phosphide, and at the same time an intermediate step towards the synthesis of P-rich iron phosphide films. Here, the P content in an iron phosphide film was increased through the electrolytic synthesis of the film, followed by the selective dissolution of Fe and Fe-rich phase. For this purpose, the oxidation or dissolution potentials of Fe and iron phosphides were determined by linear sweep voltammetry (LSV) using a reference powder sample. This information was then used to selectively dissolve Fe and Fe-rich phase in a film densely and uniformly electroplated with iron phosphide, thus allowing the preparation of the high-phosphorus film while preserving its mechanical integrity. Finally, the obtained film was evaluated as the anode of a lithium secondary battery, and its characteristics were compared with those of the film before selective dissolution.

2. Experimental Procedures

2.1. Measurement of Oxidation Potential for Reference Sample

In order to prepare a reference sample, Fe (Alfa Aesar, 99.9%), Fe_2P (Sigma Aldrich, 99.5%), Fe_3P (Alfa Aesar, 99.5%), and FeP in powder form were mixed in an equal weight ratio, and the mixture was blended with polytetrafluoroethylene (PTFE, Sigma Aldrich, 60 wt.% dispersion in H_2O) binder and carbon black (Alfa Aesar, 99.9%) conducting agent in a weight ratio of 8:2:1. The synthesis of FeP involved mixing Fe (Alfa Aesar, 99.9%) and P (Alfa Aesar, 98.9%) in a stoichiometric ratio of 1:1, followed by heat treatment in vacuum. A heating rate of 20°C h^{-1} was used to achieve a final temperature of 700°C , which was maintained for five days before the mixture was cooled with air. A reference sample was produced

by coating a mixed paste on a piece of stainless steel gauze (Alfa Aesar, 80 mesh, type 304) or Cu gauze (Alfa Aesar, 100 mesh) and drying it in an oven for 12 h. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively, in a three-electrode electrochemical cell setup.

The solution used for measuring the oxidation potential was the same as that used for plating iron phosphide: it comprised 0.72 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Junsei Chemical, Japan), 0.36 M $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (Sigma Aldrich, USA), 0.11 M $\text{H}_2\text{NCH}_2\text{COOH}$ (Junsei Chemical, Japan), and 5 mM $\text{H}_2\text{C}_2\text{O}_4$ (Sigma Aldrich, USA), the pH of which was adjusted to 2.3 by adding H_2SO_4 (Ducksan, Korea). LSV measurements were conducted at room temperature by sweeping the voltage in the anodic direction at a rate of 0.05 mV s^{-1} , starting from the open-circuit potential (OCP), up to the voltage at which the current density rapidly increased. Additional LSV measurements were conducted using bare stainless steel and Cu substrates. A Solartron 1287 potentiostat was used for the electrochemical experiments. The phases present before and after LSV were examined by X-ray diffraction (XRD, D8 Advance, Bruker, Germany).

2.2. Production of Iron Phosphide Film and Selective Dissolution

A Cu foil (Alfa Aesar, 99.8%) was selected as substrate for producing a film electroplated with iron phosphide. The native oxide layer was removed by pretreatment with dilute sulfuric acid, followed by washing with distilled water. The exposed area was set to 0.25 cm^2 . As discussed in Section 2.1, a three-electrode electrochemical cell was assembled using a Pt wire and SCE as the counter and reference electrodes, respectively, and the same electrolyte was used for electroplating. Two films were produced by applying a constant voltage of -1.7 V vs. SCE for 10 s and 40 s.

The LSV curve of a film plated for 10 s under the same conditions as those employed for the reference sample discussed in Section 2.1 was then obtained. Since a relatively well-defined peak was observed even at high scan rate, the potential sweep rate was set to 0.5 mV s^{-1} . The oxidation potentials of the Fe and Fe-rich phases in the electroplated film were determined by comparing the results obtained for the film and the reference sample, and then used to define the final LSV potential required for the selective dissolution of the iron phases. An Iviumstat unit (Ivium Technologies, The Netherlands) was used for the electrochemical experiments.

The morphology and crystal structure of the films were analysed by field emission scanning electron microscopy (FE-SEM, MIRA3, TESCAN, Czech Republic) and XRD, respectively. The surface and depth compositions were determined by energy-dispersive X-ray spectroscopy (EDS, APOLLO X, AMETEK, USA) and X-ray photoelectron spectroscopy (XPS, PHI Quantera-II, ULVAC-PHI, Japan), respectively.

2.3. Analysis of the Performance of the Films as Lithium Battery Anodes

Four samples were tested as anodes of lithium secondary batteries: two films plated with iron phosphide for 10 s and 40 s (hereafter referred to as samples 10D and 40D) and the corresponding films produced by selective dissolution (hereafter labelled 10E and 40E). A three-electrode cell was assembled using lithium metal as counter and reference electrode. A 1 M solution of lithium hexafluorophosphate in 1:1 (w/w) mixture of ethylene carbonate and dimethyl carbonate was used as electrolyte.

Cyclic voltammetry (CV) was conducted at a scan rate of 0.5 mV s^{-1} in a potential ranging from 0.01 to 2.25 V vs. Li/Li^+ . Charging/discharging cycles were repeated 30 times at a rate of 0.25C between 0.01 and 2.25 V vs. Li/Li^+ (the C rate was calculated using the actual reversible capacity measured experimentally). However, in order to minimize changes in the film characteristics due to the initial irreversible reaction [41], the first charging was

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