



Growth of nickel phosphide films as anodes for lithium-ion batteries: Based on a novel method for synthesis of nickel films using ionic liquids



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ABSTRACT

Nickel phosphide (Ni-P) films were fabricated through four types of Ni films electrodeposited using a choline chloride-based ionic liquid (choline chloride-ethylene glycol) at room temperature. Sheet-like morphology of Ni films can be obtained when 0.5 M of Ni²⁺ is used; and sphere-like one is presented by 1.0 M of Ni²⁺. Consequently, the surface morphologies of these Ni-P films were affected by the initial Ni films. And different phases of Ni₁₂P₅ and Ni₂P in the Ni-P films would be obtained after the phosphorization process. As anodes for Li-ion batteries, the electrochemical properties of these Ni-P films were investigated by cyclic voltammetry and galvanostatic charge–discharge tests. The surface morphology and thickness of thin films had a significant effect on their electrochemical performance. The Ni₂P films delivered a large reversible discharge capacity around 398.5 mAh g⁻¹ with the capacity retention of 91.4% after 50 cycles.

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1. Introduction

Rechargeable Li-ion batteries (LIBs) are currently the dominant power source for portable electronic devices and considered as one of the most promising energy storage devices [1–5]. In the last decade, great interest has been devoted seeking for new anode materials for the next-generation LIBs, which can exhibit higher capacity than graphite while possess excellent cyclability at the same time for the practical applications [6–18]. Since the pioneering work of Nazar on anode materials of transition metal phosphides [19], many studies have been carried out to investigate the reaction mechanism of these new material systems [15,20–30]. Among them, nickel phosphide (Ni-P) compounds have drawn great attention due to their high capacities and low polarization [22,31–34].

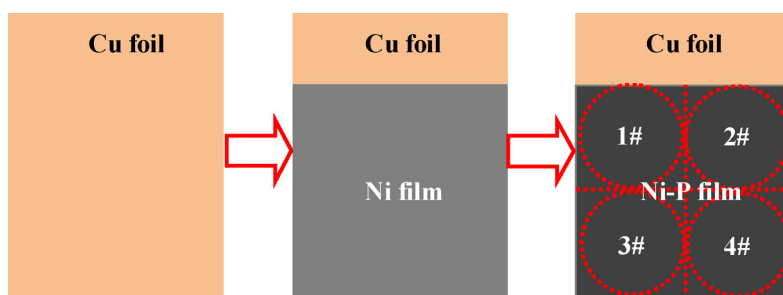
Unlike transition metal oxides, Ni-P exhibits the lowest polarization due to its metallic character [35], leading to its competent applications in electrochemistry [36–38]. In many works, the electrode is commonly prepared by mixing active material and

polymer binder, which probably negates the favorable effects of the decreasing particle size and introduces supplementary interfaces [39]. Generally, these cells need to be modified due to the lack of good electrical contact. An alternative way to obviate this problem is fabricating nano-architected film directly on current collector, which usually exhibits a long cycling life [40–42]. However, in Boyanov's work [23], AAO template was used, and it did not provide the evidence that the Ni nanopillars had been completely phosphorated. In addition, the Ni-P nanostructure was confirmed as NiP₂ just according to the EDX results. In previous works [24,28,29,31], a heat treatment after electrodeposition should be involved to obtain a Ni₃P phase, which showed unsatisfactory performances, including the initial coulombic efficiency and the cyclic stability.

For transition metal phosphides, many researchers have reported a novel synthetic strategy: the conversion of preformed metal nanoparticles into metal phosphides by solution-mediated reaction with trioctylphosphine (TOP) [43–45]. Based on our recent works, the nanoparticles can be extended to nanowires [38] and nanosheets [46]. On the other hand, it is reported that ionic liquids based deep eutectic solvents (DESS) are more advantageous media for the cathodic deposition of metals, for instance Ni [47] and Cu [48]. The ionic liquids can overcome the limits imposed by common aqueous or organic media, such as wide electrochemical window (up to 6V) and extremely low vapor pressures [49].

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Scheme 1. Schematic illustration showing the deposition process and the electrodes collected by dividing the film into four pieces.

Herein, seeing the merits of ionic liquids, we consider to fabricate Ni thin films from ethylene glycol/choline chloride (EG/ChCl) based DES, thereby make these films phosphorated into Ni-P through a facile organic-phase strategy. The structure, surface morphology and electrochemical performance of the Ni-P thin films were investigated.

2. Experimental

2.1. Electrodeposition of bulk Ni deposit on Cu substrate

The electrodeposition of bulk Ni deposit on a polished Cu foil was conducted in the ionic liquids. ChCl (AR, Aladdin) and EG (AR,

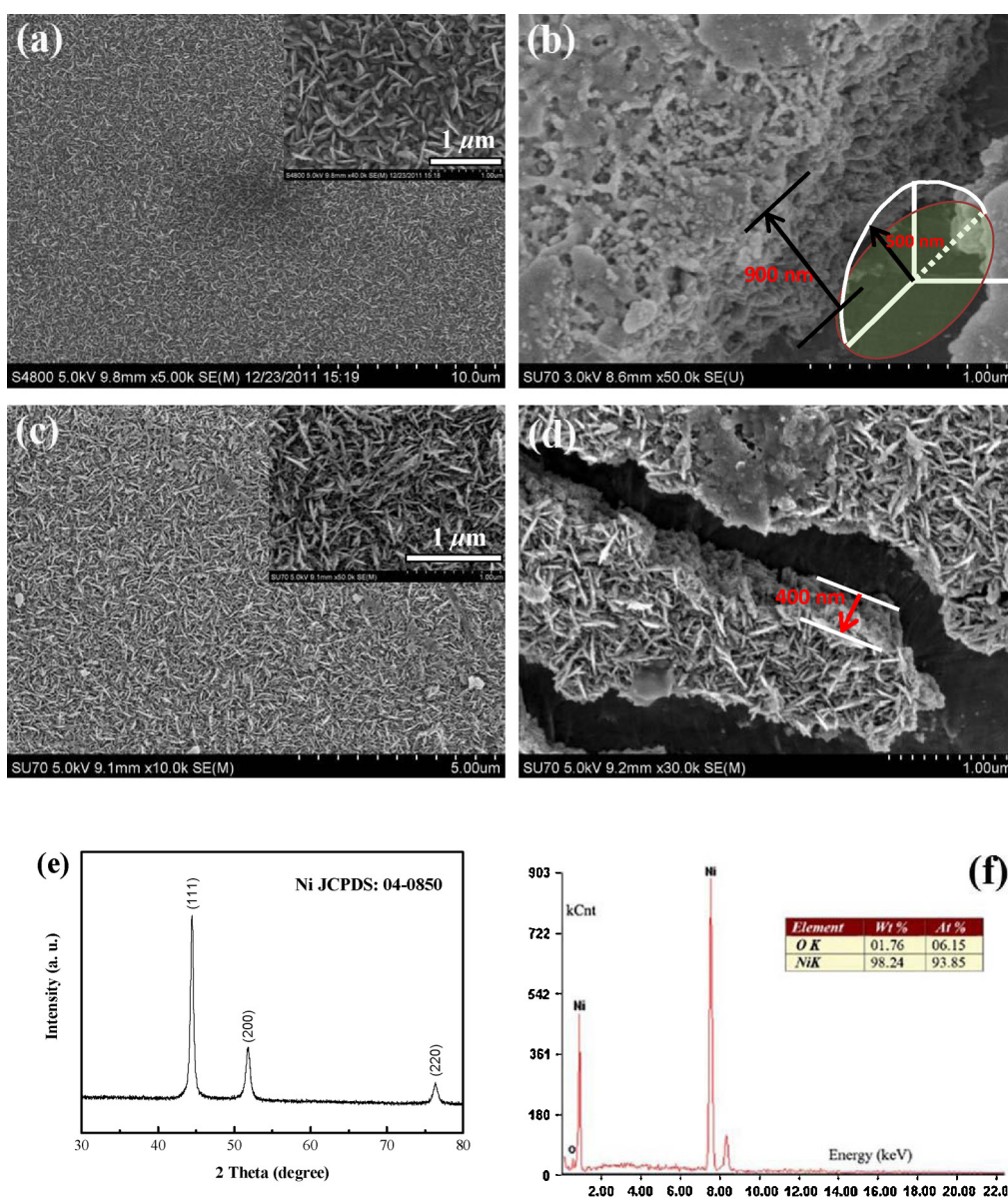


Fig. 1. Surface morphologies of N-1 (a and b), and N-2 films (c and d). (b) and (d) show the thicknesses of the films for different depositing times. The insets of (a) and (c) are the magnified images; and the scheme in inset of (b) is a 3-D calibration curve to certify the thickness of film. (e) and (f) are the XRD pattern and EDX mapping analysis corresponding to (a).

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