



Li metal coated with amorphous Li_3PO_4 via magnetron sputtering for stable and long-cycle life lithium metal batteries



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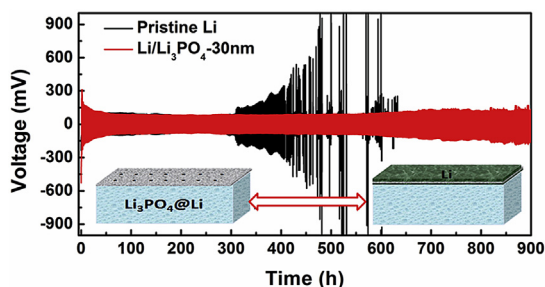
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HIGHLIGHTS

- Glassy Li_3PO_4 thin film is homogeneously deposited onto lithium metal foils.
- Li_3PO_4 thin film has an electronic conductivity of 1.4×10^{-10} S/cm.
- Li_3PO_4 thin film has an ionic conductivity of 2.8×10^{-8} S/cm.
- Li_3PO_4 coated lithium metal anodes have long cycle life performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium metal with high theoretical capacity (3860 mAh/g) and low operational voltage (-3.04 V vs. standard hydrogen electrode) reflects to be one of the most high energy density anodes for energy storage devices. While, its high chemical activity to continuously react with electrolytes causing low coulombic efficiency and formation of lithium dendrites leading safety concern limits practical applications. To conquer these challenges, amorphous Li_3PO_4 thin films with thickness of 0–200 nm are directly coated on the surface of Li metal foil via magnetron sputtering. The as-prepared Li_3PO_4 has almost insulated property with electronic conductivity of 1.4×10^{-10} S/cm and ionic conductivity of 2.8×10^{-8} S/cm. The conformal coating layer Li_3PO_4 can successfully suppress the lithium dendrites growth and improve its life span. The remarkable improvements of the Li_3PO_4 -coated Li electrodes are mainly attributed to high chemical stability as well as amorphous nature of Li_3PO_4 , which leads layer-by-layer growth Li film rather than islands form dendrites.

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1. Introduction

Lithium metal anode is a contender in terms of energy density due to its high theoretical capacity (3860 mAh/g) and low operational voltage (-3.04 V vs. standard hydrogen storage) compared

with Mg, Zn, Na metal ion anodes [1–6]. Moreover, the Li^+ stripped from lithium metal anodes has a smaller radius and monovalence, which can easily shuttle between cathodes and anodes under the conditions of preserving the framework structure with a small volume expansion/contraction [7,8]. However it has two challenges for the real applications. One is that metallic Li is too active (Gibbs energy -8.670 kJ/mol at room temperature) and hence it reacts with conventional organic liquid electrolytes to produce a solid electrolyte interface (SEI) layer, which is an ionic conductor and

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electronic insulator. The formed SEI, chemically unstable and unconfined, can be easily broken as a result of local stress during charge-discharge process leading exposure of fresh lithium which eventually brings in continuous consumption of both active Li metal and electrolyte. This finally causes low coulombic efficiency [9–11]. The other is the formation of lithium dendrites as a result of sluggish deposition of lithium ions that is correlated with the anionic mobility and electric field [12,13]. The formed lithium dendrite can puncture separators and lead to a short circuit with possible explosion due to the quickly accumulated heat [14–17].

Various attempts have been developed to circumvent these issues. In terms of stabilizing SEI layer, optimizing the electrolyte solvents and addition of additives with the aim of enlarging the electrochemical window in stability and modifying the SEI compositions have been shown to be effective ways [18,19]. Meanwhile, substitutions of the carbonate-based liquid electrolytes with solid state electrolytes are alternatives [20,21]. Moreover, artificial SEI layers via chemical or physical depositions onto the lithium metal before electrochemical activation are also practicable to improve the energy efficiency [22–25]. As for the prevention of lithium dendrites, tuning the local electric field via 3D current collectors to affect the initial nucleation of lithium deposition and improving thermal distribution through modify separators with a thermally conductive BN coating layer have been proved to be beneficial for lithium metal battery performance [14,26]. Simultaneously, lithium alloys (*i.e.* Li-Al, Li-B) are other important strategies to change lithium deposition morphology [27,28]. Thin layers, such as carbon films, PEDOT-co-PEG polymers, Al_2O_3 layers, and LiPON, directly coated on lithium metal foils have positive effects on safety and long cycle performance [25,29–32]. Zhang et al. employed amorphous carbon coatings on metallic Li foils by magnetron sputtering technique against the side reactions between Li electrode and electrolytes [23]. Recently, Li and coauthors reported that 200 nm thin film Li_3PO_4 generated by a chemical reaction with a high Young's Modulus 10–11 GPa can play roles to be an artificial ionic conducting SEI layer and to inhibit the lithium dendrite growth [22]. Wherever, it is still ambiguous and intriguing to know the intrinsic account of coating layers for the improvements. Since Bate et al. found that the polycrystalline Li_3PO_4 synthesized by chemical reactions has an ionic conductivity 10^{-18} S/cm, which is actually an ionic insulator [33]. In the case of lithium deposition/dissolution, lithium ions are accordingly difficult to pass through thick Li_3PO_4 films under high current rates (larger than 0.5 mA/cm^2 in normal cases). It is known that good chemical stability is prerequisite. While, there are limited references regarding the effect of transport properties, thickness, crystalline of these coating layers on the performance and the morphology evolutions of lithium metal. More importantly, the lithium electrochemical plate is a diffusion-limited process in which current density, electric field, and interfacial properties drive its growth modes (*i.e.* islands mode or layer-by-layer mode) [34,35]. Thus, the contribution of coating layer including of surface properties and morphologies on the early stage nucleation of lithium film should be paid special attentions.

In this study, herein, we fabricate amorphous Li_3PO_4 thin films with different thickness via magnetron sputtering onto the lithium foils to evaluate its impact on the electrochemical performance of lithium. Magnetron sputtering technique provides a facile and economic way to obtain homogeneous and compact films with thickness control via tuning sputtering time. Moreover, thin films obtained via magnetron sputtering at room temperature normally present glassy amorphous phases with the advantages of less grain boundaries, high ionic conductivity, and low surface energy as well as isotropy nature. As for the Li_3PO_4 , it is more chemically stable than the well known lithium ion conductor LiPON, which is highly sensitive to air and moisture. It is found that the obtained Li_3PO_4

thin film, an almost insulate material, has an ionic conductivity of 10^{-8} S/cm and electronic conductivity of 10^{-10} S/cm. Lithium metal with 30 nm thick coating Li_3PO_4 thin film demonstrates the best cycling performance and smallest electrochemical polarization. Besides acting as a protecting layer to prevent the reaction between lithium foil and electrolytes, its amorphous nature with homogeneous current density distribution on its surface along with tunnel effect is believed to be powerful for depressing lithium dendrite growth.

2. Experimental

2.1. Preparation of Li_3PO_4 thin film coated lithium metal foils

The Li metal foil (200 μm in thickness) was purchased from Tianqi Li Corporation, and was used as received. Li_3PO_4 thin film was deposited on Li metal foil by radio-frequency (RF) magnetron sputtering using a commercial Li_3PO_4 target (99.99%). The sputtering was performed at a fixed power (160 W) under 1.0 Pa argon pressure and target-to-substrate distance was fixed to be 5 cm. During sputtering, the substrate was rotated to guarantee a uniform coating. The sputtering time was changed from 5 min to 30 min to tune the coating thickness. The average sputtering rate is estimated to be 2 nm/min by measuring the thickness of the Li_3PO_4 film additionally deposited on silicon wafers. The surface-coated Li electrodes are denoted as Li/ Li_3PO_4 -x nm (x represents the thickness of Li_3PO_4 thin film) in the following text. For Li_3PO_4 conductivity measurement, we designed a Cu/ Li_3PO_4 /Cu structure on the quartz glass and the Cu film and Li_3PO_4 film with the thickness 200 nm and 1 μm , respectively. Our sputtering chamber is connected with the glove box. The samples can be directly transferred into the glove box without exposure to the air.

2.2. Material characterizations and electrochemical tests

The morphology was characterized by field-emission scanning electron microscope (FE-SEM, Hitachi, S3400N) and the crystalline of Li_3PO_4 film was investigated by transmission electron microscope (TEM, JEOL JEM-2100). And the compositions were analyzed with an energy dispersive X-ray spectroscopy (EDS, Oxford INCA PentaFET-X3).

As for the Li-S battery, the carbon/sulfur (C/S) composite was prepared by heating a mixture of Ketjen Black and sublimed sulfur powder (99.5%, Aladdin) in the weight ratio of 1:2 at 155 °C for 12 h. Subsequently, the C/S composite (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (binder, 10 wt%) were mixed with *N*-methylpyrrolidone on a piece of Al foil. Afterward, the sulfur cathode was dried at 60 °C in vacuum for 12 h. Finally, the cathode was punched into a disk ($\Phi = 10 \text{ mm}$) for assembling Li-S cells. Li-Li symmetric cells were assembled in a glove-box filled with an argon atmosphere. 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) (1:1:1, v/v) was used as the liquid electrolyte. The separators (Celgard2400) were dried in vacuum overnight at 50 °C. The Li-S cells were assembled by the same way except with sulfur electrode as the working electrode. 1 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) dissolved in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 by volume) (Zhangjiagang Guotai-Huarong New Chemical Materials Co. Ltd.) was used as electrolyte for Li-S batteries. The galvanostatic charge/discharge tests were performed using a CT2001A cell test instrument (LAND Electronic Co. Ltd.) at room temperature. The current density of Li-Li symmetric cells is 0.5 mA/cm^2 for each step with firstly discharge time of 0.5 h. The Li-S cells were tested in a voltage range of 1.7–2.8 V (*vs.* Li/Li⁺) at a rate of 0.5 C (1 C = 1675 mA/g). Electrochemical impedance

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