

Chemically polished lithium metal anode for high energy lithium metal batteries



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ABSTRACT

The formation of lithium dendrites during operation is a major issue that has prevented the practical application of lithium metal anode, which is considered one of the most promising anode materials for next generation lithium batteries. The formation of dendrites has been attributed to the non-uniform and locally high current densities resulting from the uneven dissolution and deposition of lithium, which is associated with the topographical and electrical inhomogeneity on lithium foil. Herein, we demonstrate a facile chemical polishing strategy to remove the pristine film on lithium foil to simplify the surface chemistry of lithium and enable uniform lithium deposition/dissolution during cycles, which can then effectively improve the electrochemical performance of lithium metal batteries.

1. Introduction

Lithium metal has been considered the ultimate anode materials for high energy density batteries due to its high specific capacity of 3860 mA h g^{-1} , low density (0.59 g/cm^3) and low redox potential (-3.040 V vs. the standard hydrogen electrode) [1–8]. However, despite these advantages, practical applications of lithium metal are hindered by several challenges, including uncontrolled and inhomogeneous deposition of lithium [9–13]. The uncontrolled growth of lithium dendrites may lead to severe electrolyte side reaction, low cycling Coulombic efficiency (CE), and internal short circuit of batteries. The cause of these problems boils down to the inhomogeneous surface layer on pristine lithium, which consist of the native layer of Li_2O , LiOH , Li_2CO_3 et al., [2,14–16] and the as-formed solid-electrolyte-interface (SEI) when in contact with the electrolyte solvents [11,17–19]. The topographical and electrical inhomogeneity on pristine lithium results in sporadic lithium nucleation/dissolution and creates the “hot spots” for lithium dendrite growth [20–22]. It is widely regarded that the initial nucleation behavior of lithium should be regulated for the subsequent uniform lithium deposition [20]. Over the past few years, considerable efforts have been devoted to improve the performance of lithium metal anode, such as introducing physical block barriers to suppress the growth of lithium dendrites [13,23–39], controlling the initial lithium deposition and SEI formation through electrolyte

modifications and current collector treatments [33,40–52], and improving the specific surface area of lithium electrode to create more deposition/dissolution sites by using 3D frameworks of graphic carbon nanocomposites, 3D copper current collectors and building up 3D lithium-penetrated composite electrodes [52–60]. Although these works has shown improvement in the lithium metal anode performance, rare attention has been paid to the modification of the native film formed on the pristine lithium metal. Cui and Zhang's groups have reported the conformal pre-treatment of lithium metal and copper foil by lithium fluoride respectively, indicating the importance of initial surface chemistry in directing the subsequent lithium dissolution and deposition [11,61]. When lithium metal comes into contact with the electrolytes, there is a partial dissolution of the pristine film by the electrolytes, resulting in the formation of primary SEI layer [14,15,19]. The inhomogeneity of the pristine film will lead to the formation of inhomogeneous primary SEI layers, thus hindering the uniform lithium nucleation and result in an uncontrollable growth of lithium dendrites and the continuous side reaction between lithium dendrite and the organic electrolyte [11,44].

Herein, we report a facile method to effectively remove the pristine layer on the surface of lithium. The uniformity of lithium nucleation/dissolution on the polished lithium metal can be significantly improved, leading to smooth deposition/dissolution of lithium during electrochemical cycling. We demonstrated that the polished lithium

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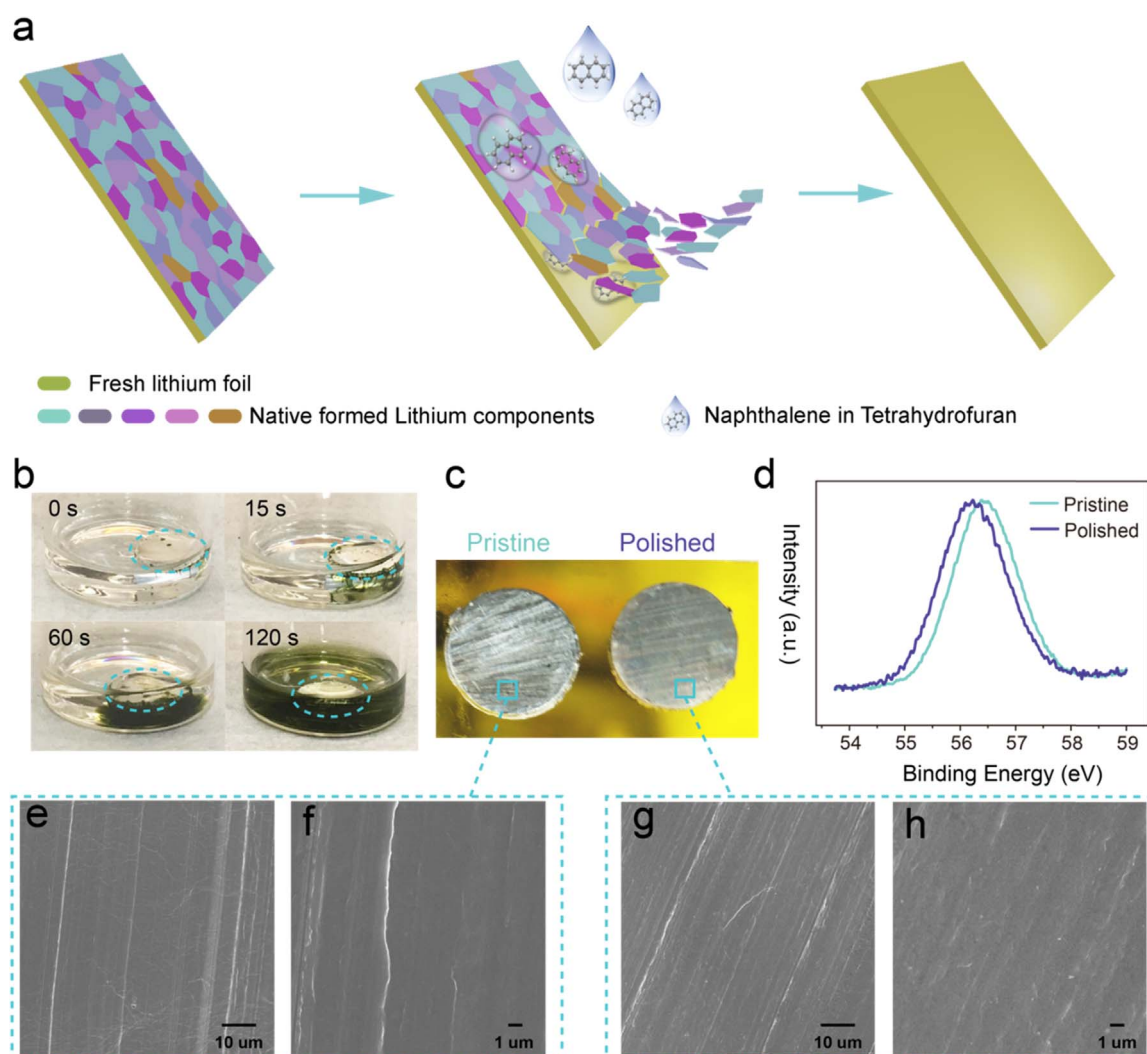


Fig. 1. Preparation and characterizations of polished lithium foil. (a) Schematic of the preparing process of polished lithium foil. The different colors represent the different components formed on the lithium foil with various surface formation energies and diffusion barriers. (b) Time-lapsed digital photos to show the polishing process of lithium foil by naphthalene in tetrahydrofuran. (c) Digital photos of pristine and polished lithium foils. (d) Li 1s synchrotron Radiation XPS of pristine and polished lithium foils. SEM images of pristine (e, f) and polished (g, h) lithium foils.

can significantly improve the electrochemical performance of lithium iron phosphate in terms of rate capability and specific capacity.

2. Results and discussion

Polished lithium is obtained through a simple etching in a naphthalene solution in tetrahydrofuran (Fig. 1a). In this process, the lithium metal layer underneath the surface film reacts with the aromatic hydrocarbons in naphthalene to form a dark green alkali solution at room temperature (Fig. 1b). Subsequently, the surface film peels off to expose the fresh lithium surface (Fig. 1a, a successful removal of the low conducting layer on lithium foil during polishing process leads to an obvious decrease of surface charge transfer resistance as shown in Fig. S1) [62–64]. As shown in Fig. 1c, the polished lithium foil shows a smoother surface than that of pristine lithium foil. The Li 1s peak of polished lithium foil shifts to lower binding energy, indicating the successful removal of the lithium components from lithium foil upon polishing (Fig. 1d, detailed XPS spectra are shown in Fig. S2). Upon careful examinations of SEM images, it is found that the pristine lithium foil was covered with rigid lithium components film while some cracks can be observed from the surface (Fig. 1e, f). After polishing, the rigid surface layer is successfully removed from the lithium foil (Fig. 1g, h).

Lithium dissolution/deposition on the polished lithium foil was then carefully examined by SEM at different electrochemical status. SEM images are false-colored for greater clarity. The original images of Figs. S2–S4 and more SEM images are included in Figs. S3, S4, S5, S6, S7, S8, S9, S10, S11, S12. There is pronounced morphological difference in the dissolution/deposition with pristine and polished lithium foils. As shown in Fig. 2a, the initial dissolution (5 min) of lithium generates cracks with diameters between 5 μm to 10 μm on the surface film of the pristine lithium foil. Magnified SEM images and SEM images of the initial dissolution of pristine lithium foil at 15 min are shown in Fig. S3. With a better ionic conductivity, more lithium is excavated from these cracks during extended dissolution, leading to the formation of deep pits on the surface of pristine lithium foil (Fig. 2b and c). The pits range in size from approximately 20 to 30 μm in diameter, (Fig. 2c) indicating the uneven removal of lithium from the surface. In contrast, there is no pit observed throughout the dissolution process on the polished lithium foil (Fig. 2d, e, f, magnified SEM images and SEM images of the initial dissolution of polished lithium foil at 15 min are shown in Fig. S4). In addition, there is also higher percentage of the surface involved in the electrochemical dissolution in the polished lithium. At the end of dissolution (Fig. 2f), some terrace-like structures are observed, indicating that the lithium dissolution on polished surface may have certain facet preference. Similar phenomena were previously observed in the micro-

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