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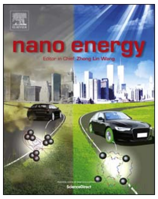

Communication

Stabilizing Li/electrolyte interface with a transplantable protective layer based on nanoscale LiF domains

Zhe Peng[a], Ning Zhao[d], Zhenggang Zhang[a], Hao Wan[a], Huan Lin[a], Meng Liu[a], Cai Shen[a], Haiyong He[a], Xiangxin Guo[b,*], Ji-Guang Zhang[c,*], Deyu Wang[a,*]

[a] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China
[b] CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
[c] Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA
[d] College of Physics, Qingdao University, Qingdao 266071, China

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ABSTRACT

Although Li metal has been regarded as one of the most promising anode materials, an unstable Li/electrolyte interface during the cycling process seriously limits its practical application in rechargeable batteries. Herein, we report a transplantable LiF-rich layer (TLL) that can suppress the side reactions between electrolyte and lithium metal. This peelable layer cross-linked by nanoscale LiF domains is obtained by electrochemically reducing NiF_2 electrodes and could be used to protect Li metal anodes. Cu-Li cells using the TLL protection can operate for more than 300 cycles with a Coulombic efficiency as high as ~ 98% in carbonate-based electrolytes. In Li-$LiFePO_4$ cells, lithium metal with a TLL still looks shiny after 1000 cycles (~ 6 months) in contrast to the black surface of bare lithium foil after ~ 500 cycles (~ 3 months). These results clearly demonstrate that the TLL could greatly limit the side reactions between lithium metal and the carbonate-based electrolytes, and may enable long-term stable operation of Li metal batteries.

1. Introduction

Lithium-ion batteries (LIBs) have been used as the primary power sources for electric vehicles (EVs), but the EV driving range still needs to be extended to compete with conventional vehicles powered by internal combustion engines [1]. It is expected that the energy densities of the state-of-the-art LIBs will reach their theoretical limit in the next decade [2]. Therefore, there is an urgent need to develop new electrode and battery systems with high energy densities [1]. In this regard, lithium (Li) metal has been widely considered as the most attractive anode material due to its ultrahigh theoretical capacity (3860 mA h g^{-1}) and low negative redox potential (-3.040 V vs. the standard hydrogen electrode). Its practical application not only can significantly improve the energy densities of conventional batteries, but also expands the cathode candidates from the Li-containing ceramics to materials without lithium, such as oxides and fluorides.

Based on the Li metal anode, the next-generation Li-metal batteries (LMB) can potentially offer 2–3 times higher specific energies than that of the state-of-art LIBs [1,3]. However, practical application of the Li metal anode is seriously limited by its interfacial instability when it is cycled in most electrolytes, which may even lead to explosions, such as those reported in Li-MoS_2 rechargeable batteries in the 1980s [4,5]. Li metal is thermodynamically unstable with organic electrolytes due to the mismatch of their energy levels, and it may react with the solvents rapidly. Although the reactions are suppressed in some solvents in static conditions by the formation of a solid electrolyte interphase (SEI) layer [6–10], most of these layers are insufficiently robust to accommodate the drastic volume change of underlying Li deposition [11,12]. Repeated cracking and reforming of the SEI layers still occurs during the Li deposition/stripping processes, consuming both the electrolyte and Li metal [13].

Interfacial engineering techniques have been applied to address the challenges of dendrite growth and poor Coulombic efficiency (CE) of Li metal anodes. These methods were mainly focused on artificial interface layers [14–20], Li metal confining spaces [21–23], and 3D current collectors [24–26]. Most of the reported systems that perform well are limited to ether-based electrolytes, which are not very stable at a voltage higher than 4 V. To avoid oxidative decomposition of the solvent, these systems had to operate below 3.5 V vs. Li/Li^+, which narrowed the range of candidate cathodes. In addition, these methods always require complicated preparation procedures, which limit their practical application.

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* Corresponding authors.
E-mail addresses: xxguo@mail.sic.ac.cn (X. Guo), jiguang.zhang@pnnl.gov (J.-G. Zhang), wangdy@nimte.ac.cn (D. Wang).

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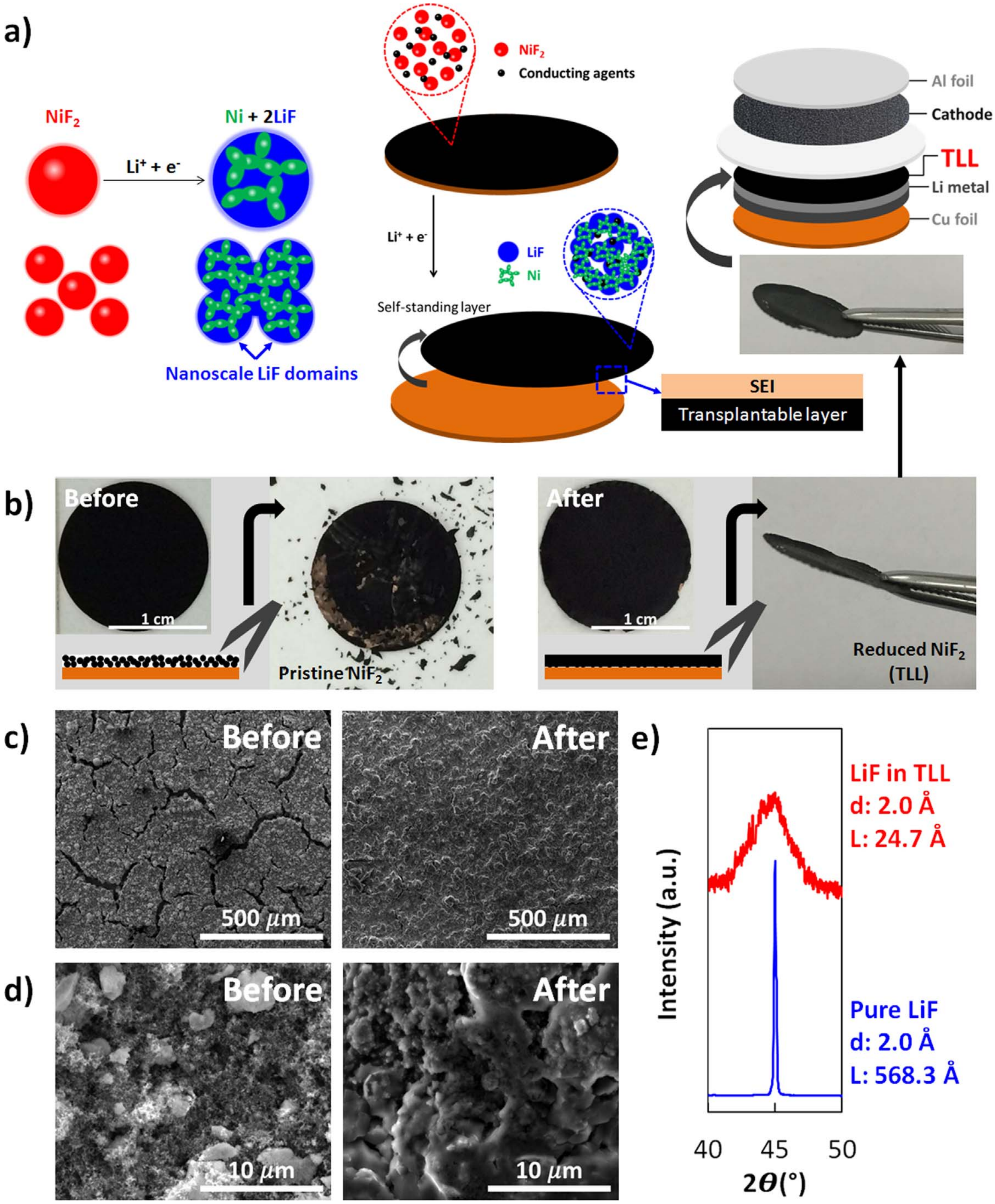

Fig. 1. a) Schematic representation of the structural evolution of the nickel fluoride (NiF_2) during electrochemical reduction, and the as-formed TLL; b) Digital photos of the NiF_2 layers before/after electrochemical reduction, with their states after being peeled off using tweezers; c, d) SEM images of the NiF_2 layer before/after electrochemical reduction; e) The interatomic layer distances, d, and domain sizes, L, of the LiF phases in the TLL and pure LiF powders, obtained by analyzing the peaks indexed to the (200) plane of LiF crystalline structure.

Recently, we have proposed a series of protective structures to extend the working life of Li metal anodes, including using a porous alumina layer to alleviate the volume variation during Li plating and stripping [27], and using Li_2O to reinforce the porous structure of the passivation layer to further extend the lifespan of Li metal anodes in carbonate-based electrolytes [28]. Based on these successes, we expect that a lithium fluoride (LiF)-rich artificial protective layer could further improve the stability of Li metal anodes, since it has been known that the presence of LiF on Li surface could be promising to stabilize SEI layers and enable smooth Li deposition and dissolution [29–36]. However, conventional LiF-containing layers formed during cycling by adding electrolyte additives such as fluoroethylene carbonate (FEC) [37–39], hydrofluoric acid (HF) [40,41], and a trace amount of H_2O [42,43], are so vulnerable that cannot protect Li metal anodes with cycling proceeding. More recently, a conformal technique for coating LiF on Li surfaces has been developed by reacting Li metal with commercial Freon R134a, the as-treated Li metal showed considerable stability in cycling [44].

In this work, we further developed a transplantable LiF-rich layer (TLL) to protect Li metal. The TLL film is composed of cross-linked