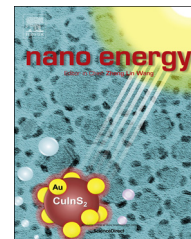


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COMMUNICATION

Dendrite-free Li deposition using trace-amounts of water as an electrolyte additive



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Abstract

Residual water (H_2O) presents in nonaqueous electrolytes has been widely regarded as a detrimental factor for lithium (Li) batteries. This is because H_2O is highly reactive with the commonly used $LiPF_6$ salt leading to the formation of HF which subsequently corrodes battery materials. In this work, we demonstrate that a controlled trace-amount of H_2O (25–50 ppm) can be an effective electrolyte additive for achieving dendrite-free Li metal deposition in $LiPF_6$ -based electrolytes, while avoid detrimental effects. Detailed analyses revealed that the trace amount of HF derived from the decomposition reaction of $LiPF_6$ with H_2O is electrochemically reduced during the initial Li deposition process to form a uniform and dense LiF-rich solid electrolyte interphase (SEI) layer on the surface of the substrate. This LiF-rich SEI layer leads to a uniform distribution of the electric field on the substrate surface thereby enabling uniform and dendrite-free Li deposition. Meanwhile, the detrimental effect of HF on the other cell components is diminished due to the consumption of the HF in the LiF formation process. Microscopic analysis reveals that the as-deposited, dendrite-free Li films exhibit a self-aligned and highly-compact Li nanorod structure which is consistent with a vivid blue color due to structural coloration. These findings clearly demonstrate a novel approach to control the nucleation and

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grow processes of Li metal films using a well-controlled, trace-amount of H₂O, as well as illuminate the effect of H₂O on other electrodeposition processes.

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Introduction

Lithium (Li) metal has been widely considered to be one of the most attractive high energy anode materials for the next-generation rechargeable batteries - such as those based upon Li-S and Li-O₂ chemistries, as well as other Li metal batteries with intercalation compounds as the cathode - because of Li metal's ultrahigh theoretical capacity (3860 mA h g⁻¹), very low negative reduction potential (-3.040 V vs. SHE), and low density (0.534 g cm⁻³) [1-3]. However, dendrite growth during repeated Li deposition/stripping cycles and a low Coulombic efficiency for these processes remain as two major problems which preclude the widespread application of Li metal anodes in rechargeable batteries. In particular, Li dendrite growth or mossy Li generation can accelerate the capacity fade of the battery due to the formation of electrically isolated Li (i.e., "dead" Li unavailable for the battery reaction). Of even greater concern, however, is the potential for the Li dendrites to penetrate through the separator, causing internal short circuiting followed by thermal runaway of the battery, which is unacceptable for commercial applications.

Over the past 40 years, tremendous effort has been devoted to observing [4,5], analyzing [6,7] and modeling [8-10] the formation/growth of Li dendrites. The concept of a solid electrolyte interphase (SEI) proposed by Peled [11] in 1979 has been extensively investigated as part of these studies. Li metal is known to be thermodynamically unstable with organic electrolyte constituents. Once Li metal contacts the electrolyte, it rapidly reacts with the solvent(s) and/or salt anions in the electrolyte to form an electrically insulating, but ionically conductive SEI layer that physically prevents the direct contact between the Li metal and electrolyte [12]. This SEI layer has been revealed to mainly consist of ROCO₂Li, ROLi, Li₂CO₃, and/or LiF, depending upon the electrolyte composition [13]. However, it has been reported by Aurbach [14] that these SEI layer components are usually not robust enough to accommodate the rapid changes in the morphology of the Li layer underneath and thus cracks occur as a result of the breakdown and reparation of the surface films during the Li deposition/stripping processes. Li metal protrusions can therefore grow out from these cracks and Li⁺ cations may preferentially deposit on them to form Li dendrites. A recent work by Sacci et al. [15] using in situ electrochemical transmission electron microscopy (TEM) revealed that the random ordering of the SEI plays a role in the subsequent Li dendrite formation. Therefore, the stability and uniformity of the SEI layer is one of the most critical factors that determine the Li deposition morphology. A more uniform SEI film leads to more

homogeneous ion conduction across the deposition area and decreases protuberant tip formation. Thus, a stronger SEI film may effectively suppress Li dendrite growth.

To improve the interfacial stability of the Li electrode, a variety of strategies have been investigated, including the use of different electrolyte solvents, salts, and additives [2,16,17]. For instance, hydrofluoric acid (HF) was proposed by Kanamura et al. as an additive to modify the SEI layer [18,19]. A small amount of HF was added to a liquid electrolyte and the HF reacted, via an acid-base reaction, with the native Li surface layers, which were mainly composed of Li₂O, LiOH, and Li₂CO₃, to produce a LiF-Li₂O bilayer. This SEI layer was reported to be dense and uniform and therefore induced a uniform current distribution during Li deposition and dissolution. Recently, Togasaki et al. reported that trace amount of H₂O accompanied with CO₂ can significantly improve the cycling performance of Li metal anode [20]. The beneficial effect of LiF on Li electrodeposition was also reported by Archer and coworkers [21], who found that simple liquid electrolytes with the lithium bis(trifluoromethanesulfonyl)imide (Li(SO₂CF₃)₂ or LiTFSI) salt and propylene carbonate (PC) solvent (i.e., 1.0 M LiTFSI-PC), when reinforced with 30 mol% LiF salt blends, could lead to stable long-term cycling of a Li metal electrode at room temperature. For such approaches, however, it is difficult to handle the HF addition in commercial electrolyte production processes since HF is highly toxic and corrosive, while LiF salt has extremely low solubility in common organic solvents. Therefore, the addition of 30 mol% LiF in the electrolyte actually results in a suspension of LiF which decreases the ionic conductivity of the electrolytes by about one order of magnitude (to only 1.3 mS cm⁻¹) which is not favorable for practical applications.

Recently, we have found that Cs⁺ cations as an additive promote the formation of an underlying SEI enriched in LiF which formed at about 2.05 V during the initial Li deposition process and lead to dendrite-free Li deposition [17]. Herein, we further demonstrate that by intentionally adding trace amounts of water (H₂O) into a lithium hexafluorophosphate (LiPF₆)-based electrolyte, HF can be generated by the hydrolysis reaction of the PF₆⁻ anions. During the initial Li deposition process, the H₂O-induced HF can then be in situ reduced electrochemically to form a thin and dense LiF-rich SEI layer on a copper (Cu) substrate at a potential above that of the Li deposition. This thin SEI layer is uniform and dense, and allows Li⁺ cations transport while minimizing the corrosion of the freshly deposited Li metal by the electrolyte, thus resulting in a dendrite-free Li film. To explore this in greater depth, the morphologies of Li films deposited using various conditions and the mechanism of the dendrite-free Li growth have been investigated by both optical and SEM analyses.

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