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Three-dimensional matrix for lithium metal anode for next-generation rechargeable batteries: Structure design and interface engineering

Long Kong, Qiang Zhang*

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

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The next-generation batteries with very high energy/power densities, affordable cost, safe operation are of paramount importance to electric vehicles and grid-scale storage. Lithium (Li) metal anode paired with conversion reaction cathodes (sulfur and oxygen) is regarded as a Holy Grail research because such battery system can employ earth-abundant elements and afford 3~5 times higher energy density than current lithium ion batteries (3500 Wh kg\(^{-1}\) for lithium-oxygen batteries and 2600 Wh kg\(^{-1}\) for lithium-sulfur batteries) [1]. Despite of unrivaled specific capacity (3860 mAh g\(^{-1}\)) and the lowest electrochemical potential (\(-3.04\) V vs. standard hydrogen electrode), Li metal anode tends to form lithium dendrites and exhibits huge volume change during repeated plating/stripping, which induces very low volumetric efficiency, electrochemical performance degradations, and even safety hazards [2,3].

The Li dendrite growth is attributed to the uneven distribution of Li plating on the metallic anode surface in the presence of pristine protrusions and inhomogeneous electric fields [4]. The higher electric field at the 'hotspot' provides large Li ion flux, which results in accumulation of Li along the axial direction and ultimately develops into Li dendrites (Fig. 1a). The homeless nature of lithium metal anode accounts for the virtually infinite volume change during electrodeposition, thereby causing large Li interface movement. This interface instability, especially at high areal capacity, contributes a fragile solid-state interface (SEI) and consumes the lithium metal and electrolytes.

Lithium dendrite formation includes nucleation and growth, which can be regulated by nucleation density, lithium ion flux, and lithium ion solvation [5]. Incorporating of lithophilic sites (nitrogen and oxygen groups) on conductive substrates or reducing local current density have been demonstrated to effectively modulate lithium deposition behavior [6–9]. Sufficient lithophilic sites can uniformly distribute lithium ions on the substrate surface and avoid high lithium ion flux on the 'hotspot'. To reduce volume change of lithium striping/plating, the robust scaffold with 3D network is considered as a Li ion reservoir, thereby alleviating the volume variation and protecting the vulnerable SEI to some extent.

Recently, Yang and co-workers from Tianjin University originally proposed a lightweight, free-standing and nitrogen-doped carbon nanofiber-based 3D matrix (NCNF) as a two-in-one strategy to circumvent issues of dendrite formation and volume change [10]. Comparing copper current collectors and routine scaffolds, 3D NCNF matrix possessed three attributes: (1) lightweight—the mass density of NCNFs was only 0.57 mg cm\(^{-2}\), much lighter than the commercial Cu current collector (7.96 mg cm\(^{-2}\)), which was beneficial to enhance the energy density based on the whole device; (2) free standing—the 3D intertwined fiber framework obviated the requests of additional binders to hold building blocks together and provided enough space to accommodate volume variation; (3) proper nitrogen-doping level—the 9.5 at% nitrogen heteroatoms afforded a plenty of Li nucleation sites to reduce the nucleation over-
potential and regulate the following Li growth (Fig. 1b, c). These attributes rendered Li deposition in void space instead of forming dendrite, while Li clumps grew and the branch-like Li dendrite was generated on copper surface (Fig. 1d, e). The full cell with a combination of pre-lithiated NCNF anode and LiFePO₄ cathode could deliver a capacity of 122.4 mAh g⁻¹ after 300 cycles, corresponding to a capacity retention of 82.4% (Fig. 1f).

To further advance lithiophilic matrix with lightweight nature as a composite lithium metal anode, the future efforts are deserved to design suitable lithium/electrolyte interface or develop artificial layer to avoid continuous formation of SEI. Moreover, to realize the high energy density of lithium metal batteries, both physical and electrochemical properties, such as porosity, interface and composition, of the matrix should be investigated and optimized to endow it with a stable cell operation under high current density (e.g. 3–10 mA cm⁻²) and large areal capacity (e.g. 3–15 mAh cm⁻²).

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