Facet Selectivity of Li deposition on Cu Current Collector for Anode-free Lithium Metal Batteries

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Li metal is considered as one of optimal candidates for high-energy anode material because it has the highest theoretical specific capacity (3,860 mAh g^{-1}) and the lowest redox potential (−3.04 V vs. standard hydrogen electrode).[1] However, safety concerns and low coulombic efficiency issues, which are caused by the inhomogeneous Li deposition/dissolution and continuous corrosion by electrolytes during battery cycling, have prohibited the use of metallic Li as anode in practical Li metal batteries.[2]

Lithium metal batteries (LMBs), which replace graphite anode with Li metal from conventional lithium ion batteries are considered as the most realistic approach to increase energy density of rechargeable battery. Furthermore, an anode-free LMB which features the only use of current collector in the anode compartment is the design to maximize the energy density of LMB. Because the current collector could affect the nucleation behaviors at the initial state of Li plating and the morphological development of the subsequently plated Li, it is a key component for achieving cycling stability of anode-free LMBs.

Cu current collector is the most widely adopted current collector for the anode of LIBs and LMBs due to its high conductivity, mechanical property, and electrochemical stability, but is known to have a large Li nucleation overpotential in comparison with Au, Ag, Zn, or Mg.[3] That is because the binding energies of Li atom on bulk Li is much larger than that of Li atom on bulk Cu (which are around 24~30 and 2.5~2.7 kcal mol^{-1}, respectively). Therefore, the surficial modulation of Cu current collector is needed to improve the affinity between Li metal and Cu and induce uniform initial Li deposition on Cu current collector.

Herein, we demonstrates the facet selectivity of Li electrodeposition on Cu surface and proposes a new strategy of modulating Cu facet structure to improve the Li plating/stripping efficiency of Li metal. The key feature of this work is 1) to provide a theoretical basis for the facet selectivity by a DFT calculation, 2) to elucidate that (100) facet is the most favorable one for Li nucleation among three major facets of (100), (110) and (111) by comparing the Li electrodeposition behavior of the corresponding single crystals, and 3) to visualize the preferential Li deposition on (100) plane on a Cu current collector with different facet by using EBSD analysis. The discovery motivates us to fabricate Cu current collector with a preferential orientation of (100) plane by means of high temperature annealing. The annealed Cu exhibits two times higher cycling stability compared with a control with a random facet distribution, verifying the efficacy of this approach. Therefore, this work provides a new insight into the development of current collector for anode-free or low Li metal-loaded LMBs.

References:

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