Abstract

Increasing global energy demand requires high energy density batteries for which the replacement of intercalation or conversion anodes with lithium metal is a crucial step towards batteries with improved energy density. State-of-the-art secondary lithium metal batteries still suffer from low Coulombic efficiency and low safety related to the thermodynamically unstable solid electrolyte interphase (SEI) between metallic lithium and the electrolyte in most of the liquid electrolytes, resulting in high surface area lithium (HSAL) growth. Various approaches can be used to suppress HSAL formation, including protective layer preparation on the lithium surface. Properties of the protective layer should be high Li-ion conductivity, electronic resistivity, small thickness, and high Young's modulus to withstand the applied stress during lithium stripping and the deposition process within the cell.

In this work, we investigated three different approaches employed as a protective layer on a lithium surface to suppress HSAL growth. The protective layers were examined with electrochemical measurements supported by scanning electron microscopy, X-ray photoelectron spectroscopy, and other techniques.

We demonstrate that the functionalization of graphene modifies its electronic and ionic properties to make it suitable for use in protective layer applications. The impact of graphene oxide (GO), reduced graphene oxide (rGO), and fluorinated reduced graphene oxide (FG) as protective layers on a lithium surface on HSAL growth suppression was studied in Li symmetric cells. Additionally, the FG protective nature was evaluated in two full cell configurations (Li-ion and Li-sulfur) in carbonate and ether-based electrolyte. The physical characteristics and electrochemical measures had shown the dual role of the FG protective layer. First, it acts as a Li-ion conductive layer and electronic insulator on metallic lithium surface; second, it successfully suppresses dendritic growth. Enhanced electrochemical performance of the full cell battery system indicates potential applications in the secondary lithium metal batteries of the future.

Metal fluorides (MgF_2 and AlF_3) were studied as precursors of protective layers on a lithium surface. The use of MgF_2-modified lithium resulted in denser lithium deposits, enhanced stability in symmetric cells and prolonged cycling in Li-sulfur batteries with fluorinated electrolyte.

Finally, the *in-situ* anionic polymerization of trimethylolpropane ethoxylate triacrylate on a lithium surface resulted in completely hindered lithium ion transport through the layer and exposure of the edge effect. Correspondingly, we designed a new cell configuration that enables more accurate electrochemical evaluation of protective layers with edge effect avoidance.

Keywords: Li-sulfur batteries, Li metal batteries, artificial SEI, protective layer, dendrite growth suppression, graphene oxide, reduced graphene oxide, fluorinated reduced graphene oxide, metal fluoride, anionic polymerization, trimethylolpropane ethoxylate triacrylate, edge effect