Sulfur Cathode Design Strategies Enabled by Stereolithography Technique and Oxidative Chemical Vapor Deposition

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It is urgent to enhance battery energy storage capability to satisfy the increasing energy demand in modern society and reduce the average energy capacity cost. Among the candidates for next-generation high energy storage systems, the lithium-sulfur battery is especially attractive because of its high theoretical specific energy (around 2600 W h $kg^{-1}$) and cost savings potential.[1] In addition to the high theoretical capacity of sulfur cathode as high as 1,673 mA h $g^{-1}$, sulfur is further appealing due to its abundance in nature, low cost, and low toxicity.

Despite these advantages, the application of sulfur cathodes to date has been hindered by a number of obstacles, including low active material loading, low electronic conductivity, shuttle effects, and sluggish sulfur conversion kinetics.[2] The traditional 2D planer thick electrode is considered as a general approach to enhance the mass loading of the lithium-sulfur (Li-S) battery.[3] However, the longer diffusion length of lithium ions required in the thick electrode decrease the wettability of the electrolyte (into the entire cathode) and utilization ratio of active materials.[4] Encapsulating active sulfur in carbon hosts is another common method to improve the performance of sulfur cathodes by enhancing the electronic conductivity and restricting shuttle effects. Nevertheless, it is also reported that the encapsulation approach causes unfavorable carbon agglomeration with low dimensional carbons and a low energy density of the battery with high dimensional carbons. Although an effort to induce defects in the cathode was made to promote sulfur conversion kinetic conditions, only one type of defect has demonstrated limited performance due to the strong adsorption of the uncatalyzed clusters to the defects (i.e.: catalyst poisoning). [5]

To mitigate the issues listed above, herein we propose a novel sulfur electrode design strategy enabled by additive manufacturing and oxidative chemical vapor deposition (oCVD).[6,7] Specifically, the electrode is designed to have a hierarchal hollow structure via a stereolithography technique to increase sulfur usage. Microchannels are constructed on the tailored sulfur cathode to further fortify the wettability of the electrolyte. The as-printed cathode is then sintered at 700 °C in a reducing atmosphere (e.g.: $H_2$) in order to generate a carbon skeleton (i.e.: carbonization of resin) with intrinsic carbon defects. A cathode treatment with benzene sulfonic acid further induces additional defects (non-intrinsic) to enhance the sulfur conversion kinetic. Furthermore, intrinsic defects engineering is expected to synergistically create favorable sulfur conversion conditions and mitigate the catalyst poisoning issue. In this study, the oCVD technique is leveraged to produce a conformal coating layer to eliminate shuttle effects, unfavored in the Li-S battery performance. Identified by SEM and TEM characterizations, the oCVD PEDOT is not only covered on the surface of the cathode but also the inner surface of the microchannels. High resolution x-ray photoelectron spectroscopy analyses (C 1s and S 2p orbitals) between pristine and modified sample demonstrate that the high concentration of the defects have been produced on the sulfur matrix after sintering and posttreatment. In-operando XRD diffractograms show that the $Li_2S$ is generated in the oCVD PEDOT-coated sample during the charge and discharge process even with a high current density, confirming an eminent sulfur conversion kinetic condition. In addition, ICP-OES results of lithium metal anode at different states of charge (SoC) verify that the shuttle effects are excellently restricted by oCVD PEDOT.

Overall, the high mass loading (> 5 mg $cm^{-2}$) with elevated sulfur utilization ratio, accelerated reaction kinetics, and stabilized electrochemical process have been achieved on the sulfur cathode by implementing this innovative cathode design strategy. The results of this study demonstrate significant promises of employing pure sulfur powder with high electrochemical performance and suggest a pathway to the higher energy and power density battery.


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