Engineered Sulfur-MoS$_2$-Graphene Heterostructure Cathodes for Diagnostics of Nanoscale Electrochemical Processes in High Energy Density Li-S Batteries

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Lithium-sulfur (Li-S) batteries have recently attracted enormous attention because of high theoretical specific energy (2600 Wh kg$^{-1}$) and high specific capacity (1672 mAhg$^{-1}$), as well as the low cost, natural abundance, and nontoxicity of elemental sulfur. They represent one of the most promising candidate technologies for emerging applications in electrical transportation, portable electronics, implanted devices, and communications. However, Li-S batteries often suffer from the dissolving and shuttling of lithium polysulfides (Li$_2$S$_x$, x = 3-8) generated as intermediates during electrochemical conversion of sulfur in the electrolyte. This effect, known as a “polysulfide shuttle”, could cause capacity fading, poor Coulombic efficiency, and shorten life time, thus hindering the practical realization of Li-S technology. In recent engineering approaches, sulfur and functionalized carbons (graphene, carbon nanotubes, mesoporous hollow carbons, yolk-shell structures) are integrated with polar hosts such as transition metal dichalcogenides, MX$_2$, M = Mo, Ti, X = S, Se) to reduce the effective diffusion length of the polysulfides via anchoring and electrocatalytic transformation of Li$_2$S$_x$ into insoluble Li$_2$S. Consequently, this strategy shows potential to greatly boost the performance and rate capabilities of the Li-S cells [1].

In this work, we report nanoengineered heterostructures composed of thin layers of sulfur, graphene, and MoS$_2$ as diagnostic composite cathodes that could be used for rational design of high-performance Li-S batteries. The morphology, interfaces, crystallinity, and elemental distributions in the cathodes were characterized at multiple scales down to the atomic level using various imaging, diffraction and spectroscopic modes of high-resolution analytical scanning/ transmission electron microscopy (AS/TEM). Sulfur was deposited onto graphene with low vapor pressure evaporation in an Ar atmosphere. The composites were prepared by heating sulfur to 150$^\circ$C above its melting point (115.2$^\circ$C). Next, graphene flakes were exposed to the sulfur vapor. Fig. 1a demonstrates the morphology and elemental distributions of sulfur island films formed on the surfaces of wrinkled graphene nanosheets. Sulfur layers could be additionally stabilized with 1,3-diisopropyl benzene (DIB) as a cross-linking agent [2]. Finally, high-aspect-ratio sulfur-graphene-2H MoS$_2$ heterostructures were produced by casting an additional MoS$_2$-flake solution (Figs. 1b and 1c). Such electron transparent sandwich structures could enable the creation of high surface area interfaces required to facilitate electronic and ionic conductivity and charge transfer as well as to enhance the binding capacity towards Li$_2$S$_x$. Using low energy scanning focused Li-ion beam (LiFIB), 2 keV Li$^+$ ions have been injected into a 2x2 µm square with ion current of 1 to 4 pA and dose of 1350 Li$^+$/nm$^2$ (Figs. 2a and 2b). Based on results of spatially-correlated STEM-EELS spectroscopic imaging (SI) analysis (Figs. 2c - 2e), this may allow to initiate local conversion of sulfur into Li$_2$S$_x$ and monitor a state of discharge and further transformations of lithiated species, including catalytic anchoring of Li$_2$S$_x$ on active sites of MoS$_2$.

References:

Figure 1. (a) HAADF STEM, graphene flakes coated with sulfur, EELS sulfur S L\textsubscript{2,3} (yellow) and carbon C K (green) maps (bottom insets) from the area marked by green box. (b, c) TEM, sandwich MoS\textsubscript{2}-sulfur (DIB)-graphene heterostructure, (b) BF-TEM and SAED pattern (inset) showing point reflections from a 2H-MoS\textsubscript{2} structure, near zone axis $B = [001]$. (c) HRTEM, wrinked graphene flakes and sulfur nanoparticles stabilized with DIB on a layered 2H-MoS\textsubscript{2} nanosheet.

Figure 2. Spatially-resolved Li\textsuperscript{+}-ion implantation and correlative LIFIB-FESEM-STEM-EELS SI. (a) LiFIB, ion-induced secondary electron ($i$SE) image of the heterostructure, red circle marks the injection area. (b) Low-voltage FESEM, SE image of the implanted region. (c-f) HAADF STEM-EELS SI, (c) survey image, green box marks an area around the injection region used to collect EELS data; (d) lithium Li K-map (cyan) and (e) sulfur S L\textsubscript{2,3} (yellow) EELS map of the lithiated region; (f) EEL spectrum acquired over the region reveals both lithium and sulfur.