High-Aspect Ratio Sulfur-MoS$_2$-Carbon Heterostructure Electrode Materials for High-Performance Li-S Batteries: Design and Multiscale Characterization by Advanced Focused Ion and Electron Beam Techniques

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The development of emerging energy storage technologies for electrical transportation, portable electronics, implanted devices, and national security increases the demands for the next generation of rechargeable electrochemical batteries with high energy density and long service life. The lithium-sulfur (Li-S) battery is a promising solution because of its 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. However, electrochemical conversion of sulfur into lithium polysulfides (Li$_2$S$_x$, x = 3 - 8) during the discharge often results in capacity fading, poor Coulombic efficiency and limited cycle life, which all are related to parasitic diffusion of Li$_2$S$_x$ from a sulfur-carbon cathode into electrolytes. This "polysulfide shuttle" effect coupled with the insulating nature of sulfur, severely limits the practical realization of Li-S technology. To reduce the effective diffusion lengths of the polysulfides via electrocatalytic transformation into insoluble L$_2$S, two-dimensional (2D) layered transition metal (TM) dichalcogenides (MX$_2$, M=Mo, Ti, X=S, Se) have been employed recently in cathodes for L-S batteries [1, 2]. Thus, new engineering approaches use integration of sulfur and TM dichalcogenides with functionalized carbon materials such as mesoporous hollow carbons, graphene and polymers that can stabilize 2D sulfur layers and improve rate capabilities of the Li-S cells [1]. In this work, we explore coupling of sulfur with nanocrystalline graphene and MoS$_2$ flakes as a prospective route for engineering of heterostructures comprising thin layers of sulfur, graphene, and TM dichalcogenides and compare it with a traditional slurry-based fabrication scheme. Using recently introduced low-energy scanning focused Li-ion beam (LiFIB) combined with various imaging, diffraction and spectroscopic modes of cold field-emission electron gun SEM (C-FESEM) and high-resolution analytical scanning/ transmission electron microscopy (AS/TEM), we characterize the surface topography, morphology, interfaces, crystallinity, and elemental distributions in the composite cathodes at multiple scales up to the atomic level. In previous work, a MoS$_2$-S$_8$ composite-based cathode was fabricated by ball milling a component mixture (1:1 by mass) with conductive carbon, and poly(ethylene) binder in a 75:20:5 mass ratio [1]. The coated cathode films, as revealed by LiFIB (Fig. 1a) and low-voltage C-FESEM (Figs. 1b and 1c), involve 10-50 μm partially exfoliated MoS$_2$ platelets and 10-30 μm rounded sulfur microparticles non-uniformly distributed throughout the cathode matrix. From corresponding X-ray maps (Fig. 1d), one can clearly see the distinct MoS$_2$ flakes, α-S$_8$ microparticles, and aggregated 30-60 nm carbons through different colors, although due to poor cohesion of the components interfaces between them appear to be discrete and limited to a few contact areas primarily near the edges of α-S$_8$ particles and MoS$_2$ flakes and surrounding carbons. On the contrary, graphene flakes coated with sulfur (Fig. 2a) demonstrate much more uniform distributions

of the active material forming thin continuous layers of sulfur over the surface's wrinkled graphene nanosheets. The composites were prepared by heating sulfur powder (Sigma-Aldrich, 99.99%) to ~150°C above its melting point (115.21°C). Next, graphene flakes (GF1200, EMS) were exposed to the sulfur vapor for 30 seconds. The S $L_{2,3}$ sulfur and C K carbon EELS maps (Figs. 2a and b) demonstrate elemental distributions in the area. Finally, MoS_2-sulfur-graphene heterostructures were produced by casting an additional MoS_2-flake solution (Fig. 2c). The results indicate that such sandwich structures involving nanolayered graphene, sulfur, and MX_2 potentially enable high surface area robust interfaces with improved electronic and ionic conductivity and charge transfer as well as the enhanced physical integrity of the composite cathodes.

References:

[1] V.P. Oleshko *et al*, (2017). *Microsc. Microanal.* **23** (S1), 1972-1973.
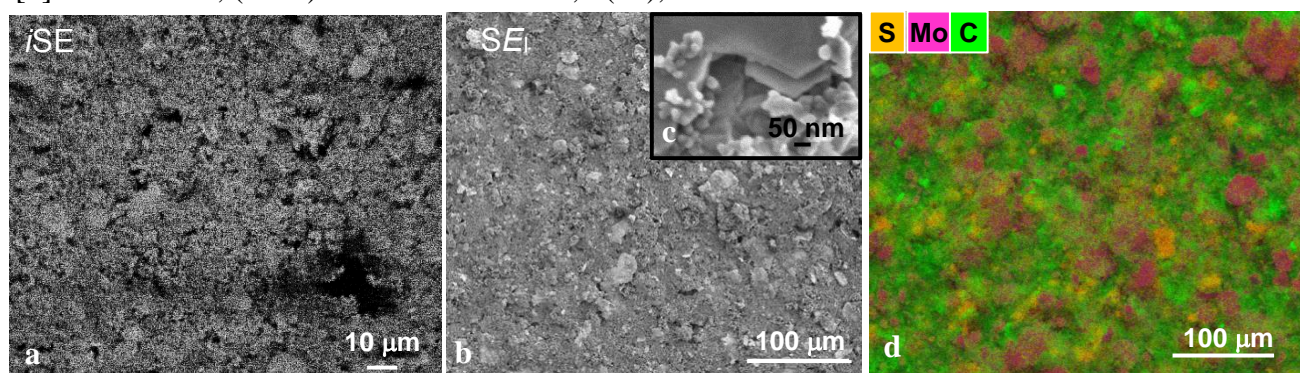[2] Y. Wei *et al*, (2018). *J. Mater. Chem.* A, **6**(14), 5899-5909.

Figure 1. MoS_2-S_8 (1:1 wt.) composite-carbon cathode: (a) LiFIB, ion-induced secondary electrons (*i*SE), accelerating voltage U=3.9 kV; (b, c) C-FESEM, SE_I, U=2 kV; (d) Overlaid S Kα (yellow), Mo Lα (pink) and C Kα (green) net X-ray maps from the same area as (b) derived by deconvolution of severely overlapped the S Kα (2.307 keV) and the Mo Lα (2.293 keV) lines followed background subtraction, U=20 kV.
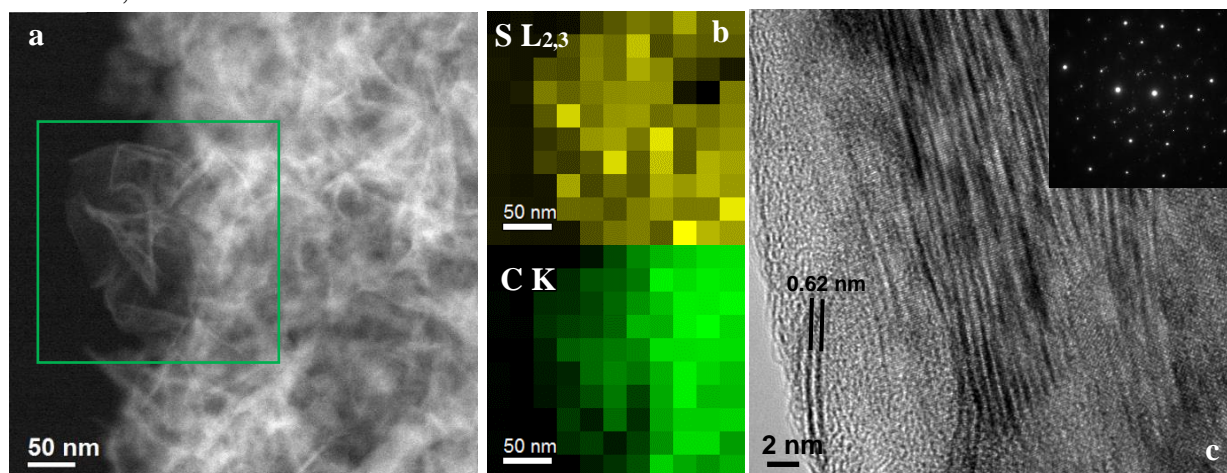

Figure 2. (a) HAADF STEM, graphene flakes coated with sulfur; (b) EELS sulfur S $L_{2,3}$ (yellow) and carbon C K (green) maps from the area marked by green box and EEL spectrum acquired in the region marked by red box; (c) HRTEM, sandwich MoS_2–sulfur-graphene heterostructure: folded layered 2H-MoS_2 structures with a 0.62 nm (002) interlayer separation and its SAED pattern (inset).