

## MoS<sub>2</sub>-S<sub>8</sub> Composite Cathodes for Long Cycle Life High Performance Li-S Batteries Studied by FESEM and High-Resolution AEM

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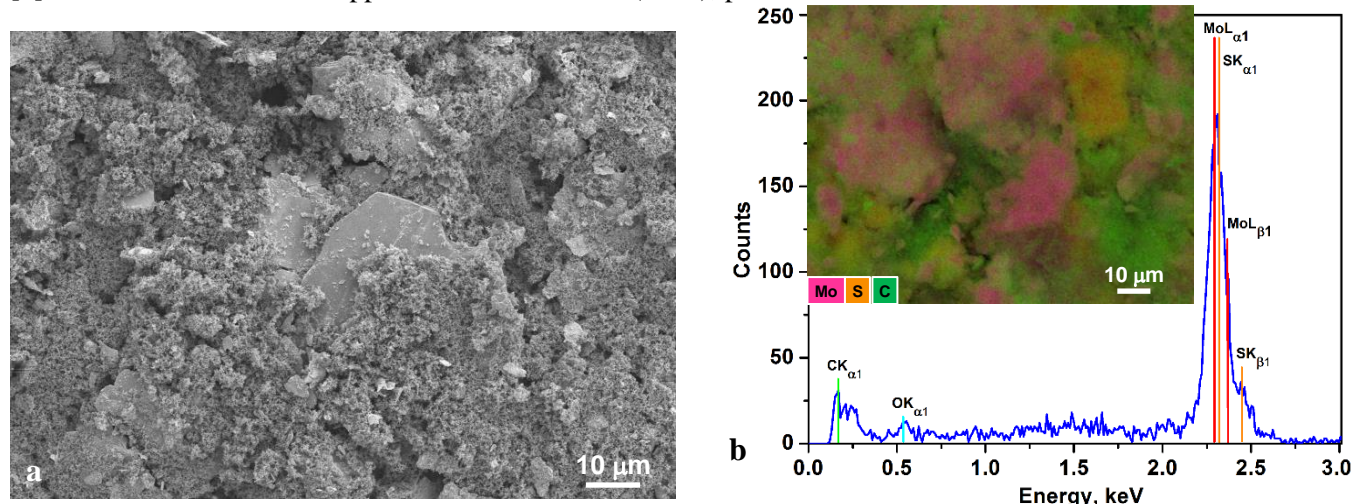
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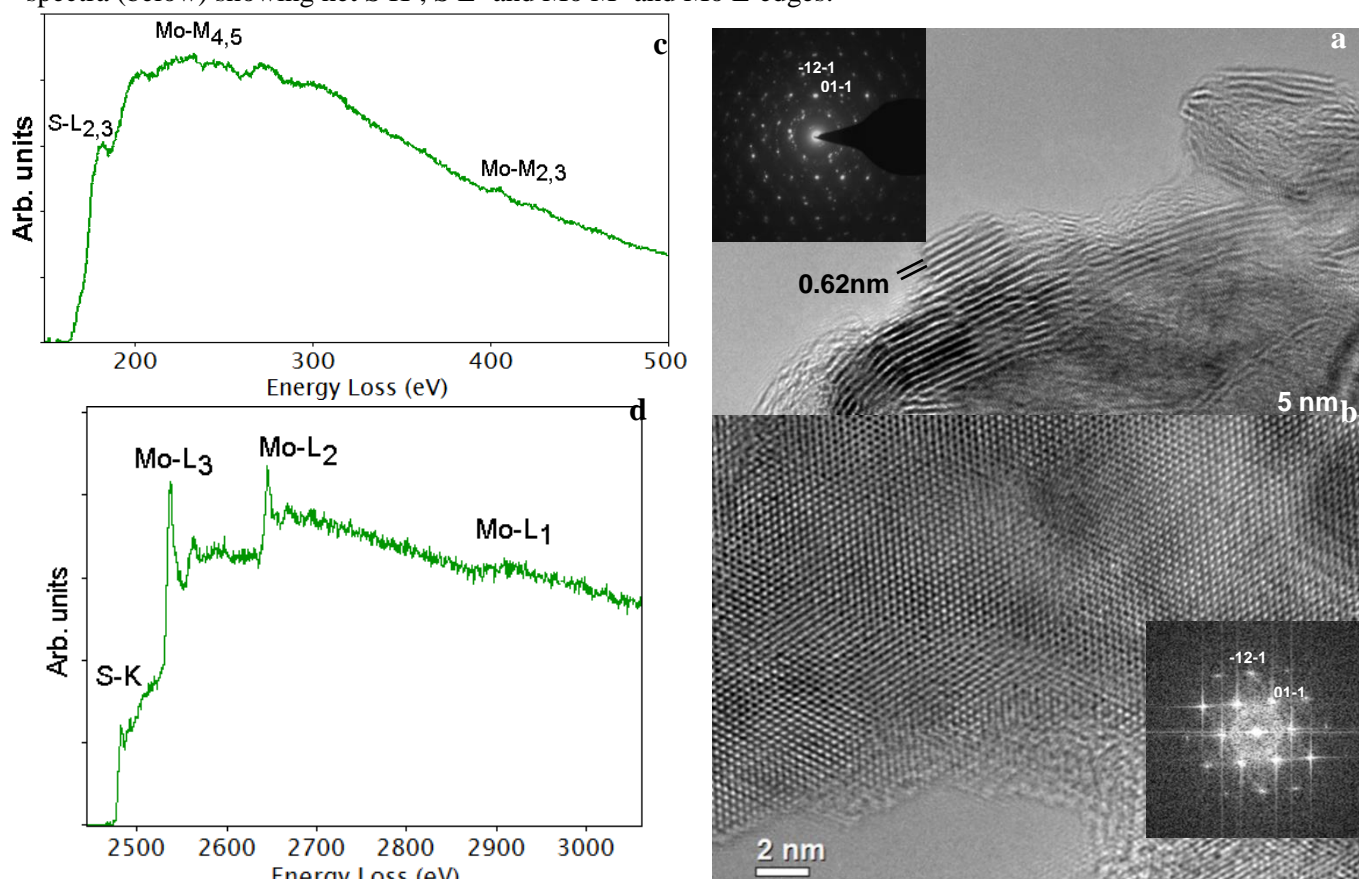
The development of next generation electrical energy storage driven by ever increasing demand is pushing electrochemical power sources beyond the barriers of current Li-ion batteries towards multicomponent composite electrode materials exploring new chemistries with higher energy densities, longer cycle life, and improved safety while being sustainable, “green”, low cost, and reliable. With theoretical specific energy (2600 Wh kg<sup>-1</sup>) and specific capacity (1672 mAhg<sup>-1</sup>), which are the highest among all solid elemental redox couples, Li-S battery is regarded as a prospective technology for near-future commercialization in emerging applications (high-altitude pseudosatellites, long-range electric vehicles (>550 km), portable electronics, and stationary grid energy storage) [1]. Remaining obstacles for the practical realization of Li-S battery technology are, however, pronounced capacity fading, poor Coulombic efficiency, and limited cycle life, which all are to various extent related to parasitic diffusion of soluble lithium polysulfides (Li<sub>2</sub>S<sub>x</sub>, x = 3÷8) during cycling from a sulfur-carbon cathode to a Li metal anode (a “polysulfide shuttle” effect). In order to decrease the effective diffusion length of the polysulfides and enhance cell performance via binding Li<sub>2</sub>S<sub>x</sub> to the cathode surface, nanostructured layered transition metal dichalcogenides MX<sub>2</sub> (M = Mo, Ti, X = S, Se), have been employed. MoS<sub>2</sub>-elemental sulfur (α-S<sub>8</sub>) composites recently introduced as a new active material for cathodes in Li-S cells exhibited extended cycle life up to 1000 cycles, high capacity retention and exceptional rate capability with the delivery of reversible capacity up to 500 mAhg<sup>-1</sup> at 5 C rate [2]. In this work, we explore mechanistic roots for these remarkable improvements using cold-electron gun field-emission SEM (C-FESEM) and high-resolution analytical scanning/transmission electron microscopy (AS/TEM) to characterize the surface topography, morphology, interfaces, and elemental distributions in MoS<sub>2</sub>-S<sub>8</sub> composite-based cathodes. The cathodes were fabricated by ballmilling of a mixture of MoS<sub>2</sub>-S<sub>8</sub> composite (1:1 by mass), conductive carbon, and poly(ethylene) binder in a 75:20:5 mass ratio. Low voltage C-FESEM observations show that 10-50 μm diameter and 20-500 nm-thick crystalline MoS<sub>2</sub> platelets and sulfur microparticles are regularly distributed throughout the cathode matrix comprising carbons and PE binder practically with no cracks usually formed in S<sub>8</sub>-carbon cathodes due to mechanical stresses induced during drying of deposited cathode films (Fig. 1a). Characterization of sulfur distributions in MoS<sub>2</sub>:S<sub>8</sub> composites by EDXS is challenging and requires appropriate standards and fitting references because of severe overlapping of MoL-series and SK-series with only a 17 eV separation between the major characteristic SKα (2.307 keV) and MoLα (2.293 keV) lines (Fig. 1b), On the other hand, with EELS (Figs. 1c and 1d), owing to its higher energy resolution, one can distinguish molybdenum (the Mo M<sub>4,5</sub>-edge (227 eV), the Mo L<sub>2,3</sub>-edge (2520 eV) and sulfur (the S L<sub>2,3</sub>-edge (165 eV) and the S K-edge (2472 eV)). Morphological, crystallographic, and compositional C-FESEM and AS/TEM analyses of the cathodes reveal 3D agglomerates formed by flakes of mechanically disrupted layered MoS<sub>2</sub> platelets and exfoliated nanosheets with large-area interfaces primarily on basal planes surrounded by aggregated 30-60 nm carbon particles and extended micro- and mesoporosity, which serve as electron and ion transport pathways, respectively. HRTEM observations (Fig. 2) indicate that 2D nature and large 0.62 nm (002) interlayer separation in 2H-MoS<sub>2</sub> crystallites provide perfect locations to accommodate and anchor lithium polysulfides suppressing the shuttle effect. These findings demonstrate significant implications from the incorporation of MoS<sub>2</sub>-S<sub>8</sub> composites into the cathodes on the performance of Li-S batteries.

## References:

- [1] V.P. Oleshko *et al*, *Microsc. Microanal.* **22** (2016), p. 1198.  
 [2] P.T. Dirlam *et al*, *ACS Appl. Mater. Interfaces* **8** (2016), p. 13437.



**Figure 1.** (a) Low voltage C-FESEM, secondary electrons, surface topography of a MoS<sub>2</sub>-S<sub>8</sub> composite-carbon cathode with 1.47 mgcm<sup>-3</sup> loading of active material; (b-d) S(T)EM/EDXS-EELS, MoS<sub>2</sub>-S<sub>8</sub> composites, spot X-ray spectrum, 3s acquisition and overlaid SK (orange), MoL (pink) and CK (green) X-ray maps (inset). (c, d) EELS spectra (below) showing net S K-, S L- and Mo M- and Mo L-edges.



**Figure 2.** HRTEM, MoS<sub>2</sub>-S<sub>8</sub> composites, (a) bended layered structures with a 0.62 nm (002) interlayer separation. SAED pattern (inset) of a defective 2H-MoS<sub>2</sub> structure, near zone axis  $B = [001]$ . (b) MoS<sub>2</sub> nanosheets, top view. FFT (inset) indicates 0.27 nm (101) and 0.16 nm (121) lattice fringes.