Supplementary Information for

Interlayer-Expanded Molybdenum Disulfide Nanocomposites for Electrochemical Magnesium Storage

Yanliang Liang,^{1†} Hyun Deog Yoo,^{1†} Yifei Li,¹ Jing Shuai,² Hector A. Calderon,³ Francisco Carlos Robles Hernandez,⁴ Lars C. Grabow,⁵ and Yan Yao^{1,6*}

¹ Department of Electrical and Computer Engineering and Materials Science and Engineering Program, University of Houston, Houston, Texas 77204, USA.

² Department of Physics, University of Houston, Houston, Texas 77204, USA.

³ Departamento de Física, ESFM-IPN, Ed. 9, UPALM-Zacatenco, México, D.F. 07738, Mexico

⁴ College of Technology, University of Houston, Houston, Texas 77204, USA.

⁵ Department of Chemical & Biomolecular Engineering, University of Houston, Houston, Texas 77204, USA.

⁶ Texas Center for Superconductivity at University of Houston, Houston, Texas 77204, USA.

[†] These authors contribute equally to this work.

* Correspondence and requests for materials should be addressed to Y.Y. (e-mail: yyao4@uh.edu)

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Experimental methods

Computational methods. Total energy calculations were performed within the framework of DFT as implemented in the Vienna ab initio simulation package (VASP).¹⁻⁴ The vdW-DF functional was adopted to treat the exchange and correlation potential including a self-consistent van der Waals (vdW) correction to account for dispersion interaction.⁵⁻⁶ A cutoff energy of 540 eV is employed for the plane wave expansion of the wave functions. To study the effect of interlayer spacing of MoS₂ on Mg binding and diffusion, a 3×3×1 supercell containing 18 Mo atoms and 36 S atoms was constructed. Experimental lattice constants for the bulk trigonal prismatic MoS₂ phase (a = 0.3160 nm, c = 1.2294 nm, $\alpha = 90^{\circ}$, and $\gamma = 120^{\circ}$) were used for all calculations.⁷ The good agreement between the computationally optimized lattice constants (a =0.315 nm, c = 1.206 nm) and the experimental reference values confirms the applicability of the chosen computational setup. To preserve a regular interlayer distance during geometry optimizations, one Mo atom in each of the two MoS₂ layers was fixed, while all other atoms were left fully relaxed. Integration over the Brillouin zone uses a 4×4×1 Monkhorst-Pack special k point mesh⁸ and convergence with respect to k points was confirmed. The Mg diffusion process in MoS₂ was studied using the climbing image nudged elastic band method⁹ using five intermediate images to sample the diffusion pathway between the stable O_h and T_h sites.

Material synthesis and characterizations. The PEO-intercalated MoS₂ composites were synthesized by following the method of Lerner et al. with some modification.¹⁰ MoS₂ powder (Aldrich) was soaked in the solution of an excess of 2.5 M *n*-butyllithium in hexane (Aldrich) for 8 h to form lithiated Li_xMoS₂. The lithiated product was delaminated in water to form a quasistable suspension of single-layered MoS₂ sheets. A controlled amount of PEO (0, 0.25, and 1 eq.

relative to MoS₂) was added to the suspension. The mixture was centrifuged, washed with water, and dried at 50 °C in vacuum to afford the PEO-intercalated MoS2 composites with different interlayer distances. The res-MoS₂ was synthesized with the same method without the addition of PEO and dried at a higher temperature of 150 °C to remove loosely adsorbed water. The composition of the synthesized composites res-, peo₁-, and peo₂-MoS₂ were determined to be $Li_{0.21}MoS_2(H_2O)_{1.0}$, $Li_{0.16}MoS_2(PEO)_{0.49}$, and $Li_{0.13}MoS_2(PEO)_{0.98}$, respectively. The samples were characterized by XRD (Rigaku MiniFlex 600) using Cu K α radiation ($\lambda = 1.5406$ Å), Additional characterizations include fourier transform infrared spectroscopy (Thermo Scientific Nicolet iS5), elemental analysis (Midwest Micro Lab), thermogravimetric analysis (TA instruments Q50), inductively coupled plasma optical emission spectrometry (Agilent 725 ICP-OES), scanning electron microscopy (SEM; Gemini LEO 1525), and physisorption analysis (Micromeritics ASAP 2020) using N₂. Transmission electron microscopy was performed in the TEAM 0.5 microscope of the NCEM-LBNL at 80 kV and in low dose conditions. The dose rate in use (15 e Å⁻² s⁻¹) allows taking 40 images at different defoci and an exit wave reconstruction procedure was performed in order to obtain phase and amplitude images with atomic resolution.

Electrochemical characterizations. The electrochemical performances of MoS₂ composites as intercalation host materials for Mg were measured with three-electrode cells. A slurry of the desired MoS₂ composite (70 wt.%), Super-P carbon (20 wt.%), and polyvinylidene fluoride (10 wt.%) dispersed in N-methyl-2-pyrrolidone was spread on a piece of carbon cloth (for Mg-ion experiment; Carbon Cloth Plain untreated, Fuel Cell Earth LLC) or stainless steel mesh (for Liion experiment) and dried as the working electrodes with a mass loading of ~1 mg cm⁻². Freshly polished magnesium foil was used as both the counter and reference electrodes. A solution of $0.25 \text{ M} [Mg_2Cl_3]^+[AlPh_2Cl_2]^-$ in THF was prepared following the method reported by Aurbach *et* $al.^{11}$ served as the electrolyte. Li-ion intercalation experiments were performed with 1 M LiClO₄ in THF as the electrolyte and Li foil as the counter and reference electrodes. THF was used in Liion cell in order to keep the same solvent used in the Mg-cells for fair comparison. Cells were measured using a potentiostat (Biologic VMP-3). The electrodes were operated within 0.2–2.0 V vs Mg²⁺/Mg, which is equivalent to 1.0–2.8 V vs Li⁺/Li as used for Li-cells. The specific capacity was calculated based on the weight of MoS₂. GITT measurements were carried out following a method reported by Weppner and Huggins.¹²



Figure S1. Illustration of Mg coordination in MoS_2 . Two stable sites for Mg intercalation in the MoS_2 structure were considered: (a – c) the octahedral site (O_h-site) where a Mg atom coordinates to three S atoms from both each of the upper and lower MoS_2 triple layers and (d – f) the tetrahedral site (T_h-site) where a Mg atom coordinates to three S atoms from one layer and one S atom from the other layer. Figures a & d, b & e, c & f show the top, side, and bird's view of the structure, respectively.



Figure S2. Compositional characterization with infrared spectra. The presence of PEO in *peo*₁and *peo*₂-MoS₂ can be confirmed by the absorption at 2880 cm⁻¹ corresponding to C–H stretch. A strong absorption peak characteristic of water is found for *res*-MoS₂.



Figure S3. Thermogravimetric analysis result of *res*-MoS₂. The weight loss of *res*-MoS₂ dried at 50 °C is shown. The 6.6% weight loss corresponds to removal of loosely adsorbed water, which was removed by drying at 150 °C in vacuum prior to further characterization and electrochemical measurements. The 9.4% weight loss above 300 °C indicates the presence of 1 equiv of tightly-bound water, which most likely exists between MoS₂ layers.



Figure S4. Morphology characterization of MoS₂ and MoS₂-PEO nanocomposites. SEM images reveal the particle size (a–d) and layer thickness (e–h) of (a&e) *com*-, (b&f) *res*-, (c&g) *peo*₁-, and (d&h) *peo*₂-MoS₂. The starting material *com*-MoS₂ is aggregates of nanoflakes; the diameter of the aggregates is 1–2 μ m and the thickness of the primary nanoflakes is roughly estimated to be < 20 nm. The simply restacked *res*-MoS₂ is large wavy flakes with diameters at the 20 μ m level and thickness of ~0.3 μ m. Upon the inclusion of PEO, both the area and thickness of the flakes continue to grow. The thickness of *peo*₁-MoS₂ is over 0.7 μ m, and that of *peo*₂-MoS₂ is well beyond 1 μ m. PEO seems to act as a polymer binder to glue delaminated flakes into large aggregates.

Table S1. Comparison of properties of Mg and Li.

	Magnesium	Lithium	Sodium
Gravimetric capacity (mAh g ⁻¹)	2205	3861	1166
Volumetric capacity (mAh cm ⁻³)	3833	2066	1128
Potential (V vs NHE) (more negative is better)	-2.372	-3.04	-2.71
Global production (kg yr ⁻¹)	6.3×10 ⁹ (high)	2.5×10^7 (very low)	10 ¹⁰ (high)
Price (carbonate; \$ ton ⁻¹)	600	5000	200
M ⁿ⁺ radius (nm) (smaller is better)	0.065	0.068	0.095
Polarization strength $(10^4 \text{ pm}^{-2})^a$ (lower is better)	4.73	2.16	1.11

^{*a*} Polarization strength (*P*) is calculated as $P = q \cdot r^2$, where *n* is the charge number of the cation and *r* is the ion radius.

	ICP-OES (ppm) ^a		Elemental analysis (wt.%)			Daniana di Camana la
	Li	Мо	С	Н	$n_{\rm H}/n_{\rm C}^{b}$	Derived formula
<i>res</i> -MoS ₂ ^c	1.107	72.82	-	1.11	-	Li _{0.21} MoS ₂ (H ₂ O) _{0.98}
peo ₁ -MoS ₂	1.389	118.6	6.97	1.09	1.86	Li _{0.16} MoS ₂ (PEO) _{0.49}
peo ₂ -MoS ₂	1.103	113.0	12.67	1.98	1.86	Li _{0.13} MoS ₂ (PEO) _{0.98}

Table S2. Chemical composition analysis of the synthesized MoS₂-PEO nanocomposites.

^{*a*} Sample solutions were prepared with the concentration of Li^+ fixed at ~1 ppm.

- ^{*b*} The measured values are close to the theoretical value of 2.0. If 1 eq. of H₂O was contained in the PEO-intercalated MoS₂ composites, the $n_{\rm H}/n_{\rm C}$ ratio would be 6.0 and 4.0 for *peo*₁- and *peo*₂-MoS₂, respectively. Therefore, the H₂O content in these composites, if any, is too low to be measured.
- ^c Sample dried at 150 °C prior to measurement.

Table S3.	5. Comparison of the rate performance of Mg-storage materials in no	n-aqueous
MgRBs.		

Material	Morphology	Capacity retention ^{<i>a</i>}	Mg-storage mechanism	Reference
MoS ₂	Microflakes	60% (1C)	Intercalation	This work
TiS ₂	Nanotubes ($\phi \sim 40 \text{ nm}$)	59% (C/6)	Intercalation	[13]
Mg _{1.03} Mn _{0.97} SiO ₄	Nanoparticles (~90 nm) supported on MWCNTs	40% (C/2)	Intercalation	[14]
Li ₄ Ti ₅ O ₁₂	Nanoparticles (7-8 nm)	41% (C/1.2)	Intercalation	[15]
Mo ₆ S ₈	N/A (likely $\sim 200 \text{ nm})^b$	67% (1C)	Intercalation	[16]
Mo ₆ S ₈	Nanoparticles (~200 nm)	$51\% (1C)^{c}$	Intercalation	[17]
MoS ₂	nanosheets supported on reduced graphene oxide	73% (C/2)	Unknown ^d	[18]
C ₆₀	Nanoparticles (~1 nm)	82% (2C)	Unknown ^e	[19]

^{*a*} Defined as the preserved capacity at a relatively high rate (usually 1C; where there is no data for 1C, the data recorded at the closest rate is used) relative to that measured at the lowest rate employed in the same work. The definition of 1C is given by the original paper; where there is no such definition, the current density required to discharge the capacity obtained at the lowest rate in one hour is considered as 1C.

^b The size of particles was not mentioned in the paper; based on our own experience, the synthesis method employed in this work typically yields nanoparticles with a diameter of ~200 nm.

^c Measurement performed at 15 °C; all other examples were measured at room temperature.

- ^{*d*} The material was discharged to a low potential where conversion reaction could possibly occur; evidence for exclusion of this possibility was not available.
- ^e Mg storage mechanism was not discussed.

	Table S4.	Surface area	measured by	physisorption.
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	Surface area	
	$(m^2 g^{-1})$	
<i>com</i> -MoS ₂	9.4	
<i>exf</i> -MoS ₂	4.3	
peo ₁ -MoS ₂	11.4	
peo ₂ -MoS ₂	7.0	

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