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Intercalation Pseudocapacitance of Exfoliated Molybdenum Disulphide for Ultrafast Energy Storage

Hyun Deog Yoo,^[a] Yifei Li,^[a] Yanliang Liang,^[a] Yucheng Lan,^[b] Feng Wang,^[c] and Yan Yao^{*[a][d]}

Abstract: We report intercalation pseudocapacitance of 250 F g⁻¹ for exfoliated molybdenum disulphide (MoS₂) in non-aqueous electrolytes that contain lithium ions. The exfoliated MoS₂ shows surface limited reaction kinetics with high rate capability up to 3 minutes of charge or discharge. The intercalation pseudocapacitance originates from the extremely fast kinetics due to the enhanced ionic and electronic transport enabled by the slightly expanded layer structure as well as the metallic 1T-phase. The exfoliated MoS₂ could be also used in a Li-Mg-ion hybrid capacitor, which shows full cell specific capacitance of 240 F g⁻¹.

Li-ion intercalates and diffuses inside the interlayer gap of layered materials such as graphite, lithium cobalt oxide, and molybdenum disulfide (MoS₂).^[1-3] Recently, intercalation pseudocapacitance has drawn much attention because of the significantly larger capacitance compared to conventional supercapacitors while maintaining the high-rate capability as a supercapacitor.^[4-7] Intercalation pseudocapacitance, which occurs when ions intercalate into the tunnels or layers of a redox-active material accompanied by a faradaic charge-transfer with no crystallographic phase change, is one of three mechanisms that give rise to pseudocapacitance.^[6] Mesoporous and nano-crystalline oxides were found to exhibit pseudocapacitive behaviors through rapid ion intercalation.^[4,5] Recently, M. Chhowalla *et al.* reported that layered molybdenum sulfides also showed the intercalation pseudocapacitance when exfoliated into nano-sheets and then restacked.^[7] However, the capacity was limited to 100 F g⁻¹ in aqueous electrolyte and less than 60 F g⁻¹ in organic electrolyte.

In this work, we improved the capacitance of exfoliated-restacked MoS₂ to 250 F g⁻¹ in an organic electrolyte containing Li ions. Electrochemical characterization confirmed the ultrafast kinetics mechanism as surface-limited intercalation pseudocapacitance. We also demonstrated a Li-Mg-ion hybrid capacitor with full-cell capacitance of about 240 F g⁻¹, six times

higher than that of conventional activated carbon based supercapacitors.

We synthesized exfoliated and restacked molybdenum disulfide (*exf*-MoS₂) according to Scheme 1. The crystallinity of *exf*-MoS₂ was substantially reduced compared to that of *com*-MoS₂ (Fig. 1a). (002) peak of *com*-MoS₂ corresponds to an interlayer distance of 0.61 nm. For *exf*-MoS₂ sample, we observed weaker and broader (001) peak corresponding to an increased interlayer distance of 0.64 nm. Note that the (001) peak of *exf*-MoS₂ corresponds to the (002) peak of *com*-MoS₂ because of the P6₃/mmc and P1 symmetry of 2H and 1T phase, respectively.^[8] Metallic 1T-phase of *exf*-MoS₂ was clearly evidenced due to the appearance of hexagonal patterns of $a\sqrt{3} \times a\sqrt{3}$ superstructure inside the (100) electron diffraction (ED) ring (Fig. 1b).^[9,10] The amorphous structure is reflected in the ring-shaped ED pattern. Although the interlayer distance slightly expanded, the oxidation state and bond length kept intact. No shift of the Mo K edge was observed for the two samples from the X-ray absorption near edge structure (XANES, Fig. 1c). The extended X-ray absorption fine structure data (EXAFS, Fig. 1d) shows the same bond length for Mo-S (1.9 Å) and Mo-Mo (2.9 Å) before and after exfoliation.^[11] *Exf*-MoS₂ was found to be mainly 1T-phase from our previous XPS study.^[12] It is well known that *com*-MoS₂ also undergoes phase transition from 2H to 1T during the first discharge step.^[8,10] Therefore, both *exf*-MoS₂ and cycled *com*-MoS₂ have similar 1T-phase with the major difference coming from the slightly expanded interlayer distance and the lower crystallinity of *exf*-MoS₂.

Scheme 1. Exfoliation of MoS₂ via chemical lithiation, delamination, and restacking approach.

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Figure 1. Material characterizations of commercial (*com*-) and exfoliated (*exf*-) MoS₂: (a) XRD patterns, (b) TEM images and the electron diffraction patterns, (c) XANES and (d) EXAFS spectra for molybdenum K edge.

In the cyclic voltammogram, current (i) was normalized by scan rate (v) to present the normalized current ($i v^{-1}$), which is equivalent to capacitance in $F g^{-1}$. The normalized current of *com*-MoS₂ reduces significantly as the scan rate increases (Fig. 2a), and the peak current is proportional to the square root of scan rate (Fig. 2b). This behaviour reveals that the intercalation of Li⁺ into *com*-MoS₂ is solid-state diffusion limited.^[13] On the other hand, *exf*-MoS₂ shows nearly constant normalized current with respect to the scan rate (Fig. 2c). The fact that peak current is linearly proportional to the scan rate (Fig. 2d) shows the reaction kinetics becomes surface limited.^[5,13] As a result, structural change from *com*-MoS₂ to *exf*-MoS₂ resulted in the shift of kinetic behavior from diffusion-limited in *com*-MoS₂ to surface-limited in *exf*-MoS₂, therefore exhibiting high rate capability.^[6]

The rapid intercalation of Li⁺ is correlated with the slightly expanded layer structure that lowers the migration barrier of solid-state Li⁺ diffusion in between the MoS₂ layers,^[14] as well as the high electronic conductivity of the metallic 1T-phase. According to the Nernst equation, the intercalation pseudocapacitance (C_p , $F g^{-1}$) is given by a function of occupancy fraction of layer lattice sites (x) as:

$$C_p(x) = Q_0 \frac{dx}{dE} = \frac{Q_0 F}{RT} x(1-x) \quad (1)$$

, where Q_0 , E , F , R , and T denote the specific capacity ($C g^{-1}$), electrode potential (V), Faraday constant ($C mol^{-1}$), Gas constant ($J mol^{-1} K^{-1}$), and temperature (K). According to Eq. 1, the pseudocapacitance is represented as the peak shaped

voltammogram that is maximized at $x = 0.5$.^[15] In *exf*-MoS₂, however, the intercalation pseudocapacitance shows quite flat voltammogram (Fig. 2c). This flat voltammogram is attributed to the variation of site energy caused by the structural disorder.^[16] The flat voltammograms have often been observed from other pseudocapacitive materials such as ruthenium oxide where multiple redox couples are involved.^[17]

The intercalation pseudocapacitance of *exf*-MoS₂ was further confirmed by electrochemical impedance spectroscopy (EIS). EIS was measured at varied electrode potential from 2.5 V to 1.0

V vs Li/Li⁺. The Nyquist plot shows significant decrease in the charge transfer resistance as the potential is lowered to 1.0 V vs Li/Li⁺ (Fig. 3a). This phenomena agrees with the prediction from the Butler-Volmer kinetics where the charge transfer resistance decreases at large overpotential.^[18] Note the real part of the capacitance (C') represents the capacitance value of the electrode at a given potential,^[19] which increases from 50 to 150 F g⁻¹ from 2.5 to 1.0 V vs Li/Li⁺ (Fig. 3b top). The characteristic frequency defined as the peak frequency in the C'' vs $\log f$ plot (Fig. 3b bottom) is about 13 mHz that corresponds to a response time of about 1.3 min.

Figure 2. Mechanistic study of Li-ion intercalation into MoS₂: cyclic voltammograms of *com*-MoS₂ (a) and *exf*-MoS₂ (c); peak current vs. scan rate and fitting for *com*-MoS₂ (b) and *exf*-MoS₂ (d).

Figure 3. EIS results demonstrate the capacitive behaviours of *exf*-MoS₂ at various potential (vs Li/Li⁺): (a) the Nyquist plot and (b) complex capacitance plot vs frequency.

Both *com*-MoS₂ and *exf*-MoS₂ shows the same specific capacity of 140 mAh g⁻¹ at 0.1C rate (Fig. 4a), which is close to the theoretical capacity of LiMoS₂ (167 mAh g⁻¹). The fact we observed the same capacity for both samples supports that the number of intercalation sites remains no change during the preparation of *exf*-MoS₂. The lower voltage profile for *exf*-MoS₂ is related with the broad distribution of site energy due to the disordered structure compared to the crystalline *com*-MoS₂.^[16] Capacitance of about 250 F g⁻¹ is preserved with the cycling of *exf*-MoS₂ at 1C rate for 30 cycles (Fig. 4b), which is calculated using $C = 3.6Q/V$, where Q is 140 mAh g⁻¹ and V is 2 V. It is noteworthy that the capacitance is far larger than the maximum capacitance of the state-of-the-art electric double-layer capacitors (EDLCs), which shows about 100-150 F g⁻¹ in non-aqueous electrolytes.^[20] The rapid intercalation enabled the high capacitance of 150 F g⁻¹ (i.e. utilization of 70%) even at 20C, which is equivalent to 3 minutes' charge or discharge (Fig. 4c). M. Chhowalla recently demonstrated ~ 60 F g⁻¹ intercalation pseudocapacitance in organic electrolyte using *exf*-MoS₂ prepared in a similar method.^[7] The fact that we obtained 300% higher capacity may be due to the smaller size of Li⁺ than EMIM⁺ cations used in their study, therefore allowing a larger amount of Li⁺ to be intercalated.

The intercalation pseudocapacitor electrode can also be applied in various configurations.^[21] We demonstrate a hybrid Mg-Li supercapacitor in Fig. 4d that can maximize the utilization

of large intercalation pseudocapacitance by pairing *exf*-MoS₂ with a magnesium metal anode.^[22] Magnesium anode shows flat deposition/dissolution voltage profile (slope ~ 0) with high gravimetric (2205 mAh g⁻¹) and volumetric capacity (3833 mAh cc⁻¹). So the capacitance, which is inversely proportional to the slope of the voltage profile, is virtually infinite (∞). Moreover, the magnesium metal anode is not susceptible to dendrite growth, in contrast to dendritic deposition of Li metal anode. Moreover, Mg metal shows excellent rate capability that could match with supercapacitor cathode.^[22] The Mg hybrid intercalation pseudocapacitor attained full-cell capacitance of about 240 F g⁻¹ at 0.1C rate, considering the total mass of both *exf*-MoS₂ and Mg metal electrodes (Fig. 4d). The full-cell capacitance is 6 times higher than that of symmetric supercapacitors based on activated carbon electrodes, which is usually 30-40 F g⁻¹.^[23]

In conclusion, exfoliated-restacked MoS₂ shows surface-limited intercalation pseudocapacitance behaviour which enables ultrafast energy storage with enhanced capacitance of 250 F g⁻¹. Even at the high rate 20 C (3 minute charge or discharge), a high capacitance of 150 F g⁻¹ still retained. The Li⁺ intercalation kinetics is facilitated by exfoliation which provides reduced diffusion barrier for Li⁺ transport and the metallic 1T-phase that enhances the electronic conductivity. This study shows the exfoliated-restacked MoS₂ as a promising intercalation pseudocapacitor material for ultrafast energy storage.

Figure 4. Li-ion intercalation pseudocapacitance: (a) voltage profile at 0.1C, (b) capacitance retention at 1C rate, (c) rate performance. (d) voltage profile of a Li-Mg hybrid capacitor with the potential of both electrodes measured simultaneously.

Experimental Section

Material synthesis and characterizations. Commercial molybdenum disulphide (*com*-MoS₂) powder (Aldrich) was soaked in n-butyllithium in hexane (Aldrich) to form Li_xMoS₂. The lithiated product was exfoliated in water to form a quasi-stable suspension of single-layered MoS₂. The suspension was centrifuged, washed with water three times, and dried as restacked sample (*exf*-MoS₂). The samples were characterized by synchrotron radiation ($\lambda = 0.78$ Å, Beamline X14A at Brookhaven National Laboratory), X-ray absorption spectroscopy (XAS, Beamline X18A at Brookhaven National Laboratory), and transmission electron microscope (TEM, JEOL 2100F).

Electrochemical characterizations. The electrochemical performances of MoS₂ samples were characterized with three-electrode cells using a potentiostat (Biologic VMP-3). Slurry of the active material (70 wt.%), Super-P carbon (20 wt.%), and polyvinylidene fluoride (10 wt.%) dispersed in N-methyl-2-pyrrolidone was spread on a piece of stainless

steel (316L) mesh and dried to form the working electrode. Li-ion intercalation experiments were done with 1 M lithium perchlorate (LiClO₄) in tetrahydrofuran (THF) as the electrolyte and Li foil as the counter and reference electrodes. A solution of 0.25 M [Mg₂Cl₃]⁺[AlPh₂Cl₂]⁻ and 0.5 M lithium chloride (LiCl) in THF served as the electrolyte for a Li-Mg-ion hybrid supercapacitor.

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Keywords: Energy storage • Intercalation pseudocapacitance • Molybdenum disulphide • Exfoliated structure • Supercapacitor

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COMMUNICATION

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