

Pseudocapacitive Charge Storage in Thick Composite MoS₂ Nanocrystal-Based Electrodes

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A synthesis methodology is demonstrated to produce MoS₂ nanoparticles with an expanded atomic lamellar structure that are ideal for Faradaic-based capacitive charge storage. While much of the work on MoS₂ focuses on the high capacity conversion reaction, that process is prone to poor reversibility. The pseudocapacitive intercalation-based charge storage reaction of MoS₂ is investigated, which is extremely fast and highly reversible. A major challenge in the field of pseudocapacitive-based energy storage is the development of thick electrodes from nanostructured materials that can sustain the fast inherent kinetics of the active nanocrystalline material. Here a composite electrode comprised of a poly(acrylic acid) binder, carbon fibers, and carbon black additives is utilized. These electrodes deliver a specific capacity of 90 mAh g⁻¹ in less than 20 s and can be cycled 3000 times while retaining over 80% of the original capacity. Quantitative kinetic analysis indicates that over 80% of the charge storage in these MoS₂ nanocrystals is pseudocapacitive. Asymmetric full cell devices utilizing a MoS₂ nanocrystal-based electrode and an activated carbon electrode achieve a maximum power density of 5.3 kW kg⁻¹ (with 6 Wh kg⁻¹ energy density) and a maximum energy density of 37 Wh kg⁻¹ (with 74 W kg⁻¹power density).

1. Introduction

Fast charging batteries are highly desired for portable electronics, electric vehicles, and regenerative energy storage. Traditional Li-ion batteries offer high energy density storage by utilizing reversible redox reactions, but slow ionic diffusion leads to long charging times (\approx 1–10 h).^[1] Electrochemical capacitors (ECs), such as electrochemical double layer capacitors (EDLCs), offer

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some advantages over batteries, including fast charging times (<1 min) and long lifetimes (>500 000 cycles).^[2] However, EDLCs generally have low energy densities (5–10 Wh kg⁻¹) compared to batteries (100–250 Wh kg⁻¹), since they do not involve redox reactions.^[3]

Pseudocapacitors are another type of EC that have the potential to combine the attractive high energy density storage of batteries with the fast rates of EDLCs.^[4,5] Pseudocapacitance was originally described by Conway who identified Faradaic mechanisms that result in capacitive electrochemical features. The most useful of these charge storage mechanisms for energy storage are redox pseudocapacitance and intercalation pseudocapacitance.^[6,7] Redox pseudocapacitance occurs when a Faradaic charge transfer process takes place at or near the surface of a material, accompanied by adsorption of charge balancing ions.^[8–14] Conway originally described the pseudocapacitive mechanism to also

include lithium intercalation into some layered host materials,^[6] but the majority of the work published in this field focuses on surface redox-based electrochemical reactions in materials such as RuO₂^[8-12] and MnO₂.^[14] This bias toward materials showing surface pseudocapacitance has led to intercalation pseudocapacitance (another distinguishable pseudocapacitive mechanism) being dismissed or confused in some cases with traditional battery reactions. However, several papers clearly distinguish key differences between intercalation pseudocapacitance and batterylike reactions.^[15–19] Intercalation pseudocapacitance is similar to familiar battery-type intercalation, but unlike traditional battery materials, the charge storage mechanism and electrochemical response is not dominated by diffusion limitations. Another key feature that distinguishes intercalation pseudocapacitance from traditional battery-type intercalation reactions is that these materials do not undergo phase transitions in association with charge storage.^[18,19] As a result, materials that store charge dominantly through intercalation pseudocapacitance display fast kinetics and long cycle lifetimes.^[17,18,20,21]

The electrochemistry of hydrous ruthenium oxide in acidic solutions exhibits classic surface redox pseudocapacitance and has been studied for over 30 years because of its relatively high capacitances, high proton conductivity, and high electronic conductivity.^[8–10,12] However, the high cost of ruthenium has led

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groups to develop materials based on less expensive transition metals. We have developed a variety of oxide-based nanostructures that store charge through intercalation pseudocapacitance, such as MoO_2 ,^[18] MoO_3 ,^[16,22] and Nb_2O_5 ,^[17,22-24] As mentioned above, intercalation pseudocapacitance is distinguishable from diffusion dominated charge storage, and as a result, the characteristic electrochemical signatures are markedly different.^[4,7,25] For example, the galvanostatic charge and discharge curves of pseudocapacitors are typically pseudolinear with respect to intercalant concentration, in contrast to batteries, which show plateaus.^[26,27] Since intercalant diffusion does not dominate the charge storage in pseudocapacitors, the energy hysteresis between guest-ion insertion and deinsertion is typically small, which can be seen as a small peak separation in a cyclic voltammogram.^[17,22-24] These properties lead to two key technologically relevant properties of pseudocapacitors: (1) The majority of the full theoretical capacity can be accessed within minutes to seconds. (2) The reactions are highly reversible, leading to low parasitic heat generation and long cycle lifetimes.

Much of the work on pseudocapacitors has focused on transition metal oxide-based materials, but metal sulfides are attractive pseudocapacitive materials as well, because the interaction between the guest ion (Li⁺, for example) and the sulfide lattice should be weakened compared to oxides. Furthermore, this weakened interaction should lead to faster ion migration through the lattice. In support of those ideas, we have recently demonstrated high levels of pseudocapacitive charge storage in TiS₂ nanoplatelets^[19] and mesoporous MoS₂ thin films.^[21] MoS₂ is a particularly attractive pseudocapacitive electrode material because the already large van der Waals gap observed 6.2 Å in micrometer sized samples increases up to 6.9 Å in nanostructured samples.^[28,29] The increased van der Waals spacing should further reduce the guest–host interaction, making this an ideal pseudocapacitive material.

MoS₂ also has a second advantage, which is that lithium insertion into the semiconducting 2H phase of MoS₂ induces a phase transition to the metallic 1T phase of MoS_2 .^[30-33] This metallic phase is more conductive than the semiconducting phase of MoS₂, which is an advantage for fast Faradaic-based charge storage. The thermodynamically stable 2H phase of MoS₂ consists of sulfur atoms coordinated in a trigonal prismatic arrangement around the metal, while in the 1T phase, the atoms conform to an octahedral arrangement around the metal center.^[34] The physical rearrangement of the molybdenum coordination environment induces a change in the electronic structure of the MoS2, leading to metallic conductivity.^[31] In agreement with this idea, our group has recently used conductive atomic force microscopy to demonstrate that ordered mesoporous 1T-MoS₂ thin films are significantly more conductive than the 2H form.^[21] It was also recently reported that 10 nm thick exfoliated 1T-MoS₂ has a low sheet resistance $(2 \text{ k}\Omega \text{ sq}^{-1})$,^[35] corresponding to a calculated bulk conductivity of ≈ 500 S cm⁻¹. In hydrogen evolution applications, the intrinsically high electronic conductivity of 1T-MoS₂ is utilized to decrease the overpotential required for hydrogen evolution.^[36] However, the high electronic conductivity of MoS₂ has not been fully leveraged in Li-ion battery applications because many studies have focused on high capacity conversion reaction of MoS₂, which interrupt the metallic 1T form of MoS₂.^[29,37-46]

Additionally, the volume change on cycling for the conversion reaction limits cycle lifetimes to $\approx 100-300$ cycles.^[47] Therefore, utilizing MoS₂ as an intercalation host, and not as a coversion material, is a route to developing fast charging energy devices with long cycle lifetimes.

We note that Li⁺ intercalation in MoS₂ is not a new idea.^[48–50] MoS₂ was seriously considered as a commercial secondary battery in the 1980s because the reversibility is extremely favorable when the lithium concentration in MoS₂ is limited to 1 mole,^[50–53] usually by limiting the lower cut-off voltage window to above 0.8 V versus Li/Li⁺.^[54] In our previous paper, we demonstrated that mesoporous MoS₂ thin films exhibited high levels of pseudocapacitive charge storage, emphasizing the promise of this material system as a fast charging, high power, and long lifetime material.^[21] That study motivated us to see if those observations were limited to thin films, or if those exciting properties could be recreated in thick film composite electrodes, as we have done here.

MoS₂ can be synthesized using a variety of different techniques. Monodispersed 5 nm MoS₂ nanocrystals can be synthesized directly by low temperature colloidal synthesis methods.^[55] The hydrothermal method is another versatile technique, which has been used to synthesize a variety of nanostructured MoS₂ architectures.^[29,56,57] However, both of these methods typically lead to very disordered crystal structures. The energy and power density of pseudocapacitive materials are, to a high degree, dependent on the crystallinity.^[16] Therefore, in this work, we use a two-step process, first creating MoO2 nanocrystals as a precursor using straightforward hydrothermal methods, and then converting those MoO₂ nanocrystals to MoS₂ nanocrystals. This two-step process enables precise control of both the nanoscale architecture and atomic-scale crystallinity. The synthesis method is versatile, and should be applicable to other nanoscale architectures such as wires, belts, and a broad range of porous architectures. Here we specifically use thermal sulfurization in H₂S to convert the MoO₂ to MoS₂, which preserves the carefully constructed nanoscale architecture formed from the solvothermal reaction.^[44,56,58-60] This oxide-to-sulfide conversion is typically achieved above 600 °C, which can lead to well crystallized MoS₂ with good preservation of the preformed nanoscale architecture.^[56] It is worth noting that sulfur vapor can also be used instead of H₂S to convert molybdenum oxides to MoS₂.^[61] Extensive discussion on the various methods used to synthesize MoS₂ can be found in several recent reviews.^[47,62–64]

Commercial electrodes for Li-ion batteries are required to have high active material volumetric loadings to maximize the energy density of the cell. In order for this requirement to be satisfied in pseudocapacitive-based composite electrodes, close attention also needs to be paid to the electrode architecture. The three main components that form a composite electrode are the active material, the conductive additive, and the nonconductive polymeric binder. Optimization of these parameters strongly influences the energy density and power density of the final electrode.^[65,66] Furthermore, nanoparticle active materials tend to agglomerate, making them difficult to disperse homogeneously within the electrode matrix.^[67,68] This random agglomeration results in electronically resistive interparticle contact, ultimately leading to poor power density due to inhomogeneous current gradients. Therefore, even if a material



shows a basic pseudocapacitive response in thin films, the characteristic fast charge/discharge rates cannot be realized if the composite electrode architecture is not optimized for pseudocapacitive charge storage. Porous electrode architectures, which are highly electronically conductive, represent an effective design strategy to maintain the fast rates inherent to pseudocapacitive active materials.

In this study, we combine all of these ideas to synthesize MoS_2 nanocrystals with an expanded layer spacing for use as a high rate and long lifetime pseudocapacitor. The nanocrystals are fabricated into carbon fiber-based composite electrode architectures, and the electrodes show extremely fast charging and discharging kinetics along with long cycling lifetimes. We further utilize precycling steps to convert the 2H phase into the highly conductive 1T phase, which then synergistically couples to the highly conductive carbon fiber mesh electrode architecture. Detailed electrochemical kinetic analyses performed on the nanocrystal-based electrodes are used to quantify the amount of capacitive charge storage. These values can then be compared to electrodes containing micrometer size MoS_2 to fully establish advantages of the MoS_2 nanocrystal composite electrodes.

2. Results and Discussion

2.1. Materials and Characterization

The MoS_2 nanocrystals (nc- MoS_2) studied in this report were synthesized by the sulfurization of hydrothermally prepared MoO_2 nanocrystals. The X-ray diffraction (XRD) patterns of bulk MoS_2 (b- MoS_2) and nc- MoS_2 match the Joint Committee on Powder Diffraction Standards (JCPDS) reference pattern number 37-1492 (**Figure 1**a). We have refined the b- MoS_2 structure in Celref using the hexagonal P63/mmc hexagonal space group and aluminum foil as an internal standard. The lattice parameters for b-MoS₂ are *a* and $b = 3.163 \pm 0.002$ Å and $c = 12.3092 \pm 0.0002$ Å, which is in excellent agreement with previously reported values for MoS₂.^[69] The lattice parameters for nc-MoS₂ are a and $b = 3.14 \pm 0.01$ Å and $c = 12.544 \pm 0.003$ Å. The c-axis lattice parameter is expanded in the nanoparticles to 6.27 Å, compared to 6.15 Å for the bulk sample, in agreement with previous reports for nanosize MoS₂.^[28,29] Furthermore, significant XRD peak broadening is observed for the nc-MoS₂ due to both finite size effects and lattice defects. The domain size calculated from the Scherrer equation is 7 nm, which is smaller than the primary particle size observed from the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Figure 1b-e, respectively. This difference in the calculated Scherrer size versus observed size clearly indicates that the XRD peak broadening is due to a combination of finite size effects and lattice disorder. In agreement with this idea, defects and curvature of the MoS₂ layers can be clearly seen in the TEM images (Figure 1d,e).

Beyond the primary particle size and lattice structure, Figure 1b further shows that in powder form, the nanocrystals aggregate into a nearly ideal interconnected porous network. The surface area and pore sizes in that network can be characterized using nitrogen porosimetry. The surface area for both b-MoS₂ (2 m² g⁻¹) and nc-MoS₂ (35 m² g⁻¹) was calculated from the nitrogen adsorption isotherms shown in Figure 2a using the Brunauer-Emmett-Teller (BET) method.^[70] The surface area of the nc-MoS₂ is almost 20-times larger than b-MoS₂ and leads to a higher density of redox active surface sites for pseudocapacitive charge storage. This is coupled to short intragrain diffusion distance, which favor intercalation pseudocapacitance. The pore size distribution shown in Figure 2b was calculated using the Barrett-Joyner-Halenda (BJH) method^[71] and was used to characterize the pores that are created in the nc-MoS₂ by adhesion of the nanocrystals to each other. The pore size distribution is remarkably narrow for a material formed by random nanocrystal agglomeration, and the 25 nm pore diameter is



Figure 1. a) X-ray diffraction of b-MoS₂ and nc-MoS₂ shows that both materials crystallize in the 2H hexagonal crystal structure (JCPDS 037-1492). The nc-MoS₂ shows significant peak broadening, however, which we assign to both finite size effects and lattice disorder. b) Scanning electron microscope image of nc-MoS₂ shows a network of agglomerated nanocrystals. c–e) Transmission electron microscope images of dispersed nc-MoS₂ show sub-50 nanometer primary particles. Significant defects are observed and are believed to be at least partly responsible for the facile ion insertion into the bulk of the nanocrystal.



Figure 2. Nitrogen isotherm of both b-MoS₂ and nc-MoS₂ a). The calculated surface area for nc-MoS₂ is 35 m² g⁻¹ while the bulk is 2 m² g⁻¹. This 17.5-fold increase in surface area, in part, leads to the pseudocapacitive charge storage mechanism. BJH pore size distribution calculated from the adsorption isotherm in part (a) for nc-MoS₂ b). The porosity shown in the BJH distribution arises from adhesion of the nanocrystals to each other, which creates pores.

well suited to allow facile electrolyte diffusion into the nanoparticle aggregates.

The chemical surface properties of b-MoS₂ and nc-MoS₂ were examined using X-ray photoelectron spectroscopy (XPS), as shown in **Figure 3**. These high resolution spectra can be fit with a single oxidation state for both Mo and S, corresponding to the Mo⁴⁺ and S²⁻ valence states. The peak area ratio between these two elements further yields a Mo:S = 1.05:2.00 stoichiometry ratio for both samples. Since the surface chemistry is identical in bulk and nanosized samples, strong conclusions can be drawn about the effect of size, surface area, and atomic disorder on the enhanced electrochemical performance in the nanosized materials.

2.2. Electrochemistry

The reversible lithium insertion and deinsertion process for MoS_2 is represented by the following equation

$$MoS_2 + xLi^+ + xe^- \leftrightarrow Li_x MoS_2$$
, where $: 0 \le x \le 1$ (1)

Intercalation of Li-ions proceeds through the weakly bonded van der Waals gaps of MoS_2 .^[47,72] The lithium ion binding energy is higher for adsorption into the octahedral interstitials compared to the tetrahedral interstitials, and hence is preferentially stored in the octahedral sites between sulfur layers.^[73] Below x = 0.1 in Li_xMoS₂, intercalation into the 2H-MoS₂ occurs without much change to the initial atomic lattice structure.^[57] However, increasing the concentration of Li between the range 0.1 < x < 1 causes an advantageous irreversible phase change from the semiconducting 2H phase to the metallic 1T



Figure 3. X-ray photoelectron spectroscopy of b-MoS₂ a,b) and nc-MoS₂ c,d). The data can be well fit with a single 4+ oxidation state for Mo and a 2- oxidation state for S. The elemental stoichiometry calculated from the data is 1.05:2.00, Mo:S. These data thus show that the surface of the nc-MoS₂ is the same as the commercial bulk powder, and both surfaces are consistent with bulk MoS₂.

phase at ≈ 1.0 V versus Li/Li^{+,[31,74]} This phase change does not involve a significant structural rearrangement but instead is accomplished by a glide process of the highly polarizable sulfur layers with respect to the molybdenum plane.^[31]

Figure 4 shows dQ/dV plots of the first ten formation cycles at 1C of b-MoS₂ and nc-MoS₂ (in carbon fiber-based electrodes). The 2H to 1T phase transition is observed electrochemically as the large differential charge response at \approx 1.2 V versus Li/Li⁺ in Figure 4a,c. Figure 4b,d shows the same data with cycle 1 omitted (cycles 2–10), so that the evolution of lower intensity peaks can be more easily observed. The data clearly demonstrate the nc-MoS₂ electrodes require multiple cycles to convert to the 1T phase while b-MoS₂ is rapidly converted just after two cycles. This type of behavior is often seen in nanocrystal-based phase transitions where many isolated nucleation events are needed to fully transform a sample.^[75] During the ten formation cycles at 1C, new cathodic and anodic peaks develop, and correspond to the lithiation/delithiation of the electronically conductive MoS₂ 1T phase.^[76] Raman spectroscopy was also performed on lithiated nc-MoS2 to verify the formation of the 1T MoS₂ phase (Figure S1, Supporting Information). The results show the development of four additional peaks between 120 and 350 cm^{-1} , which can be assigned to the 1T phase of MoS₂; along with the loss of the 2H E_{1g} peak at 281 cm⁻¹.^[21,36,77,78] All other peaks in the Raman spectra are shared by both the 2H and 1T phases. The combination of both electrochemical and spectroscopic characterization provides strong evidence that nc-MoS₂ is converted to the 1T phase during these first ten cycles.

Electrochemical impedance spectroscopy was then used to characterize changes in conductivity as a function of precycling. Figure 4e shows the charge transfer resistance of both nc-MoS₂

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Figure 4. Derivative (dQ/dV) of the galvanostatic charge discharge plot of the first ten cycles of nc-MoS₂ a), and b-MoS₂ c) showing the irreversible phase transition and subsequent formation of the highly electronically conducting 1T-MoS₂ phase. dQ/dV of cycles 2–9 of nc-MoS₂ b) and b-MoS₂ d) which shows that the 2H to 1T phase change occurs over ten cycles, while in b-MoS₂ the phase change has occurred after the second cycle. Charge transfer resistance of b-MoS₂ (black) and nc-MoS₂ (blue) electrodes during the first ten formation cycles calculated from the corresponding Nyquist plots. The impedance measurement was collected at 0.8 V versus Li/Li⁺ e). Atomic representation of the 2H to 1T phase transformation. This transformation only involves a small shift in the easily polarized sulfur layer, which is nondestructive to the nanoscale structure f).

and b-MoS₂, which was obtained from their respective Nyquist plots (Figure S2a,c, Supporting Information). The equivalent circuit model used to fit our data, and representative fits using that model are shown in Figure S2d,f,g. This model fits our data well and has been used to fit the impedance spectra of hydrous RuO₂, another pseudocapacitive material.^[10] During the formation cycles (0.8–3.0 V vs Li/Li⁺), the charge transfer resistance is reduced by the 2H to 1T phase change and increased by the formation of the solid electrolyte interphase (SEI). The net result for both nc-MoS₂ and b-MoS₂ is that the charge transfer resistance increases during the first two cycles, mainly due to SEI formation, followed by a gradual decay during the next eight cycles mainly due to the formation of the electronically conductive 1T phase.

Electrode architectures for high rate pseudocapacitive charge storage were optimized in order to maximize the properties of the electronically conductive MoS_2 1T phase. One effective way to achieve highly conductive and porous composite electrodes is to utilize carbon fibers. The shape anisotropy of the carbon fibers can lead to a highly porous mesh that extends from the current collector throughout the electrode.^[79,80] In this work, the electrode components are sonicated together in ethanol to disperse the nanocrystals homogeneously with the carbon fibers and carbon black, which upon drying lead to a highly conductive and porous electrode. We chose to use a poly(acrylic acid) binder since it has demonstrated high rate performance in other systems.^[81,82] SEM images of these electrodes are

shown in **Figure 5**c and Figure S3a (Supporting Information), which demonstrate that the carbon fiber-based electrodes consist of a mesh-type network that appears to be macroporous. A traditional electrode formulation of polyvinylidene fluoride (PVDF) binder and carbon black was used as a comparative baseline to understand the synergy between the electrode architecture, composition, and the pseudocapacitive active material (Figure 5d and Figure S3b, Supporting Information). In Figure S3c,d, we also present cartoons of the traditional carbon black electrodes and the carbon fiber-based electrodes.

The kinetic performance of nc-MoS₂ is shown for these two different electrode formulations in Figure 5a. The nc-MoS₂ active material in the carbon fiber-based electrodes show much better kinetic performance compared to the traditional electrodes. We believe that both particle dispersion and electronic conductivity are dominating factors leading to the superior performance of the carbon fiber-based electrodes. The traditional electrodes were mixed by hand with mortar and pestle, and the final composite electrode probably suffer from poor nanoparticle dispersion, since nanoparticles tend to agglomerate. In contrast, the carbon fiber-based electrodes were mixed using sonication and show extremely good kinetic performance. Sonication assisted mixing homogeneously distributes the nanocrystals throughout the electrode,^[83] enabling synergistic coupling between the nc-MoS₂ 1T-conductive phase and the conductive carbon scaffold. It has previously been shown that improving dispersion in nanocrystal-based electrodes can





Figure 5. Galvanostatic kinetic analysis, after ten formation cycles, comparing $nc-MoS_2$ electrodes made using carbon fibers and mixed using sonication (green), and electrodes made using only carbon black and mixed using a traditional mortar and pestle (red) a). Charge transfer resistance of $nc-MoS_2$ /carbon fiber-based electrodes (green) and $nc-MoS_2$ /carbon black-based electrodes (red) during the first ten formation cycles calculated from Nyquist plots collected at 0.8 V versus Li/Li⁺ b). The charge transfer in the carbon fiber-based electrode is both lower in absolute value and decreases with cycle number because the newly formed 1T MoS_2 is electronically well connected to the electrode architecture. By contrast, the charge transfer resistance in the traditional carbon black-based electrodes monotonically increases, likely due to SEI formation. Backscatter electron images of the carbon fiber-based electrode c) and carbon black only electrode d). The brightness in backscattered images is related to the atomic Z number, so the dark regions are carbon rich and the light regions are MoS_2 rich.

produce markedly better rate performance compared to traditional electrodes. $^{\left[67\right] }$

In order to further understand the disparity in kinetics between the two different electrode formulations, we also performed electrochemical impedance spectroscopy on the carbon black-based nc-MoS₂ electrodes. The Nyquist plots are shown in Figure S2b,e (Supporting Information), and the same equivalent circuit model mentioned previously was also used to fit these data. We found that the pristine charge transfer resistance is significantly higher in the carbon black-based electrode architecture compared to the carbon fiber-based electrode architecture. Furthermore, the charge transfer resistance of the carbon black-based electrodes increases over the first ten formation cycles, in stark contrast to the decrease in charge transfer resistance of the carbon fiber-based electrodes over the same interval (Figure 5b and Figure S2, Supporting Information). These data suggest that the improved rate kinetics in the carbon fiberbased electrodes are a combination of the dispersed nanocrystals in the composite electrode and the good electronic coupling of the nanocrystals to the carbon scaffolding.

Using the optimized carbon fiber-based electrode architecture enables the quantification of important metrics related to pseudocapacitors in a standard slurry-type electrode. We can now move on to compare these metrics between b-MoS₂ and nc-MoS₂ fabricated in the same electrode architecture to understand how nanostructuring affects the electrochemical properties. The kinetic analysis of the nc-MoS₂ shown in **Figure 6** shows markedly better rate performance compared to b-MoS₂. The nc-MoS₂ electrodes retain 50% of the original 1C capacity at 100C while the b-MoS₂ electrodes retain only 17%. Remarkably, these thick film electrodes based on nc-MoS₂ store more than 90 mAh g⁻¹ in less than 20 s.

We calculated the resistor-capacitor (RC) time constants for the three electrode systems developed in this work to better understand the nature of the fast kinetic response (see experimental section). After ten cycles between 0.8 and 3.0 V versus Li/Li⁺ the RC time constant for the traditional carbon black-based electrode (no carbon fiber) with nc-MoS₂ active material is 2.74 ms. In contrast, the RC time constants of b-MoS₂ and nc-MoS₂ in optimized carbon fiber-based electrodes are 1.86 and 1.26 ms, respectively. The optimized electrode architecture decreases the RC time constant twofold for nc-MoS₂. The synergistic coupling of the metallic nanocrystals and the conductive carbon fiber backbone leads to low electrode resistance that is responsible for the enhancement in the RC time constant. These RC time constant values are fairly short compared to other pseudocapacitive material.^[84]

In order to compare these exciting performance results discussed above to other state of the art MoS2-based pseudocapacitors, we have aggregated important performance characteristics of nonconversion type reactions (including both intercalation and surface reactions) in Table 1. At low specific currents, the nc-MoS₂ reported here delivers similar capacity to the best materials reported to date. Most materials reported in the table show specific currents between 3 and 4 A g⁻¹ as their fastest rates, and the nc-MoS₂ reported here delivers 142 mAh g⁻¹ at a specific current of 3.3 A g⁻¹, a value two to threefold higher than other materials included in the table. Moreover, when nc-MoS₂ is cycled at the very high rate of 16.7 A g^{-1} , the delivered capacity is still nearly double the capacities reported for the other materials at a significantly lower specific current. In our recent work on nanostructured MoS₂ thin films, we found similarly fast kinetics,^[21] but what makes this report significant, is the ability to preserve those rates in thicker composite electrodes. This is enabled through the porous electrode morphology and coupling of the highly conductive 1T-MoS₂ nanocrystals to the composite electrode architecture.





Figure 6. Galvanostatic kinetic analysis comparing b-MoS₂ to the nc-MoS₂ in optimized carbon fiber-based electrodes a). The nanostructured material stores nearly four times the charge at 100C compared to b-MoS₂. Galvanostatic lithium insertion and deinsertion profiles at different specific currents of b-MoS₂ b) and nc-MoS₂ c). The galvanostatic traces for the nc-MoS₂-based electrodes are pseudolinear and are quite different from the standard plateaus observed for b-MoS₂.

The fast charge transfer kinetics in nc-MoS₂ can also be understood by the physical charge storage mechanism of ions in the material. Figure 6b shows the galvanostatic charge and discharge traces for b-MoS₂ between 1C and 100C. These traces display the traditional stepped plateau features that are indicative of charge storage accompanied by a phase transition in a battery material. Structural studies have shown that indeed, bulk 1T Li_xMoS₂ undergoes multiple first order phase changes during Li-ion storage.^[76] Phase transformations are in part responsible for the sluggish kinetics in battery-type materials because the nucleation and propagation of new phases are typically slow. In contrast to b-MoS₂, Figure 6c shows galvanostatic traces for nc-MoS₂ that display a pseudolinear voltage response with respect to Li-ion concentration. This sloping response is a hallmark of pseudocapacitance and is also indicative of a solid-solution storage mechanism where no phase change occurs to accommodate the lithiation.^[18,19] As described in the Introduction, pseudocapacitance occurs whenever the charge (*Q*) depends on the change in potential (d*E*), yielding capacitance (*C* = d*Q*/d*E*).^[17] Although these charge storage redox processes are Faradaic in nature, their phenomenological behavior, and response to experimental variables such as sweep rate, are those typical of capacitors.

Generally, the dependency of the current response on the sweep rate in a cyclic voltammetry experiment can be utilized to distinguish the charge storage process according to Equation $(2)^{[86,87]}$

$$i = av^b$$
 (2)

In the framework of this analysis, the measured current i is fit to a power law with scan rate v, and the exponential term b can be determined from the slope of the log (i) versus log(v) plot. Values of b = 0.5 indicate that the current is proportional to the square root of the scan rate, which is consistent with traditional diffusion dominated charge storage.^[86] On the other hand, when b = 1 the current is linearly proportional to the scan rate, which is characteristic of a capacitor-like charge storage mechanism.^[86] Figure 7 shows several of the cyclic voltammograms used to calculate the *b*-values at the current maxima in the anodic and cathodic regimes. The *b*-values that are calculated for b-MoS₂ are labeled on the cyclic voltammetry (CV) plots next to the corresponding peaks used in their calculation. The various peaks display values between 0.65 and 0.83. These values are indicative of a diffusion dominated charge storage mechanism, as expected for micrometer size MoS₂. The b-values for nc-MoS₂ samples are generally much higher, and are found to be between 0.93 and 1.00, indicating that the dominant charge storage mechanism in the nanocrystal-based electrodes is capacitor-like. The fast rate performance in nc-MoS₂ is enabled by this capacitive-type charge storage mechanism, quantified using Equation (2).

Another related analysis using cyclic voltammetry enables the measured current (*i*) at a fixed potential (*V*) to be quantitatively separated into a diffusion contribution and a capacitive contribution^[88]

$$i(V) = k_1 \nu + k_2 \nu^{0.5} \tag{3}$$

In Equation (3), $k_1\nu$ and $k_2\nu^{0.5}$ correspond to capacitive and diffusion contributions to the measured current, respectively, where ν is the scan rate in mV s⁻¹. Equation (3) enables the capacitive charge storage at specific potentials to be quantified along with total capacitive contribution over the entire voltage range. Figure 7 shows the results of this analysis for b-MoS₂ and indicates that charge storage is largely diffusion controlled at current maxima in the cyclic voltammograms, which is supported by the calculated *b*-values from Equation (2). The

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Table 1. Gravimetric capacity of nanostructured MoS₂-based half-cells.

Material type	Guest ion	Slow rate [A g ⁻¹ , mAh g ⁻¹]	Fast rate [A g ⁻¹ , mAh g ⁻¹]	Capacity retention cycles, % retention	Reference
nc-MoS ₂	Li+	0.167, 182	16.7, 91	3000, 81	This study
Hydrothermal MoS_2	Li ⁺	0.2, 200	3, 50	1400, 83 ^{a)}	[48]
Fullerene type MoS_2	Na^+	0.1, 160	4, 61	30, 47	[50]
Exfoliated MoS ₂ (thin film)	H+	5 mV s ⁻¹ , 57 ^{b)} (potentiostatic)	100 mV s ⁻¹ , 49 ^{b)} (potentiostatic)	5000, 75	[85]

^{a)}The capacity increased from \approx 200 to 220 mAh g⁻¹ over \approx 500 cycles, so we normalized the capacity retention by the maximum capacity value and not the initial capacity of 200 mAh g⁻¹; ^{b)}The capacitance reported in this study was converted to capacity using the reported voltage window of 0.85 V. The galvanostatic trace used to calculate the capacitance are nearly linear, so the relationship capacity = (capacitance · voltage)/3.6 is an excellent approximation for this system.

total integrated capacitive charge storage is about 60% (b-MoS₂), which indicates that the parent atomic structure of MoS₂ is an extremely good candidate for pseudocapacitive charge storage.

When we perform the same analysis on $nc-MoS_2$, we find that over 80% of the charge storage is capacitive in nature. Furthermore, the capacitive current is significantly enhanced at the peak maxima voltages compared to $b-MoS_2$, again in



good agreement with the calculated *b*-values from Equation (2), which are close to 1 in all cases. The broad noncapacitive cathodic peak in Figure 7d ≈1.6–1.1 V versus Li/Li⁺ is attributed to the 2H to 1T phase transformation. Even though this phase transition was largely completed before running these CV scans, some slow CV scan rates were used for this analysis to compare the slower diffusion processes in b-MoS₂ to the fast storage processes in nc-MoS₂. However, it has been reported that the 1T MoS₂ phase can convert back to the 2H phase at higher voltages,^[76] and this apparently occurs in the nc-MoS₂ samples cycled at the slowest rates (see Figure S4, Supporting Information). As

indicated in Figure 7d, the 2H to 1T phase transition in the nc-MoS₂ is largely diffusion limited. We expect that even higher total capacitive contributions are possible by elimination of this phase transition by limiting the time that the nc-MoS₂ electrode spends in the fully delithiated state (3.0 V versus Li/Li⁺).

The origin of this fast capacitive charge storage mechanism in $nc-MoS_2$ can be described through structural considerations.



Figure 7. Analysis of the charge storage in the current maxima for $b-MoS_2$ a) and $nc-MoS_2$ b) using *b*-values calculated from Equation (2). This analysis shows that the Faradaic charge storage associated with the peak maxima in CV has a significant diffusion contribution in $b-MoS_2$, while the same Faradaic processes are capacitive-like in $nc-MoS_2$. Quantification of the capacitive and diffusion charge storage in $b-MoS_2$ c) and $nc-MoS_2$ d) as a function of voltage at 0.1 mV/s. This analysis indicates that the $nc-MoS_2$ -based electrodes store charge largely through a capacitive mechanism.

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Much of the structural information available on the electrochemical phase stability of MoS2 has focused on the 2H (semiconductor with hexagonal symmetry) to 1T (metal with trigonal symmetry) transformation discussed above.[31,32,36,74,89] Once this conversion is complete, the 1T-metallic MoS₂ phase has been reported to undergo several first-order phase transformations^[76] between 1 and 2.8 V versus Li/Li⁺; therefore, the fast kinetics observed here raises a fundamental question about the underlying charge storage processes occurring with nc-MoS₂ because these phase transitions should be slow. We have shown in both an oxide and sulfide-based material system that phase transformation suppression is a hallmark of pseudocapacitive charge storage.^[18,19] We thus postulate that similar effects are also occurring here. If charge storage kinetics are not limited by the nucleation and propagation of new phases, charge storage can proceeded directly through fast migration of ions through the weakly interacting sulfide lattice. The sloping voltage profiles observed in the galvanostatic measurements in Figure 7 for nc-MoS₂ electrodes strongly suggests that phase transitions are indeed being suppressed here.

High levels of capacitive charge storage are often associated with long cycle life, and this system is no exception. The cycling stability measured for b-MoS₂ and nc-MoS₂ is shown in **Figure 8** and indicates capacity retention for both samples is above 80% after 3000 cycles at 20C. The excellent cycling performance is associated with reduced structural changes (after the initial formation of the 1T phase) and the expansion in the c-axis direction.^[57] The charge storage capacity in nc-MoS₂ at 20C is nearly 70% greater after 3000 cycles compared to b-MoS₂ as a result of its superior charge transfer properties. Referring back to Table 1, the nc-MoS₂ composite electrodes also cycle more reversibly than all of the intercalation-based entries in the table as a result of the pseudocapacitive charge storage mechanism.

While the half-cell experiments described above provide a clear picture of fundamental redox processes occurring in these MoS_2 -based electrodes, they do not fully demonstrate the potential of these materials in practical devices. To this end, a final set of experiments was performed to assess the technological relevance of this new pseudocapacitive electrode. Hybrid lithium capacitor devices were fabricated using an activated carbon (AC) cathode and a nc-MoS₂ anode. AC is a typical material used in EDLCs for high rate applications, but the energy density is low compared to Faradaic storage processes because charge is stored



Figure 8. Cycle lifetime of nc-MoS₂ and b-MoS₂ electrodes cycled at 20C. Cycle 1 reported here was started after the kinetic study (1C–100C) shown in Figure 7. The long cycle lifetime and high capacity of the nc-MoS₂ is correlated with the established pseudocapacitive charge storage mechanism.



Figure 9. Average discharge energy density versus average discharge power density for a full cell utilizing a nc-MoS₂ anode and an activated carbon cathode. The voltage of this device operates between 0.4 and 3.2 V. Average discharge energy density versus cycle number for an asymmetric nc-MoS₂/activated carbon full cell. b) The voltage of this device operates between 0 and 3.0 V. The fast kinetics and long lifetime is a result of the highly reversible pseudocapacitive charge storage mechanism. These data were mass normalized using the total active mass of both electrodes (\approx 4 mg).

only in the double layer of the electrode-electrolyte interface.^[2,3] Figure 9a shows that the hybrid lithium capacitor device made from a nc-MoS₂ and AC electrode delivers 37 Wh kg⁻¹ at slow rates. In comparison, symmetric AC devices cycled in a similar electrolyte, and between a similar voltage window, deliver a maximum energy of ≈ 20 Wh kg⁻¹.^[90] The redox-based charge storage mechanism found in the nc-MoS₂ is responsible for producing a higher energy density than the double layer charge storage of AC-based devices. If an appropriate pseudocapacitive cathode was used instead of AC, even higher energy density would be expected. The maximum power density of the nc-MoS₂ hybrid devices is 5.3 kW kg⁻¹ (with 6 Wh kg⁻¹ energy density), while symmetric AC devices in similar conditions are reported to deliver only 3.5 kW kg⁻¹ (with 2 Wh kg⁻¹ energy density).^[90] Furthermore, the energy densities and power densities of this sulfide-based material are comparable with other state of the art

oxide hybrid lithium-ion capacitors, such as Nb₂O₅-AC,^[90] TiO₂-AC,^[91] and Li₄Ti₅O₁₂-AC^[92] chemistry. Figure 9b further shows the excellent reversibility of the nc-MoS₂ full cell, which can be cycled 8000 times with little decay in the delivered energy. These data thus indicate that nc-MoS₂ full cells overlap with the power density typically thought to be limited to double-layer type EC devices, while also overlapping with the energy density of some Li-ion battery materials.

3. Conclusions

We have successfully synthesized high surface area MoS₂ nanocrystals with expanded van der Waals gaps, which show high levels of pseudocapacitive charge storage when built into a composite electrode. We have also demonstrated that the electrode architecture can be a dominating factor in the development of composite pseudocapacitors electrodes. The high capacitive contribution measured for the nc-MoS₂-based electrodes is due to the interplay between the nanoscale architecture of the active material and the composite electrode. The high surface area and expanded layer structure of nc-MoS₂ enable fast Faradaic reactions, which leads to charge storage that appears capacitive even though ion migration occurs over distances that normally would be limited by semi-infinite diffusion. We have shown that over 80% of the charge storage is capacitive in nanocrystal-based electrodes, which enables over 90 mAh g⁻¹ to be accessed in only 20 s. Furthermore, the cycling stability of nc-MoS₂ shows over 80% retention after 3000 cycles as a result of the pseudocapacitive charge storage mechanism. Full cell devices utilizing an activated carbon cathode and an nc-MoS₂ anode show extremely attractive charge storage behavior and little capacity fade after 8000 cycles. Moreover, the energy density of devices based on nc-MoS₂ could be almost doubled if a cathode with similar kinetic performance is developed.

The results of this study highlight the importance of sulfidebased pseudocapacitive active charge storage materials. The large 2D galleries of MoS₂ and other metal chalcogenides make them particularly interesting to the pseudocapacitive charge storage field. The next frontier will be developing new sulfide materials that enable intercalation pseudocapacitance over even larger length scales. This work also highlights the important need for composite electrode architectures that are optimized for nanostructured pseudocapacitive active materials. The electrodes discussed in this work represent a significant accomplishment, but if practical devices are to be made from pseudocapacitive materials like these, attention needs to be paid to the synergistic coupling of the active material and the composite electrode in order to move to even thicker composite electrodes. We hope this demonstration of attractive electrochemical properties in sulfide-based pseudocapacitors will stimulate the exploration of other chalcogenide-based materials.

4. Experimental Section

Synthesis: All starting materials were obtained from commercial suppliers and used without further purification. The synthesis of nanosized- MoO_2 has been reported in ref. [18] and is briefly described

here. MoO_2 nanocrystals were prepared solvothermally by dissolving anhydrous $MoCl_5$ (Strem Chemicals) in a mixture of ethanol and deionized water and heating at a reaction temperature of 180 °C for 6 h. The MoO_2 nanocrystals were converted to MoS_2 with H_2S gas. The reaction was carried out in a tube furnace at 600 °C under flowing H_2S/H_2 (H_2S 5 mol%: H_2 95 mol%, Air Gas) for 10 h. A graphite boat was used to convert $\approx 100-200$ mg of MoO_2 to MoS_2 .

Characterization: Powder XRD was performed in a PANalytical X'Pert Pro operating with Cu K α (λ = 1.5418 Å) using a 0.03° step size, a voltage of 45 kV, and a current of 40 mA. XRD patterns were recorded in the range of $5^{\circ} < 2\theta < 80^{\circ}$. TEM was performed using an FEI Technai T12 operating at 120 kV. Nitrogen porosimetry was carried out using a Micromeritics TriStar II 3020. The surface area was calculated from the adsorption branch of the isotherm between 0.04 and 0.30 P/Po using the BET model. The pore diameter and pore volume were also calculated from the adsorption branch of the isotherm using the BJH model. XPS analysis was performed using a Kratos Axis Ultra DLD with a monochromatic Al (K α) radiation source. A charge neutralizer filament was used to control charging of the sample, a 20 eV pass energy was used with a 0.1 eV step size, and scans were calibrated using the C 1s peak shifted to 284.8 eV. The integrated area under the peaks was found using the CasaXPS software, and atomic ratios were also found using this software. The atomic sensitivity factors used were from the Kratos library within the Casa software.

Electrochemistry: The carbon fiber-based electrodes were made from a slurry consisting of 70 wt% nc-MoS₂ or b-MoS₂ (Alfa Asear) powder used as the active component for Li storage, 10 wt% vapor grown carbon fibers (Sigma-Aldrich), 10 wt% carbon black (Alfa Asear) used as conductive additive, and 10 wt% polyacrylic acid solution $(M_w = 250 \text{ K}, \text{ Sigma-Aldrich})$ used as binder. The polyacrylic acid was used as a predissolved 5 wt% solution in 200 proof ethanol. A typical slurry was prepared with 40 mg nc-MoS₂, 5.7 mg carbon black, 5.7 mg carbon fiber, 114 mg 5 wt% polyacrylic acid solution, and 1 mL 200 proof ethanol. These four components were sonicated for 30 min to obtain a homogeneous dispersion. Ethanol evaporation over one hour resulted in a homogeneous thick paste that was cast onto 25 μ m carbon coated Al foil (gift from Coveris) using doctor blading. The slurry was dried at ambient temperature for 1 h and further dried at 25 °C under vacuum overnight to evaporate the excess solvent. The traditional electrode was made from a slurry consisting of 70 wt% nc-MoS₂, 20 wt% carbon black (Alfa Asear), and 10 wt% polyvinyl difluoride (gift from Kynar) dissolved in n-methyl-2-pyrrolidone (Alfa Asear). Components were mixed using a mortar and pestle, and again cast onto 25 µm carbon coated Al foil using doctor blading. The electrodes were dried in a vacuum oven at 110 °C overnight. The mass loading of all the electrodes in this study were \approx 1 mg cm⁻² of active material. These electrodes were assembled into in-house built Swagelok cells using lithium metal as counter electrode, glass fiber (Watman) as separator, and 1 ${\rm M}$ LiPF₆ in a 1:1 ethylene carbonate/dimethylcarbonate solvent (Sigma-Aldrich) with 5% (v/v) fluorinated ethylene carbonate (TCI America) as the electrolyte. Halfcell cycling was carried out on a Bio-Logic VSP potentiostat/galvanostat using a 1C rate that corresponds to 167 mAh g^{-1} . The half cells were precycled ten times between 0.8 and 3.0 V versus Li/Li+ to drive the 2H-1T phase transition before the kinetic analysis and cycling stability measurements.

Raman spectroscopy was performed using a Renishaw inVia Raman confocal microscope (excitation wavelength 514 nm and 200 mW laser power) to study the 2H–1T phase change in bulk and nano MoS₂. The electrodes used for Raman spectroscopy studies are the same as the ones described above. Raman spectroscopy was performed on the pristine and lithiated (0.8 V) states of both bulk and nano MoS₂ after the 11th cycle to ensure the majority of the 2H phase was fully converted to the 1T phase. These slurry electrode samples were electrochemically cycled at 1C from 0.8 to 3.0 V on an Arbin BT-2000 using the same Swagelok configuration and electrolyte formulation described above.

Full Cells: Swagelok cells were also used to cycle the full cells. Those devices were made with a nc-MoS₂ anode and an activated carbon cathode. The electrodes were matched in a 1:5 MoS_2 :AC active



material ratio. The activated carbon electrodes were fabricated from YP50F activated carbon (85 wt%), carbon nanotubes (CNTs) (5 wt%), and PVDF (10 wt%). These components were mixed in *n*-methyl-2-pyrrolidone (Alfa Asear) to form a homogeneous slurry and cast onto a stainless steel sheet by doctor blading. The cast electrode sheet was dried in vacuum at 110 °C for 12 h. The electrodes were removed from the substrate to form free-standing electrodes with mass loadings of 4–6 mg cm⁻². As with the half cells described above, the nc-MoS₂ electrodes in all full cells were precycled ten times between 0.8 and 3.0 V versus Li/Li⁺ to drive the 2H–1T phase transition before the full cell device testing. The same electrolyte used in the half-cell testing was used for the full cell testing. The active mass of both electrodes was used to calculate the energy density and power density.

Electrochemical Impedance Spectroscopy: Electrochemical impedance spectroscopy was carried out on a Bio-Logic VSP potentiostat/ galvanostat. The impedance measurements were performed on twoelectrode Swagelok cells between 900 kHz and 100 mHz using a 10 mV input under no bias. Impedance data were collected at 0.8 V versus Li/Li⁺ after each insertion cycle. A 5 min potentiostatic hold was applied before each impedance measurement during which time the current dropped from ≈200 to ≈20 mA g⁻¹. The impedance spectra were fit using the Z fit plug-in available in EC-Lab V10.40 (Bio-Logic). RC time constants were calculated at 0.8 V after ten cycles between 0.8 and 3.0 V. These values were derived from the frequency at the maximum imaginary resistance of the semicircle in the Nyquist representation. At this point, $\omega = 1/RC$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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