Electrochemical Characterization of Liquid Phase Exfoliated Two-Dimensional Layers of Molybdenum Disulfide

Andrew Winchester,‡ Sujoy Ghosh,§ Simin Feng,‡ Ana Laura Elias,‡ Tom Mallouk,§ Mauricio Terrones,‡,§,‖ and Saikat Talapatra*‡,§

†Department of Physics, Southern Illinois University, Carbondale, Illinois 62901, United States
‡Department of Physics and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, Pennsylvania 16802, United States
§Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States
‖Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

ABSTRACT: We report on the electrochemical charge storage behavior of few-layered flakes of molybdenum disulfide (MoS2) obtained by liquid phase exfoliation of bulk MoS2 powder in 1-dodecyl-2-pyrrolidinone. The specific capacitances of the exfoliated flakes obtained using a 6 M KOH aqueous solution as an electrolyte were found to be an order of magnitude higher than those of bulk MoS2 (∼0.5 and ∼2 mF cm−2 for bulk and exfoliated MoS2 electrodes, respectively). The exfoliated MoS2 flakes also showed significant charge storage in different electrolytes, such as organic solvents [1 M tetraethylammonium tetrafluoroborate in propylene carbonate (Et4NBF4 in PC)] and ionic liquids [1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6)]. The values of specific capacitances obtained using Et4NBF4 in PC and BMIM-PF6 were ∼2.25 and ∼2.4 mF cm−2, respectively. An analysis of electrochemical impedance spectroscopy using an equivalent circuit modeling was performed to understand the charge storage mechanism of these exfoliated MoS2 flakes using different electrolytes. Our findings indicate that liquid phase exfoliation methods can be used to produce large quantities of electrochemically active, two-dimensional layers of MoS2 and can act as an ideal material in several applications related to electrochemistry.

KEYWORDS: 2D layered materials, molybdenum disulfide, liquid phase exfoliation, electrochemical, charge storage

INTRODUCTION

Molybdenum disulfide (MoS2) is an indirect band gap semiconductor that belongs to the group VI family of transition metal dichalcogenides (TMDs). The crystalline structure of this material, consisting of stacked S−Mo−S sheets, gives rise to various physicochemical properties ranging from solid lubricants to catalysts. For example, crystals of MoS2 have been known to be a photoactive material; early work by H. Tributsch established that MoS2 crystals, along with other semiconducting TMDs such as MoSe2 and WSe2, could be used as stable photoelectrochemical electrodes.1,2 Subsequent work on polycrystalline thin films of MoS2 showed a comparable photoelectric response similar to that of single crystals.3,4 More recently, methods for producing thinner films with larger yields via intercalation, exfoliation, and chemical means have been explored.5–10 MoS2 has also been evaluated as a photocatalyst for the production of H2 gas, with potential for becoming a lower-cost replacement for platinum.6,11–13

As described above, bulk crystals of MoS2 are known to have an indirect band gap of ∼1.2–1.3 eV,14,15 which has led to much of the initial photoelectrical research on this material. However, because of its layered structure, it is possible to exfoliate this system into fewer layers and observe significant changes in its physical and chemical properties. For example, it has been shown both theoretically and experimentally that via isolation of individual layers of the crystal, significant changes in the band structure of MoS2 are observed. In particular, a direct band gap of ∼1.7–1.9 eV is opened in monolayer MoS2.16–18 Therefore, it is important to study the influence of the number of layers and the addition of edges in MoS2 on the photocatalytic efficiency of evolving hydrogen gas.11,13

Recently, it has been demonstrated that with an increase in the available surface area from the bulk crystal to few or single layers of MoS2, it is possible to observe enhanced charged storage in lithium ion battery systems19,20 and supercapacitors.21–23 Therefore, it is very important to control the number of layers, the amount of reactive edges, and defects within these semiconducting TMDs to fabricate the next generation of energy-storage and harvesting systems.

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In this work, we study fundamental electrochemical properties of MoS$_2$ exfoliated into few-layer stacks by examining the behavior of the resulting material in different electrolytes. Our findings indicate that upon exfoliation, the electrochemical charge storage capacity of these layered systems increases by an order of magnitude compared to that of their bulk counterpart when measured in different electrolytes (KOH, Et$_4$NBF$_4$ in PC, and BMIM-PF$_6$). We obtained a maximal specific capacitance of $\sim$2.4 mF cm$^{-2}$ with BMIM-PF$_6$ as the electrolyte (applied voltage window of 3.5 V). Electrochemical impedance spectroscopy (EIS) in conjunction with circuit analysis indicates that in an aqueous electrolyte (e.g., KOH), nearly pure capacitive behavior is observed in the charge storage mechanism, whereas for polymers and other ionic electrolytes, diffusive behavior is more prevalent.

**EXPERIMENTAL SECTION**

The few-layer MoS$_2$ dispersions were obtained via a liquid phase exfoliation technique, as reported by Coleman et al.$^{24,25}$ Commercial MoS$_2$ powder (Sigma Aldrich, <2 μm) was added to 1-dodecyl-2-pyrrolidinone (N12P) at a concentration ratio of approximately 10 mg/mL. The mixture was then treated ultrasonically using a Fisher Scientific Sonic Dismembrator 500 horn tip sonicator operating between 20 and 40% amplitude. The dispersions were treated for 1 h continuously using an ice/water bath to maintain a stable temperature between 20 and 40% amplitude. The dispersions were treated for 1 h

with a Princeton 2263 model potentiostat using a two-electrode parallel-plate-type arrangement. Cyclic voltammetry (CV) measurements were performed at scan rates between 10 and 500 mV s$^{-1}$ with vertex potentials of $\sim$0.8 to 0.2 V (KOH), $\sim$1.0 to 1.7 V (Et$_4$NBF$_4$), and $\sim$2.0 to 1.5 V (BMIM-PF$_6$). Galvanostatic charge–discharge was performed with charging and discharging intervals of 1.0 s at constant currents of 0.1 mA (aqueous and organic) and 1.0 mA (ionic liquid). Electrochemical impedance spectroscopy (EIS) measurements were performed using a 10 mV RMS ac signal and no dc bias over frequency ranges of 100 kHz to 100 mHz (KOH), 1 MHz to 10 mHz (Et$_4$NBF$_4$), and 1 MHz to 100 mHz (BMIM-PF$_6$).

**RESULTS AND DISCUSSION**

In Figure 1, the structural characterization and optical characterization of the exfoliated MoS$_2$ flakes are shown. Figure 1a shows a typical dispersion of MoS$_2$ flakes in N12P. A representative UV–vis spectrum of such a dispersion displaying the region from 400 to 800 nm is shown in Figure 1b. This region clearly displays the A and B peaks centered at $\sim$680 nm (1.83 eV) and $\sim$620 nm (1.99 eV), respectively. The peaks are due to exciton splitting and show a separation of $\sim$60 nm ($\sim$0.16 eV), which is characteristic of the 2H-MoS$_2$ phase.$^{7,15,26}$ The spectrum also displays the broader C absorption peak located at $\sim$455 nm (2.73 eV) and possibly also the D absorption peak (typically between $\sim$400 and $\sim$450 nm), although these peaks are largely masked by the significant scattering background at higher frequencies in this sample. These indicate that the structure of the MoS$_2$ sheets is left largely intact during the exfoliation process. Via further examination of the absorbance data via means of a Tauc plot,$^{27}$ the band gap of the material can be estimated. Analysis of the Tauc plot in the linear absorbing region (Figure 1b, inset) gives a value of $\sim$1.75 eV for the direct band gap, which agrees with theoretical and experimental values reported in the literature for few-layer MoS$_2$.\textsuperscript{16–18,26} Therefore, from the optical band gap value obtained from the UV–vis analysis, we can perhaps assume that the exfoliation results in MoS$_2$ flakes containing three or four layers.

Panels c and d of Figure 1 illustrate TEM micrographs of the exfoliated MoS$_2$ flakes. TEM samples were prepared by directly dropping small amounts of the dispersions onto holey-carbon-coated grids. The grids were allowed to completely dry in an oven at 60 °C before being imaged. An electron diffraction pattern from one of the MoS$_2$ flakes, shown in Figure 1d, is also presented in the inset. From the ED data, it is extremely difficult to say if the samples obtained using this process have stacked multilayers with rotated stacking or are stacked in-layer multidomain materials, but in general, it can be assumed that because the samples are exfoliated from bulk MoS$_2$ powder, which are typically in-layer multidomain material, we believe that the exfoliated samples are perhaps in-layer multidomain material. In any event, the crystalline nature of the flakes is evident from this diffraction pattern.

In Figure 2, we show data obtained from our electrochemical measurements. The electrochemical behavior of exfoliated MoS$_2$ was studied by constructing two electrodes in a parallel-plate geometry, as is typically used in electrochemical double-layer capacitor (EDLC) measurements. Electrodes for these EDLCs were fabricated by vacuum filtering small portions of the dispersions, approximately 1–10 mL, through thin Teflon filters (Millipore) to create thin, flexible films of MoS$_2$. The filters were then cut into small pieces, of areas ranging between $\sim$0.25 and $\sim$0.5 cm$^2$, and were then pressed together with a porous separator (Ahlstrom Qualitative Filter Paper).
Values for the capacitance were calculated from the CV curves using the relation $C_{eq} = \int i \, dV/(sA\Delta V)$, where the integral provides the area of the CV curve, $s$ is the scan rate for the particular curve, $A$ is the area of a single electrode exposed to the electrolyte, and $\Delta V$ is the applied potential window through which the device is scanned. The highest value calculated for KOH at a scan rate of 10 mV s$^{-1}$ was $\sim$2 mF cm$^{-2}$. This value is at least 1 order of magnitude higher than the values obtained using bulk MoS$_2$ as EDLC electrodes ($\sim$0.5 mF cm$^{-2}$). This also indicates that exfoliation results in an increase in the specific surface area of the MoS$_2$ (by at least 1 order of magnitude) because double-layer capacitance is proportional to specific surface area. The typical surface area of bulk MoS$_2$ is $\sim$30 m$^2$ g$^{-1}$; therefore, we can estimate the specific surface areas of the exfoliated samples to be on the order of a few hundreds of square meters per gram. The capacitance was also calculated from the charge–discharge curves using the relation $C_{eq} = I/(A \times dV/dt)$, where $I$ is the constant discharge current, $A$ is the area of a single electrode exposed to the electrolyte, and $dV/dt$ is the slope of the discharge curve, giving values that typically agreed with that from CV measurements.

Electrochemical characterization of MoS$_2$ electrodes was further investigated using two additional electrolytes: 1 M tetraethylammonium tetrafluoroborate in propylene carbonate (Et$_4$NBF$_4$ in PC) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF$_6$). EDLC electrodes were prepared in the same manner as indicated above. Cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy characterization were conducted for each electrolyte, again showing capacitive behavior. The CV curves (Figure 2d,e) are much less rectangular and symmetric than those of the KOH-based EDLCs. This is likely due to effects from resistive leaking, often seen in EDLC devices. In particular, the CV curves for the Et$_4$NBF$_4$ display a rather sharp, asymmetric peak starting at approximately 1 V. This rapid increase in current occurs for several reasons; for example, the surface roughness of the electrodes can lead to charge puddles that might show jumps in the current during CV measurements. Further, the humidity level can also influence the CV measurements because Et$_4$NBF$_4$ is known to readily absorb water from its surroundings. The charge–discharge curves for all three electrolytes display only small losses of retained capacitance over numerous cycles (Figure 2f), leading to these systems showing good device stability. Here we note that the data presented in Figure 2f are from the first set of measurements of the EDLC devices. The electrodes were not conditioned before the cycling. The initial loss of capacitance during the first few cycles is perhaps due to the time required for the system to attain electrochemical stability. Calculations of the capacitance for a scan rate of 10 mV s$^{-1}$ give values of

Figure 2. (a) Exploded view of the geometry used to prepare EDLC devices. (b) Cyclic voltammetry at various scan rates of a MoS$_2$ EDLC using KOH as the electrolyte. (c) Charge–discharge cycles for the MoS$_2$ EDLC using KOH as the electrolyte. (d) Cyclic voltammetry at a scan rate of 50 mV s$^{-1}$ for a system using Et$_4$NBF$_4$ as the electrolyte. (e) Cyclic voltammetry at a scan rate of 50 mV s$^{-1}$ for a system using BMIM-PF$_6$ as the electrolyte. (f) Plot of the percent capacitance retained as a function of the number of cycles for each of the electrolytes.
∼2.25 and ∼2.4 mF cm\(^{-2}\) for Et\(_4\)NBF\(_4\) and BMIM-PF\(_6\), respectively.

The values of specific capacitances obtained for our samples are comparable to the values of specific capacitances obtained in a very recent study by Cao et al.,\(^{22}\) for hydrothermally prepared as well as exfoliated MoS\(_2\) materials. They have shown that MoS\(_2\) prepared by hydrothermal methods can be used for preparing EDLC electrodes by utilizing laser patterning to create small electrode feature sizes with areal capacitances of 8 mF cm\(^{-2}\) at a scan rate of 10 mV s\(^{-1}\) in aqueous electrolytes. In this work, MoS\(_2\) prepared via a liquid phase exfoliation method was also studied, showing a capacitance of ∼3.1 mF cm\(^{-2}\). Previous work on MoS\(_2\) by Soon et al.\(^{21}\) showed that edge-oriented nanowall films of MoS\(_2\) can show extraordinary pseudocapacitance in a number of active redox systems at very low scan rates. As in this work, however, we do not see characteristics of Faradic charge transfer with aqueous electrolytes at higher scan rates between 10 and 500 mV s\(^{-1}\). Other recent work, performed by Huang et al.,\(^{33}\) showed that hydrothermally prepared composites of MoS\(_2\) and polyaniline work together in a synergistic way to achieve very high capacitances (∼575 F g\(^{-1}\)) with very stable devices (loss of ∼2% capacitance over 500 cycles) in an aqueous environment (1 M H\(_2\)SO\(_4\)). This work gives a perspective on how these materials can be utilized in different ways to make optimal use of their properties.

To further characterize these samples, electrochemical impedance spectroscopy (EIS) was utilized. The impedance spectrum of the KOH device was acquired within the frequency \((f)\) range of 100 kHz to 100 mHz with a 10 mV RMS voltage and no dc bias. The resulting Nyquist plot of the real and imaginary parts of the impedance, shown in Figure 3a, could be used to directly estimate the equivalent series resistance (ESR) of the device.\(^{28,29}\) Looking at the high-frequency intercept of the real axis for the KOH-based system (Figure 3b), for example, gives a value of approximately 23.9 Ω for the ESR. To gain deeper insight, the impedance spectrum can be fit to an equivalent circuit; a suitable circuit can give some general idea about what physical processes may be occurring in the system.\(^{28,30}\) A simple circuit (inset of Figure 3a), similar to a Randles circuit,\(^{28}\) was found to represent the KOH-based system for a wide range of frequencies. The presence of a constant phase element (CPE) corresponds to nonideal capacitor behavior; CPEs are frequently used to represent effects such as surface disorder, electrode porosity, and adsorption processes.\(^{31}\) This is likely caused by the electrode being comprised of random stacks of MoS\(_2\) sheets, creating a very disordered surface geometry with a large distribution of pore sizes. The R\(_1\) resistor element is the device ESR corresponding to the series resistance of the electrolyte, filter papers, and charge barriers between the stainless steel current collectors and the MoS\(_2\) electrode material. The R\(_2\) resistor element is most likely due to a charge transfer barrier in the system.\(^{28,31}\) The presence of a second constant phase element could be attributed to a very small contribution to the total capacitance from a pseudocapacitance process, such as the adsorption of ions onto the electrode.\(^{28,31}\) When the impedance spectra for the Et\(_4\)NBF\(_4\) (Figure 3c,d) and BMIM-PF\(_6\) (Figure 3e,f) electrolytes were fit, it was found that simple modifications to the circuit for the KOH-based system allow the more complicated behavior of the organic and ionic electrolytes to be modeled. The presence of

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**Figure 3.** Experimental and fitted EIS spectra with equivalent circuit inset for KOH (a), Et\(_4\)NBF\(_4\) (c), and BMIM-PF\(_6\) (e). High-frequency intercepts are shown in panels b, d, and f for KOH, Et\(_4\)NBF\(_4\), and BMIM-PF\(_6\), respectively.
an additional constant phase element and resistors leads to a model very similar to that of the ideal transmission line model of a porous electrode containing a series of RC elements in parallel,28 with the BMIM-PF6-based electrolyte displaying a leakage pathway through a R resistor element. This additional “RCPE” element perhaps corresponds to a part of the system with a different relaxation time, caused by mobility differences of anions and cations or to processes such as adsorption of ions onto the electrodes.28,31

To further compare the models to experimental data, the capacitance from the constant phase elements was calculated. Using the relation \( C = P/(f^n \times \sin(n\pi/2)) \), where \( P \) and \( n \) are fitting parameters and \( f \) is taken to be the lowest frequency measured in the impedance spectrum, allows for the individual contributions to the total capacitance to be calculated. The total calculated values matched the values found experimentally (see Table 1). The fitting parameter values could also be used to glean some further insight into the systems. Notably, the values for \( n \) provide some information about the capacitive behavior occurring at the electrodes. The value of \( n \) indicates how “pure” the capacitive behavior is; a value of \( n \) equal to 1 gives ideal capacitor behavior.31 The relatively higher values of \( n \) for the KOH-based device when compared to those of the other two electrolytes could be related to ion size and surface accessibility: KOH ions are smaller than the bulky organic ions of the other two electrolytes and can therefore access the MoS2 surface area more readily. The lower value for \( n \) in the BMIM-PF6 and Et4NBF4 electrolyte systems indicates that a diffusive behavior is more prevalent.31 A comparison of several values related to the modeled circuit for each electrolyte and values of capacitances obtained from our experimental measurements are listed in Table 1.

### CONCLUSION

We have demonstrated the effect of exfoliation on the electrochemical charge storage behavior as well as electrochemical interaction of MoS2 with different electrolytes. A systematic investigation of electrochemical properties in aqueous, organic, and ionic electrolytes has shown a significant increase in the charge storage capacities of two-dimensional (2D) layers obtained via exfoliation compared to those of bulk powders. The mechanism of the charge storage process for each electrolyte was examined through electrochemical impedance spectroscopy, revealing that these systems show a predominantly physical charge storage process. The random nature of the restacked MoS2 electrodes also leads to diffusive behavior in these systems. While exfoliated MoS2 flakes by themselves as an electrode material have shown only modest results thus far, their ability to act in redox systems boosts their potential applications. We believe that exfoliated materials obtained and studied in this work can further be utilized in creating functional composites, similar to work done on hydrothermally prepared MoS2. These findings indicate that an exfoliation process could lead to large scale synthesis of electrochemically active 2D layer materials, which could have a significant impact in several applications related to electrochemical processes such as electrochemical catalysis as well as photocatalytic applications.

| Table 1. Impedance Spectra Fitting Parameters with Calculated Capacitances |
|-----------------------------|-----------------------------|-----------------------------|
| KOH | Et4NBF4 | BMIM-PF6 |
| **R1 (ESR) (Ω)** | 23.908 | 13.669 | 43.832 |
| **R2 (Ω)** | 279.85 | 15.152 | 12.619 |
| **P1** | 31.198×10^-5 | 9.0641×10^-7 | 2.4362×10^-6 |
| **n1** | 0.91348 | 1 | 0.6779 |
| **P2** | 7.1717×10^-4 | 1.8373×10^-6 | 3.5472×10^-5 |
| **n2** | 0.80817 | 1 | 0.77989 |
| **P3** | not applicable | 1.650×10^-5 | 4.1587×10^-5 |
| **n3** | not applicable | 0.63268 | 0.77438 |
| **CPE1 capacitance (F)** | 3.843×10^-5 | 9.0641×10^-7 | 5.847×10^-6 |
| **CPE2 capacitance (F)** | 1.168×10^-4 | 1.8373×10^-6 | 6.259×10^-5 |
| **CPE3 capacitance (F)** | not applicable | 1.069×10^-4 | 7.455×10^-5 |
| **total capacitance (F)** | 1.552×10^-4 | 1.096×10^-4 | 1.430×10^-4 |
| **experimental capacitance (F)** | 2.78×10^-4 @ 1000 mV s^-1 | 1.91×10^-4 @ 1000 mV s^-1 | 1.90×10^-4 @ 200 mV s^-1 |

### REFERENCES