MoS$_2$-Graphene Composite Electrode for High Energy Hybrid Li-Ion Capacitors

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A hybrid Li-ion capacitor represents an emerging class of devices, which results from the coupling of high energy density battery-type electrode materials at one side and high-power EDLC electrode at other side. Here, we develop a simple and scalable method including ball-milling, followed by heating process to synthesize MoS$_2$/graphene composite material. The structural and morphological analyses were carried out by powder X-ray diffraction (PXRD) analysis and scanning electron microscopy (SEM) technique. The composite electrode delivers high specific capacity (725 mAh g$^{-1}$ at 0.1 A g$^{-1}$ and 265 mAh g$^{-1}$ at 5 A g$^{-1}$). The hybrid device composed of MoS$_2$/graphene composite electrode as negative electrode and commercial activated carbon as the positive electrode exhibits a high energy density of 117 Wh kg$^{-1}$ at 200 W kg$^{-1}$ and a maximum power density of 3.9 kW kg$^{-1}$ at 79 Wh kg$^{-1}$. The hybrid device showed a long cycle stable Li storage capacity (62% after 5000 cycles at 1 A g$^{-1}$).

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There has been an ever-increasing need for safe, high-energy density and high-power energy storage systems that store electricity generated from renewable sources. The goal is to reduce and finally replace the combustion of fossil fuels, especially for transport applications. Electrochemical energy storage technology has proven to be a highly successful energy storage system due to its high energy efficiency and high performance.\textsuperscript{2,3} Hence, they have been widely applied in portable electronic devices, smart grids, and hybrid and electric vehicles. The current commercial Li-ion batteries are unable to meet the high acceleration rate of emerging hybrid and electric vehicles due to their limited power density.\textsuperscript{4} In contrast, supercapacitors have received much attention due to their several advantages, such as superior charge/discharge rate (within seconds), extremely high specific power (>10 kW kg$^{-1}$), longer cycle life (>10,000 cycles), and safety as compared to batteries.\textsuperscript{5–8} However, supercapacitors suffer from unsatisfactory energy density (5–10 Wh kg$^{-1}$).\textsuperscript{8} Therefore, design and fabrication of supercapacitors with high energy density with maximum power density is of great importance. This could be achieved by fabrication of a supercapacitor system with combination of asymmetric electrodes in which one electrode stores charge by Faradaic process and other electrode stores charge by a capacitive mechanism.

The hybrid capacitor concept was proposed by Amatucci’s group using carbon based capacitive electrode combined with Li$_4$Ti$_5$O$_{12}$ as negative Faradaic electrode.\textsuperscript{9} Faradaic electrodes, such as Ni(OH)$_2$, Co$_3$O$_4$, Fe$_3$O$_4$, Fe$_2$TiO$_5$ etc. and their hybrids are the most commonly used electrodes in hybrid supercapacitors.\textsuperscript{10,11} Recently, several research efforts have been dedicated to increase the performance of electrode materials for hybrid supercapacitors.\textsuperscript{9} Carbon, carbon composites, and heterocaten (e.g. N$_2$, O$_2$, P, S) doped carbon electrodes have gained much attention in the field of electrochemical energy storage systems due to their large specific surface area.\textsuperscript{12–20} Two dimensional (2D) materials, such as transition metal dichalcogenides,\textsuperscript{21,22} graphene,\textsuperscript{23–28} and MXenes\textsuperscript{29,30} have been extensively explored as negative electrodes for hybrid supercapacitors owing to their unique characteristic properties. MXenes and Xene based composite materials can exhibit a high volumetric capacitance of 900 F cm$^{-3}$ due to their remarkable physical and chemical characteristics.\textsuperscript{29,30} However, synthesis of MXene with controlled structures and properties are still challenging and remains very expensive.\textsuperscript{30} Additionally, MXenes are unstable under ambient conditions, their use in practical applications is limited.\textsuperscript{3} MoS$_2$ with its well-defined layered structure is considered to be a proper choice for energy storage devices due to its large interlayer distance (~0.615 nm), high theoretical capacity (670 mAh g$^{-1}$) and tunable electronic properties.\textsuperscript{31,32} The bulk MoS$_2$ is composed of molybdenum atoms sandwiched between sulfur layers which form S-Mo-S planes and these planes are held together by weak van der Waals interactions. A fast lithium ion diffusion is possible inside the structure due to its large interlayer distance (~0.615 nm) compared to graphite (0.334 nm).\textsuperscript{33} However, bare MoS$_2$ is not a good negative electrode material for hybrid capacitors due to its poor electronic conductivity and drastic volume change during charging/discharging process.\textsuperscript{34–35} Various strategies have been employed to circumvent these issues, such as reducing the particle size of MoS$_2$ into nanoscale\textsuperscript{36–39} and incorporating carbon materials into MoS$_2$ to increase the conductivity, structural stability, and intercalation sites.\textsuperscript{40–43} Most of the synthesis methods of MoS$_2$ and MoS$_2$/carbon composite materials involve complex synthesis routes and are difficult for scaling up.\textsuperscript{44,45} In this work, we developed a MoS$_2$/graphene composite material by a simple method using water as a solvent, including ball milling the precursor materials, followed by a heating process under N$_2$ atm. The graphene in the composite material enhances the electronic conductivity and the kinetics of Li-ion transport of MoS$_2$ and it also controls the volume expansion of MoS$_2$ during charging and discharging cycles. The electrochemical performance of MoS$_2$/graphene composite electrode was tested within a wide potential range from 0.01–3 V (vs Li/Li$^+$) in a half cell using Li metal as the reference electrode. A hybrid Li-ion capacitor was fabricated with MoS$_2$/graphene composite material (negative electrode) and commercially available activated carbon (positive electrode) and the cell was tested in the potential window of 0–4 V (vs Li/Li$^+$). The results show excellent electrochemical properties in energy, power, and cycling stability, holding great promise for application in various energy storage devices.

**Experimental**

Ammonium tetrathiomolybdate (ATTM), ((NH$_4$)$_2$MoS$_4$, 99.97%, Alfa Aesar), and graphene nanoplatelets (Alfa Aesar) were ball milled in water for 12 h at room temperature. The mixture was dried at room temperature and heated at 600 °C for 2 h in N$_2$ atm to obtain MoS$_2$/graphene composite material (30:70, 40:60, 50:50, 60:40, and 70:30).
MoS₂/graphene composite electrodes were prepared by mixing (magnetic stirring) the composite powder (70 wt%) with carbon (Super P-10 wt%) and binder (polyvinylidene fluoride-PVDF) (20 wt%, average Mw ∼ 455,000) in N-methyl-2-pyrrolidone (NMP) solvent. The slurry was casted onto copper foil current collector using doctor blade technique and then vacuum dried at 100 °C. 8 mm diameter discs were punched from the dried sheets with mass loading of ∼1 mg cm⁻². For the positive electrode, 70 wt% of commercial activated carbon (AC) powder (MSE Supplies LLC), 10 wt% of Super P and 20 wt% PVDF in NMP were mixed and the slurry was coated on to aluminum foil. The mass loading of activated carbon electrode was varied between 1 and 2 mg cm⁻². Half-cells were assembled in a coin cell (CR2032 coin cell) using Li foil as the counter electrode and 1M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (50:50 vol%) as the electrolyte in a 1M LiPF₆ in EC/DEC (50:50 vol%) as the electrolyte and polymer membrane as the separator.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 1 MHz to 0.1 Hz (VersaSTAT 3) with an AC amplitude of 10 mV. The cyclic voltammetry (CV) (Biologic VMP3) and galvanostatic charge/discharge (NEWARE BTS3000 battery test station) tests of half cells were carried out in the voltage window of 0.01–3.0 V vs Li/Li⁺. The CV and galvanostatic charge/discharge tests of hybrid device was carried out in the voltage window of 1.0–4.0 V.

The specific discharge capacitance of these cells can be calculated using the following formula:

\[ C = \frac{I \times t}{\Delta V \times m} \quad [1] \]

where \( C \) is the specific capacitance (F g⁻¹) of the cell, \( I \) is the current (A), \( t \) is the discharge time (s), \( \Delta V \) is the potential window (V), and \( m \) is the mass of the electrodes (g).

The energy density \( (E, \text{Wh kg}^{-1}) \) and power density \( (P, \text{W kg}^{-1}) \) of the hybrid cell can be calculated using the Eqs. 2 and 3, respectively.

\[ E = \frac{-C \times \Delta V^2}{2} \quad [2] \]

\[ P = \frac{E}{t} \quad [3] \]

Where \( E \) is the energy density and \( t \) is the discharge time of the hybrid cell.

**Results and Discussion**

The MoS₂/graphene composite material was synthesized by solid-state synthesis route as explained in experimental section. Figure 1 shows the schematic representation of the steps involved in the synthesis process. The MoS₂ is synthesized by thermal decomposition of ATTM at 600 °C under N₂ atm. The graphene acts as a support for the nucleation and growth of layered MoS₂ sheets. The PXRD analysis of pure graphene nanoplatelets, pure MoS₂, and MoS₂/graphene composite materials (MG37 = 30 wt% MoS₂ and 70 wt% graphene) are presented in Fig. 2a. The diffraction peaks of MoS₂ and the composite materials are assigned to those of hexagonal phase of MoS₂ with a space group of \( \text{P6}_3/mmc \) symmetry ((AMCSD 0009788). The amount of graphene in the MoS₂/graphene composite material has a significant effect on the crystallinity of MoS₂. As we can see from the PXRD patterns, the intensity of (002) peaks increases when the amount of MoS₂ increases in the composite material. The crystallite size \( (D) \) of MoS₂ particles can be calculated using the Scherrer equation:

\[ D = \frac{K \lambda}{\beta \cos \theta} \quad [4] \]

where \( K \) is the shape factor, \( \lambda \) is the wavelength of radiation used, \( \beta \) is the full width at half maximum, and \( \theta \) is the diffracted angle of the peak. The average crystallite size calculated for pure MoS₂ from PXRD data is 4.5 nm. Figures 2b–2d show the SEM images of the pure MoS₂, graphene nanoplates, and MoS₂/graphene composite material. The pure MoS₂ has formed as sheets with particle size ranging from ∼100 nm to ∼10 μm. The graphene nanoplates purchased from Alfa Aesar has particles with size ranging from 100–200 nm. Figures 2e and 2f show the EDS pattern collected for pure MoS₂ and MoS₂/graphene composite material, respectively.

To understand the Li storage mechanism of MoS₂/graphene composite electrode, half cells were assembled using CR2032 coin cell with Li metal as the counter and reference electrode. Figure 3a shows the first three CV curve obtained for the half-cell at a scan rate of 0.2 mV s⁻¹ in the potential range of 0.01–3 V vs Li/Li⁺. The peak around 1 V in the first cathodic sweep is attributed to the phase transition of trigonal prismatic (2H) MoS₂ to octahedral (1T) LiₓMoS₂ after lithiation.

\[ \text{MoS}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2 \quad [5] \]
The peak around 0.4 V is related to the conversion reaction from \( \text{Li}_x\text{MoS}_2 \) to \( \text{Li}_2\text{S} \) and Mo atom as follows:

\[
\text{Li}_x\text{MoS}_2 + (4 - x)\text{Li}^+ + (4 - x)e^- \rightarrow 2\text{Li}_2\text{S} + \text{Mo}
\]  

These two peaks are not visible in the second cycle, which indicates an irreversible phase transformation of \( \text{MoS}_2 \). The peaks at 1.9 V and 1.30 V in the second cathodic sweep is due to the multistep \( \text{Li}^+ \) insertion mechanism as follows:

\[
2\text{Li}^+ + S + 2e^- \rightarrow \text{Li}_2\text{S}
\]  

In the anodic sweep, the peak around 1.7 V is associated with the oxidation of Mo atom to \( \text{MoS}_2 \), and the latter peak at 2.3 V suggests the oxidation of \( \text{Li}_2\text{S} \) to sulfur. The CV plot obtained at various scan rates are presented in Fig. 3b. The CV plots have similar shape and the pseudo capacitive behavior of \( \text{MoS}_2 \) electrode is retained even at higher scan rates. To elucidate the contributions of two energy storage mechanism, capacitive and diffusion limited process, power law equation was applied as:

\[
\text{MoS}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2
\]
The above equation can be rearranged as:

\[
i(V) = k_1 v + k_2 v^{1/2}
\]

where, \(i\) is peak current value, \(v\) is the scan rate, \(k_1\) and \(k_2\) represent the current contributions from the surface capacitive effects and the diffusion-controlled intercalation process, respectively. \(k_1\) and \(k_2\) are determined values obtained from the slope and intercept of Eq. 9. The capacitive and diffusion contribution of the MoS₂/graphene composite electrode was calculated based on the Eq. 9 and is shown in Fig. 3c. At low scan rate 0.2 mV s\(^{-1}\), the capacitive and diffusion contributions are 37\% and 63\% respectively. When the scan rate is increased to 1 mV s\(^{-1}\), the capacitive contribution has increased to 57\% and the diffusion contribution has decreased to 43\%. These results suggest that at slow scan rates, the diffusion limited contribution largely rises from the electron transfer reaction as shown in Eq. 8. At increased scan rates, double layer contribution increases significantly.
The Li storage property of the MoS\(_2\)/graphene composite electrode was further investigated by galvanostatic charge/discharge cycling, and which is presented in Figs. 3d and 3e. The first three charge/discharge profiles of the composite electrode (MG46) are given in Fig. 3d. The composite electrode shows an initial discharge capacity of 1040 mAh/g at a current density of 0.1 A g\(^{-1}\) in the voltage window of 0.01–3 V (vs Li/Li\(^{+}\)). The sudden decay in the discharge capacity after first cycle could be due to the reaction between polysulphides and carbonates from the electrolyte (irreversible loss of MoS\(_2\)).\(^{53}\) The Li\(^+\) intercalation/de-intercalation reaction in MoS\(_2\) happens around 1 V and 0.5 V and which can be seen as the small plateau in the first discharge cycle. Figure 3e shows the discharge capacities of different MoS\(_2\)/graphene composite electrodes at various current densities ranging from 0.1 A g\(^{-1}\) to 5 A g\(^{-1}\). MG6 and MG55 shows similar discharge capacities at lower current load, however MG46 performs much better than any other sample at higher current load. The specific discharge capacities of MG46 at 0.2, 0.5, 1, 2, and 5 A g\(^{-1}\) are 670, 570, 480, 395, and 265 respectively. The specific discharge capacity of MG46 at lower current loads is comparable to the discharge capacities at same current load reported in the literature. However, the discharge capacity of MG46 at higher current load (1 and above 1 A g\(^{-1}\)) is lower than the numbers reported in the literature. Wang et al.\(^{35}\) reported a discharge capacity of \(~450\) mAh g\(^{-1}\) for a MoS\(_2\) carbon composite electrode at 5 A g\(^{-1}\) whereas the MG46 shows a discharge capacity of 265 mAh g\(^{-1}\) for the same current load. The galvanostatic charge/discharge measurement of pure MoS\(_2\) is also given for comparison. Pure MoS\(_2\) electrode shows a very high initial discharge capacity of 1267 mAh g\(^{-1}\) at a current density of 0.1 A g\(^{-1}\), however, its specific capacities decay rapidly in the following cycles with the increasing current densities. The rapid decay in the capacity could be due to the restacking and agglomeration of MoS\(_2\) during the galvanostatic charge/discharge measurements.

Figure 3f shows the Nyquist plots of coin cells assembled with pure MoS\(_2\) and MG46 composite electrode. The high frequency semicircle could be attributed to resistance of the solid electrolyte interface (SEI), the medium frequency semicircle to the charge transfer resistance of the electrode-electrolyte interface.\(^{64}\) The inclined line is correlated to the Warburg impedance (Li ions diffusion character in the electrochemical process). MG46 composite electrode has lower resistance (~137 \(\Omega\)) than pure MoS\(_2\) (236 \(\Omega\)) due to the lower charge resistance. These numbers are comparable with the literature reported values for MoS\(_2\) and MoS\(_2\)/graphene composite materials.\(^{52}\) Figure 4a shows the charge/discharge profiles of MoS\(_2\)/graphene composite electrode for first, 500 and 1000 cycles within the potential window of 0.01–3 V (vs Li/Li\(^{+}\)) at a current density of 1 A g\(^{-1}\). The long-term cycling stability of the composite electrode is given in Fig. 4b and it shows an initial discharge capacity of 556 mAh g\(^{-1}\), 75\% of its initial capacity is remained after 1000 charge/discharge cycles.

Activated carbon is considered as one of the best electrodes for supercapacitors due to its higher surface area and physical adsorption of ions. In this work, commercial activated carbon is used as the positive electrode for the hybrid device. Figure 5a shows the galvanostatic charge/discharge cycles of activated carbon with Li metal electrodes and LiPF\(_6\) in EC/DEC electrolyte at various current densities from 0.1–5 A g\(^{-1}\) in the voltage window of 1.5 to 4.5 V (vs Li/Li\(^{+}\)). The specific capacity of activated carbon at various current load is given in Fig. 5b. Activated carbon shows an average discharge capacity of 98 mAh g\(^{-1}\) at a current density of 0.1 A g\(^{-1}\). The discharge capacity of activated carbon at 0.2, 0.5, 1, 2, and 5 A g\(^{-1}\) are 91, 84, 79, 72, and 61, respectively. The activated carbon electrode has excellent cycle stability, and it shows 94 mAh g\(^{-1}\) when the current density decreased to 0.1 A g\(^{-1}\). Wang et al. reported a stable discharge capacity of 87 mAh g\(^{-1}\) for commercial activated carbon (21KS) at 0.1 A g\(^{-1}\).\(^{43}\)

The hybrid device was assembled with CR2032 coin cell using pre-lithiated MG46 electrode and activated carbon electrode in 1 M LiPF\(_6\)/EC/DEC organic electrolyte. Four different mass ratios of positive electrode to negative electrode was used to optimize the energy density and power density of the hybrid device. Galvanostatic charge/discharge tests of the hybrid cells were conducted in the voltage window of 0.01–4 V at various current loads. During the charging of the hybrid cell, the Li\(^+\) ions in the electrolyte move to the negative electrode and intercalate in to MoS\(_2\)/graphene composite electrode. At the same time, PF\(_6\) ions move toward the positive electrode and adsorb on the surface of activated carbon and the electrons are transferred to the negative electrode through external circuit.\(^{43,55}\) During discharging process, the Li\(^+\) ions are deintercalated from the MoS\(_2\)/graphene electrode and PF\(_6\) ions are desorbed from the activated carbon electrode. Figure 6a shows the galvanostatic charge/discharge profiles of hybrid cell with a mass ratio of 1:1. This cell shows excellent charge/discharge reversibility at various current loads and exhibits a specific capacity of 60 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\).

The maximum possible energy density of the hybrid cell can be obtained by an accurate mass balancing of positive and negative

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**Figure 5.** Electrochemical performance of activated carbon. (a) the charge/discharge curves and (b) cycling stability of commercial activated carbon within the potential widow of 1.5–4.5 V (vs Li/Li\(^{+}\)) at various current densities.
This can be done by matching the capacities of both electrodes at a particular discharge rate and is given by:

\[ Q_n \times m_n = Q_p \times m_p \]

where \( Q_n \) is the capacity of negative electrode, \( m_n \) is the mass of negative electrode, \( Q_p \) and \( m_p \) are the capacity and mass of positive electrode, respectively. However, the capacity matching in hybrid cells is very challenging due to the very large difference in the rate capability of positive and negative electrodes. The various challenges and approaches for mass balancing of hybrid ion capacitor electrodes can be seen elsewhere. In order to optimize the positive and negative electrode mass ratio, another 3 hybrid cells were assembled with mass ratios of 1:1.5, 1:2, and 1:3. Figure 6b shows the energy density/power density characteristic (Ragone plot) of hybrid cells with different mass ratio of positive and negative electrode. From Fig. 6b, it is very clear that the hybrid cell assembled with a mass ratio of 1:1 shows the highest energy density among other samples. This cell exhibits a maximum energy density of 117 Wh kg\(^{-1}\) with a power density of 200 W kg\(^{-1}\) and a maximum power density of 3.9 kW kg\(^{-1}\) with an energy density of 79 Wh kg\(^{-1}\). This cell shows lower power density at 2 A g\(^{-1}\) compared to other cells assembled with different mass ratio. This could be due to the higher capacitive contribution from the positive electrode of other cells (higher mass of activated carbon). Wang et al. reported a maximum energy density of 87.74 Wh kg\(^{-1}\) and a maximum power density of 35.81 kW kg\(^{-1}\) for a similar system (voltage window 1–4 V). However, the reported energy density in this work is lower than the energy density reported for a MoS\(_2\)–reduced graphene oxide system (188 Wh kg\(^{-1}\) at 200 W kg\(^{-1}\)).

The Fig. 6c shows the long-cycling performance hybrid device at current density of 1 A g\(^{-1}\). After 5000 charge/discharge cycles, 62% of its initial capacity is remained. The capacity loss of this hybrid device could be due to the inefficient charging and slower Li\(^+\) transport of negative electrode. The hybrid device shows around 100% coulombic efficiency during the long cycle stability measurements. EIS measurements of hybrid device were carried out for the fresh cell, after 50 cycles and after 5000 cycles of charging and discharging and is presented in Fig. 6d. EIS results show that as the number of cycles increased from 0 to 5000, the total resistance of the cell is also increased (\(~30 \Omega\) to \(3500 \Omega\)). This increase in resistance could be due to the electrolyte consumption and decomposition and formation and growth of new SEIs.

**Conclusions**

In summary, we have synthesised a MoS\(_2\)/graphene composite material by solid-state synthesis route, including ball milling and heat treatment process. The phase formation of the composite material was confirmed by the PXRD analysis. The composite electrode has excellent Li storage capability (725 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) and 265 mAh g\(^{-1}\) at 5 A g\(^{-1}\)) as the anode for a hybrid capacitor which is mainly due to the contact between MoS\(_2\) and the graphene through Mo–O bond, which make sure a good ion and electron transfer in the material. The CV analysis show that the composite electrode has more Li diffusion contribution at lower scan rate and a higher capacitive
contribution at higher scan rate. The hybrid device assembled with activated carbon as positive electrode and MoS2/graphene composite as negative electrode exhibits a high energy density of 117 Wh kg\(^{-1}\) at 200 W kg\(^{-1}\) and a maximum power density of 3.9 kW kg\(^{-1}\) at 79 Wh kg\(^{-1}\). The hybrid device showed a long cycle stable Li storage capacity (62% after 5000 cycles at 1 A g\(^{-1}\)). Overall, the current work provides a better insight for designing negative electrodes for hybrid Li-ion capacitor with high energy density.

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