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Design of Mixed-metal Silver Decamolybdate nanostructures for high specific Energies at high Power density

Vipin Kumar,[†] Sebastian Matz,[‡] Dirk Hoogestraat,[‡] Venkateswarlu Bhavanasi,[†] Kaushik Parida,[†] Katharina Al-Shamery[‡] and Pooi See Lee^{†}*

V. Kumar, V. Bhavanasi, K. Parida, P. S. Lee

School of Materials Science and Engineering, 50 Nanyang Avenue, Nanyang Technological University, Singapore-639798

*E-mail: pslee@ntu.edu.sg

S. Matz, D. Hoogestraat, K. Al-Shamery

Physical Chemistry 1, Institute for Chemistry, Carl von Ossietzky University of Oldenburg, 26129, Oldenburg, Germany

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In the modern technological society, research on the energy-storage devices is gaining significant attention. Electrical energy can be stored in the form of electrochemical energy using ultracapacitors or supercapacitors.^[1] Supercapacitors can be classified into two major classes based on their charge-storage mechanisms:^[2] (1) electric double layer capacitors (EDLC) arise from the potential dependence of the surface charges stored electrostatically (non-Faradic process). They directly store electrical energy via excess or deficiency of the conduction-band electrons at the surface or near-surface region of the interface,^[3] (2) pseudocapacitors are Faradic in nature, involving passage of charges (transfer of the valence-band electrons) across the double layers.^[4,5]

At present, supercapacitors are the important class of the alternative energy-storage devices due to their fast charging/discharging rate, high rate of reversibility and ultra-long cycling stability compared to batteries. Binary transition metal oxides, e.g., RuO₂,^[6] MnO₂,^[7] Nb₂O₅,^[8] Co₃O₄,^[9] MoO₃,^[10] etc., have been studied as prospective negative or positive supercapacitor (pseudocapacitor) electrode materials hitherto. In the pseudocapacitors perspective, Trasatti et al.^[6] stated that the specific capacitance obtained in oxide based systems (i.e., RuO₂-distorted rutile structure) is the sum of the inner (diffusion controlled, $i \propto$

$v^{1/2}$) and outer (surface controlled, $i \propto v$) active sites available on the material. This point was examined by Dunn et al.^[11] and Lindquist et al.^[12] in the case of TiO_2 (anatase structure), and the findings were commensurate with Trasatti et al.^[6] Recently, Dunn et al.^[13] reported that the high-rate electrochemical energy storage (surface controlled, $i \propto v$) or exceptionally rich ionic transport can be achieved in $\text{T-Nb}_2\text{O}_5$. These are attributed to the layered structure (empty octahedral sites between the chains) of $\text{T-Nb}_2\text{O}_5$. Our efforts on coating an ultrathin carbon layer onto $\text{T-Nb}_2\text{O}_5$ nanowires have also shown the high rate Li^+ ions storage capability.^[8] It is suggested that the crystal structure of the electrode material is one of the important factors that governs the mode of redox reactions (surface controlled-capacitive contribution or diffusion controlled-intercalation contribution).^[14]

Poly-acid salts of molybdenum, A_xMoO_z (where A could be a monovalent, divalent or trivalent metal ion),^[15] are interesting host materials for ion insertion applications, particularly in electrochemical energy-storage devices, i.e., batteries,^[16–18] and supercapacitors.^[19–21] Due to their unique crystal structure (layers of molybdenum oxide octahedra separated by the metal ions), metal-molybdates,^[22–24] become subject of increasing research interest. A_xMoO_z types of materials are the special class of inorganic oxide materials which possess mixed state of conductivity (ionic as well as electronic), however, their physical, chemical and electrochemical properties are largely dependent on the crystal structure (arrangement of the octahedra and tetrahedra in the unit cell).^[22,23] Besides, multiple oxidation states of molybdenum ions (Mo^{3+} to Mo^{6+}), molybdates of metal or transition metal elements provide robust chemical stability (due to covalent bonding) and excellent ionic conductivity with respect to the electrolyte ions due to the conductive paths paved with metal or transition metal ions.^[25,26] Recently, Mai et al.^[21] demonstrated the use of transition metal molybdates, i.e., CoMoO_4 in nanowire-like morphology as an electrode in pseudocapacitors with a specific capacitance of 62.8 F g^{-1} (at a current density of 1 A g^{-1} , in a potential window of $\Delta V = 1 \text{ V}$), and further improved the capacitance to 187 F g^{-1} (at a current density of 1 A g^{-1}) by forming

heterostructure of $\text{MnMoO}_4/\text{CoMoO}_4$ nanowires. Moreover, other transition metal molybdates, e.g., NiMoO_4 ,^[20,27,28] MnMoO_4 ,^[19,29] and BiMoO_4 ,^[30] in various morphologies have also been demonstrated as prospective pseudocapacitive electrode materials in supercapacitors. The performance of the electrode materials was further improved by positioning multiple transition metal elements into the host structure of molybdates, for example, the combination of Ni-Co-Mo is demonstrated to be an excellent electrode material in supercapacitors.^[31,32] In spite of exerting a lot of efforts [mixing more than one transition metal element (Mn, Co, Ni, etc.), reduced-graphene oxide (rGO),^[33] and conductive polymer (polyaniline),^[34] the working potential window of the electrode materials could not be extended to more than 1 Volt. Most recently, Liu et al.^[20] and Senthilkumar et al.^[32] showed that an asymmetric device (aqueous electrolyte) fabricated using activated carbon (AC) and nanocomposites of Ni-Co-Mo offers a wide operating potential window of 1.4 V and 1.6 V, which delivers a high energy density of $\sim 20 \text{ Wh kg}^{-1}$ and $\sim 21 \text{ Wh kg}^{-1}$ at an applied current density of 2 A g^{-1} , respectively. Despite the fact that the transition metal molybdates show a noticeable improved energy density, they sacrifice power density, for example, rGO- CoMoO_4 nanocomposites,^[35] and α - NiMoO_4 nanoplates,^[36] delivered a high energy density of 54.8 Wh kg^{-1} and 52.7 Wh kg^{-1} at a power density of 197.4 W kg^{-1} and 300 W kg^{-1} , respectively. Albeit, the reasons for this lack of power density are not known yet, it is possibly caused by the non-uniform distribution of the transition metal ions within the structure of molybdates.

In this study, we synthesize and demonstrate silver molybdate ($\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$) as a pseudocapacitive electrode material for the first time, to our knowledge. Silver molybdate can be crystallized in various crystal structures, for example, cubic (Ag_2MoO_4), orthorhombic ($\text{Ag}_2\text{Mo}_3\text{O}_{10}$), triclinic ($\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$) and hexagonal ($\text{Ag}_{1.02}\text{Mo}_{5.52}\text{O}_{17} \cdot 0.92 \text{ H}_2\text{O}$). Most recently, ultra-long nanowires of silver-molybdates in the orthorhombic phase ($\text{Ag}_2\text{Mo}_3\text{O}_{10}$) have been employed in photocatalysis, surface enhanced Raman spectroscopy (SERS), UV-Vis and photoluminescence applications.^[37] Antimicrobial, photocatalytic and

photoluminescence properties of Ag_2MoO_4 nanostructures have also been studied in the recent years.^[38] Silver molybdate in triclinic ($\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$) phase possesses a wide range of applications, such as a novel non-Pt electrocatalyst for oxygen reduction reactions (ORR), fast ion-conducting glass, electrode in battery applications, etc.^[39–41] Silver molybdate in triclinic structure consists of a unique arrangement of ions, in which a chain of Ag ions resides in-between MoO_6 octahedra or vice-versa.^[24] For simplicity, the structure can be broken down into two basic units, one consisting of six octahedra sharing edges and another made of a square arrangement of four octahedra sharing edges. An infinite zigzag chain of octahedra running along the a axis is formed by the six identical octahedra sharing edges and a group of four octahedra lies in-between these chains voids, which are then filled with silver ions.

Hydrothermal synthesis is advantageous as it involves the growth of nanomaterials in an aqueous solution at elevated temperature and pressure, which increases the solubility of the precursor that allows to change the solution conditions in order to favor the formation of the desired phase of the material.^[42] Among the various phases (orthorhombic, triclinic, hexagonal, cubic, etc.) of silver molybdate, the triclinic phase ($\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$) is the most interesting phase due to its unique layered structure.^[43] In the crystal structure of $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$, layers of MoO_6 octahedra are separated by the array of silver ions, positioned (five-coordinate site) at the void sites between MoO_6 octahedra. $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ is highly active and selective in catalysis reactions (oxygen-reduction reactions).^[39] The formation of this phase is mainly dependent on the reaction conditions, such as annealing temperature and atmosphere.^[37]

Figure 1. (a) XRD pattern of the sample annealed at 455 °C, (b) atomic arrangement of Ag, Mo and O atoms in triclinic phase of silver molybdate, (c) DSC/TGA characteristics of the as-synthesized hydrothermal product and (d) FESEM micrographs of T-Ag₆Mo₁₀O₃₃ nanorods. Inset of Figure 1(d) shows the magnified view of T-Ag₆Mo₁₀O₃₃ nanorods.

The crystallographic phase of the material is evaluated using X-ray powder diffraction (XRD). **Figure 1(a)** shows the XRD pattern of the product annealed at 455 °C. The diffraction peaks of the product are well matched with the standard diffraction pattern of Ag₆Mo₁₀O₃₃ in triclinic crystal structure (ICDD card # 13-7646, $a = 7.59 \text{ \AA}$, $b = 8.31 \text{ \AA}$, $c = 11.42 \text{ \AA}$ and $V = 671.8 \text{ \AA}^3$). XRD patterns of the as-synthesized and the as-annealed samples are shown in the Supporting Information, **Figure S1**. The crystallographic structure of T-Ag₆Mo₁₀O₃₃ is shown in Figure 1(b), in which layered arrangement of MoO₆ octahedra and Ag ions can be seen clearly, Ag ions in T-Ag₆Mo₁₀O₃₃ are present between the layers of MoO₆ octahedra.

DSC/TGA was carried out to provide insight on the thermal behavior of the product. A typical DSC/TGA curve of the as-synthesized product is shown in Figure 1(c). The observation of three endothermic peaks (at 295 °C, 455 °C and 536 °C) in the DSC curve shows the change in the phase of the material. The mass loss in the TGA curve below 250 °C is attributed to the removal of the water molecules from the lattice of the material. The consecutive mass loss is due to decomposition of the material, a further gain in the mass as well as the observation of an endothermic peak (at 455 °C) indicates the oxidation of the material ($\text{Ag}_2\text{Mo}_3\text{O}_{10} + 2\text{O}_2 \rightarrow \text{Ag}_6\text{Mo}_{10}\text{O}_{33}$).^[37] An endothermic peak identified at 536 °C shows melting of the constituents. Thus, the as-synthesized product was air annealed at 455 °C to obtain pure triclinic phase of silver molybdate.

To further evaluate the effect of annealing temperature on the arrangement of MoO_6 octahedra, Fourier transformation infrared spectroscopy (FTIR) was carried out, and the results are shown in the Supporting Information **Figure S2**. In the IR analyses, MoO_3 is chosen as the reference to identify the shift in the bands due to positioning of silver ions. Field-emission scanning electron microscopy (FESEM) analysis, Figure 1(d), revealed that the as-annealed (at 455 °C) product stabilizes in nanorod-like morphology; a magnified view of the nanorods can be seen in the inset of Figure 1(d). The as-obtained nanorods are found to be about 300 nm in diameter, as revealed by Transmission electron microscopy (TEM), **Figure S3(a)**. The observation of well defined fringes in the High resolution transmission electron micrograph (HRTEM) indicates excellent crystalline quality of the material, as presented in **Figure S3(b)**. FESEM micrographs of the as-prepared and the as-annealed (295 °C and 536 °C) samples are shown in the Supporting Information, **Figure S4**.

Surface chemical states of the $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods were studied by X-ray photoelectron spectroscopy (XPS). A typical survey and high-resolution spectra of the most dominant signals found in the $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods are shown in **Figure 2**. The detailed spectra are well fitted by a nonlinear least-squares routine using mixed Lorentzian-Gaussian (Voigt) peak

shapes, as shown in Figure 2(b-d). The survey spectrum reveals strong signals from the constituents of the nanorods, namely Mo 3d, Ag 3d, O 1s and the corresponding Ag MNV, Mo MNV and O KLL Auger lines (Figure 2(a)). Furthermore, a complex C 1s signal appears that is originating from graphite paper (used as a substrate). Parts of the oxygen and carbon signals are caused by exposure of the sample in atmosphere these are within the sensitivity of XPS measurements and the samples are determined to be free of impurities. A charge referencing is not applied, as the use of the flood gun prevents a significant charge build-up. The dominant low binding energy component in the O 1s region (Figure 2(d)) which is attributed to oxygen in MoO₃ at 530.42 eV fits nicely to the expected value of this species at 530.45 eV. This is in accordance with a very recent and detailed XPS analysis of Baltrusaitis et al. on molybdenum oxides and this was used as a energy reference,^[44] and corresponds to similar results from Scanlon et al.^[45]

Due to spin-orbit splitting, the high-resolution spectrum of Mo (Figure 2(b)) contains three pairs of peaks separated by the splitting energy of 3.14 eV.^[45] The strongest signal at a 3d_{5/2} binding energy of 232.25 eV corresponds to Mo⁵⁺ oxidation state in MoO₃. The shoulder on the low energy side of the signal can be fitted by a 3d_{5/2} peak at 231.29 eV. It is caused by an X-ray induced reduction of Mo⁶⁺ to Mo⁵⁺.^[44,45] The small signal on the high energy side of the Mo⁵⁺ cannot be easily assigned, but its introduction was necessary to obtain an acceptable fit. It is either an additional species located at 233.31 eV or a satellite effect caused by final states effects (e.g., charge transfer, spin-spin coupling, etc). All peaks were fitted with a FWHM of 1.05 eV. The Mo 3d peak widths of metallic molybdenum and highly crystalline MoO₂ and MoO₃ oxides range from 0.8 to 0.9 eV under monochromatic X-ray excitation.^[45] In nanostructured materials a broadening of core level signals is quite typical,^[46] a FWHM of approx. 1.4 eV was found for α -MoO₃ nanobelts.^[47]

As shown in Figure 2(c), the XPS spectrum of silver 3d region also features a pair of spin-orbit doublets at binding energies of 367.79 eV and 373.79 eV (1.17 eV FWHM). The binding

energy difference of 6.00 eV between the two doublets matches well with reported values.^[48] Silver exhibits an anomalous chemical shift of oxide peaks to lower binding energies compared to the metallic signal. The binding energy of $\text{Ag}^{2+} 3d_{5/2}$ in AgO is at 367.6 eV, $\text{Ag}^+ 3d_{5/2}$ (Ag_2O) can be found at 367.9 eV.^[49] The exact assignment is trivial, and it has been suggested that both oxides can be distinguished by their peak shape than their absolute binding energy.^[46] Based on this, the measured Ag 3d signal should be attributed to the Ag^+ species.

Figure 2. XPS (a) survey spectrum and (b), (c) and (d) high-resolution spectra of Mo, Ag and O, respectively, presented in T-Ag₆Mo₁₀O₃₃ nanorods.

The detailed spectrum of O 1s is shown in Figure 2(d), featuring a complex, convoluted signal with an obvious asymmetry. It can be decomposed into three distinct peaks at 530.42 eV, 531.69 eV and 533.15 eV. The two major signals may be related to oxidic oxygen.^[44,45,48] As discussed before, the first signal corresponds to O²⁻ in MoO₃.^[44,45] In the same energy range

the O 1s in pure Ag₂O is expected.^[48] The crystal structure of T-Ag₆Mo₁₀O₃₃ suggests oxygen in two different chemical environments, oxygen in MoO₆ octahedra adjacent to the silver layer and those away from it. While the latter is similar to a pure binary Mo-O oxide, the species in the vicinity to the silver layer may be responsible for the second signal at 531.69 eV. The electronegativity difference of O (3.5 eV) and Mo (2.2 eV) favors the formation of polar covalent bonds, whereas, the difference between O (3.5 eV) and Ag (1.9 eV) have a tendency to form ionic bonds, this and the larger spacing would explain a shift of O 1s to higher binding energies for oxygen close to the silver layers. The peak position of O atoms in T-Ag₆Mo₁₀O₃₃ matches closely to that found in BiMoO₄;^[50] since the electronegativity of Bi (2.02 eV) and Ag (1.9 eV) is close to each other, this indicates bipolar bonding nature of O atoms in molybdates. A weak signal in the same energy region can also be found in the analysis of Ag₆Mo₁₀O₃₃ nanorods.^[51] An alternative consideration would be the assignment of the 531.69 eV species to defective oxide found in many transition metal oxide samples.^[51] The weak third signal at 533.15 eV can eventually be related to a hydroxyl-containing surface contamination, in conjunction with the high binding energy Mo species at 233.31 eV.

In summary the XPS analysis ensures that the Mo species and most likely also Ag in T-Ag₆Mo₁₀O₃₃ nanorods are in Mo⁶⁺ and Ag⁺ oxidation states, respectively. Next to the dominant MoO₃ related oxygen signal a strong second feature is found, which maybe a large defect signal or a sign of the different chemical environment of O atoms close to the silver layer.

Electrochemical properties of transition metal (Mn, Co, Ni, etc.) or semi-metal (i.e., Bi) molybdates have been studied in alkaline medium (e.g., KOH or NaOH) due to the electrochemical activity of metal ions within the layers of MoO₆ octahedra.^[28,29,33,34]

Electrochemical measurements of T-Ag₆Mo₁₀O₃₃ were carried out in a three-electrode cell configuration (half-cell configuration) using 2 M KOH solution as electrolyte, **Figure 3**. Cyclic voltammograms (CVs) of T-Ag₆Mo₁₀O₃₃ are carried out at various sweep rates, as

shown in Figure 3(a). The stepwise oxidation and reduction (0.235 V/0.55 V, 0.620 V/0.403 V) of Ag ions, located at various sites in the structure (Mo-O-Mo/Ag/ Mo-O-Mo) indicate the pseudocapacitive behavior of the material. The nonlinearity associated with charge/discharge curves further confirms the existence of faradic redox reactions, as shown in **Figure S5**. The pseudocapacitive behavior of T-Ag₆Mo₁₀O₃₃ mainly comes from the reversible redox reaction of Ag⁺ ions, as explained on the basis of the Pourbaix diagrams of Ag and Mo, **Figure S6**. In the defined potential window and pH range, Ag ions can change reversibly to Ag(OH)₂⁻, whereas, Mo ions exist in the form of MoO₄²⁻ ions which do not partake in the redox reactions. There is a noticeable peak shift observed as the sweep rate increased from 1 mV s⁻¹ to 100 mV s⁻¹, which could be due to an increase in resistance from several origins, such as internal resistance active material, solid-electrolyte interface resistance, etc.^[13]

Figure 3. (a) Cyclic voltammograms (CVs) of the as prepared electrode at various scan rates, (b) and (c) linear fitting of the peak current vs. scan rate for the first and second set of redox peaks in CVs, respectively, (d) specific charge as a function of the scan rate.

Figure 3(b) and (c) present a relationship between $\log(i)$ vs. $\log(v)$ from 1 mV s^{-1} to 100 mV s^{-1} for both (1 and 2) cathodic and anodic peaks, respectively. Assuming that the measured current i obeys a power law relationship with the sweep rate v , according to Equation 1.^[6,13]

$$i = av^b \quad (1)$$

Where a and b are the adjustable parameters, b can be determined from the slope of the plot $\log(i)$ vs. $\log(v)$. According to the approximations, $b = 1$ indicates surface controlled current and $b = 0.5$ is corresponding to the current controlled by the semi-infinite linear diffusion. From Figure 3(b), the slope of the lines is calculated to be ~ 1 (for the first pair of anodic/cathodic peaks), indicating that the kinetics are controlled by the surface redox reactions. However, there is a change in slope observed for the second set of anodic/cathodic peak, as shown in Figure 3(c). This change in slope is corresponding to a decrease in b -values to ~ 0.7 , for both cathodic and anodic peak currents. Therefore, it is evident from the $\log(i)$ vs. $\log(v)$ analysis that T-Ag₆Mo₁₀O₃₃ exhibits both surface as well as diffusion controlled kinetics of redox reactions. Figure 3(d) shows the relationship between charge (C g^{-1}) stored by the electrode vs. sweep rate (mV s^{-1}). The maximum charge that can be stored by T-Ag₆Mo₁₀O₃₃ is as high as 398 C g^{-1} at a sweep rate of 1 mV s^{-1} and it could maintain a charge of 135 C g^{-1} at a high sweep rate of 100 mV s^{-1} . The contribution of the graphite paper in the overall performance is found negligible, as determined using cyclic voltammetry **Figure S7**.

Figure 4. (a) Normalized C_{sp} vs. $(v)^{-1/2}$ allows for the separation of intercalation redox reactions contribution from the surface redox reactions induced capacitance. Region-1 and Region-2 emerge when scan rate varied from 1-100 mV s^{-1} , extrapolated diagonal dashed line in Region-1 helps to determine surface redox reaction induced capacitance, and (b) projection of the contribution of surface and intercalation redox reaction contribution at the various scan rates.

The contribution of surface-controlled and diffusion-controlled kinetics to the overall performance can be determined using the method developed by Trasatti et al. to evaluate the charge-storage in RuO_2 (a well known pseudocapacitive material),^[6] and recently used by Lee et al. in case of Ni-Co oxide,^[52] and MoO_3 .^[53] In the relationship between normalized capacitance (C_{sp}) and the inverse of the square root of the sweep rate ($(v)^{-1/2}$), the linear region in the plot indicates capacitance or charge limited by the semi-infinite linear diffusion, however, capacitive contributions do not depend on the sweep rates. The extrapolated y – intercept in the plot of C_{sp} vs. $(v)^{-1/2}$ yields the infinite sweep rate capacitance. **Figure 4(a)** shows the plot of normalized capacitance vs. $v^{-1/2}$ for $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ from a sweep rate of 1 mV s^{-1} to 100 mV s^{-1} . Similar to the behavior of the peak currents in Figure 3(b) and (c), there are two distinct regions in Figure 4(a). In region – 1 (sweep rate 1-10 mV s^{-1}), the normalized C_{sp} is found to be independent or scantily depend on the sweep rates. An extrapolated y intercept estimated the capacitive or surface controlled contributions to the overall performance, which is determined to be approximately ~53 % (~47 % is attributed to the

diffusion kinetics). Whereas, in region – 2 (sweep rate $>10 \text{ mV s}^{-1}$), normalized capacitance decreases rapidly as a function of the sweep rates. Attributed to partake of the diffusion controlled kinetics in the region – 1, a high normalized C_{sp} was realized. Therefore, at a sweep rate of 1 mV s^{-1} , the contribution of diffusion kinetics is found maximum and decreases as the scan rate increases, and eventually becomes independent at a sweep rate $>10 \text{ mV s}^{-1}$. The kinetics of diffusion processes is strongly dependent on crystallite size as well as crystalline quality of the material.^[54] Figure 4(b) presents the estimated contributions of the surface-controlled and diffusion controlled kinetics to the overall performance of $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$.

In order to unveil the characteristics of the redox reactions, an ex-situ XPS is performed. **Figure 5(a-b)** and (c-d) presents the high resolution XPS spectra of Ag and O ions after respective charging and discharging of the electrode (in a potential window of -0.4 V to $+0.85 \text{ V}$), respectively. The obvious changes are recognized in the XPS spectra after charging and discharging of the electrode at an applied current density of 10 A g^{-1} . As depicted in Figure 5(a), a pair of peaks (1 and 1') is identified at the binding energy of 373.1 eV and 366.9 eV in the high resolution spectra of Ag ions during charging process. The observation of a peak at the high binding energy is due Ag^{2+} ions in AgO , as reported elsewhere.^[55] Whereas, the other peak at a binding energy of 366.9 eV for Ag 2s is due to Ag^+ ions in Ag_2O .^[56] The observed broad peak at a binding energy of 377.2 eV is due to physically adsorbed K^+ ions.^[57] It is noteworthy that the change in the oxidation states of Ag ions during charging is accompanied by the change in O^{2-} ions, as shown in Figure 5(b).

Figure 5. (a-c) and (b-d) XPS high-resolution spectra of Ag and O ions, respectively, after charging and discharging of $\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods, the applied current density was 10 A g^{-1} .

As shown in Figure 5(b), the intense peak in the spectra of O1s bears a little incremental change of 0.1 eV with respect to pristine electrode, moreover, a pair of peaks (2 and 2') is also identified at the binding energy of 531.5 eV and 528.7 eV, which are due to O^{2-} ions in the lattice of Ag_2O and AgO ,^[55,58] respectively. On the other hand, during discharging process the position of peaks (1 and 1') remain unchanged, while the concentration reduced to almost 30%, which indicates reversibility of the Ag species during discharging process, as shown in Figure 5(c). Likewise, as depicted in Figure 5(d), the concentration of the O^{2-} ions in AgO decreased significantly during discharge process, which further shows the reversibility of the electrochemical reactions. Whereas, the other peak which was due to oxygen ions in Ag_2O shifted to 532.5 eV and decreased in concentration (less than 10%), however, the exact cause

of this shift is not clear, but we assume that this change happened due to involvement of Ag^+ ions in the form Ag-OH species, as discussed in the previous reports.^[59]

To exploit T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ in practical applications, an asymmetric device is fabricated using activated carbon (AC) and T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ as positive and negative electrodes, respectively. As can be seen from the CV analysis of AC (Supporting Information **Figure S8**) and T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ (Figure 3(a)) electrode, it is evident that the charges can be stored in a potential window between -1.2 V and +0.85 V. Ideally, the as-fabricated device should achieve a maximum potential window of 2.05 V, but due to the activity of T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ in the negative potential regime, it reduces the effective potential window to 1.6 V. To achieve a maximum device performance, the charge-storage capacity of both the electrodes should be balanced and that was achieved by adjusting the mass of the electrodes. **Figure S9(a)** shows CV curves of the as-prepared asymmetric device collected at different working potentials at a sweep rate of 50 mV s^{-1} . Attributed to the pseudocapacitive behavior of T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$, a set of well defined redox peaks are observed in the CV analysis of the device. Galvanostatic charge-discharge (CD) curves of the device in various working potentials at an applied current density of 5 A g^{-1} are shown in Figure S9(b). CD curves further confirm that the device is completely functional within the adjusted potential window.

Figure 6(a) depicts the CVs of the as-prepared asymmetric device at various scan rates (10 - 100 mV s^{-1}). The distorted rectangular CVs render the information about the pseudocapacitive contribution of T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$. The galvanostatic charge/discharge test is carried out from 0 to 1.6 V at various current densities, as shown in Figure 6(b). Figure 6(b) further confirms that the device is fully functional in the entire potential window and exhibits pseudocapacitive behavior, which is suggestive of a good charge-storage performance. The specific capacitance of the full cell at different current densities is calculated from Figure 6(b), and is shown in Figure 6(c). The specific capacitance is calculated according to Equation (2).

$$C_{sp} = \frac{I}{m} \left(\frac{-\Delta V}{\Delta t} \right)^{-1} \quad (2)$$

Where I/m is the discharge current density, taking the total mass of the device into account, and $-\Delta V/\Delta t$ is the slope of the discharge curve after IR drop correction. As shown in Figure 6(c), the C_{sp} of the device could reach up to 65 F g^{-1} at a current density of 2 A g^{-1} , while it maintains 28 F g^{-1} at 20 A g^{-1} , which indicates good rate characteristics of the device. To show feasibility of the device at higher current densities, equivalent series resistance (ESR) for the device is calculated from the slope of the curve plotted between iR drop and applied current density, as shown in **Figure S10**. The linear dependence of iR drop on applied current density indicates that the device bear almost identical ESR of about 21Ω (calculated from the curve taking complete loading mass of the materials into account) at all applied current densities. The long term cycling stability of a supercapacitor device is crucial, to demonstrate its reliability in device applications. To show cycling stability of the asymmetric supercapacitor, continuous charge/discharge tests up to 2500 cycles at a scan rate of 50 mV s^{-1} are carried out, as shown Figure 6(d). The capacity of the asymmetric device fades about 17% in the first 250 cycles and additional 15% upon 1000 cycles. After this initial stage degradation, the device maintains its stability and achieves about 68% of initial capacity after 2500 cycles. The possible reason of this initial stage degradation can be explained on the basis of the inset of Figure 6(d). The first stage degradation (17%) could be ascribed to the irreversibility of the redox reactions (descent in the peak current) and increase in the components resistance (shift in the peak position). However, second stage degradation (15%) could be due to an evolution of oxygen (a small tail at $\sim 1.5 \text{ V}$, in the inset CV indicates this behavior). Electrochemical impedance spectroscopy (EIS) was used to evaluate the charge transfer resistance which is about 13Ω .

To better understand the mechanism of the degradation during cycling, electrochemical impedance spectroscopy (EIS) of the cell before and after 2500 cycles was carried out. Figure

6(e) shows that the charge transfer resistance of the device increased slightly due to fractional formation of new compounds, namely, MoO_2 and AgO after cycling, as revealed by XRD pattern in **Figure S11(a)**. Moreover, the morphology of the active material changed from nanorods to fractured nanorods after prolonged cycling of 2500 cycles, as depicted in **Figure S11(b-c)**. The aforementioned causes could be accountable to the capacity degradation of the asymmetric device. However, to understand the exact mechanism of this degradation, further studies should be carried out.

Figure 6. (a) Cyclic voltammograms of an asymmetric device at various scan rates (10-100 $mV s^{-1}$), (b) Galvanostatic charge/discharge curves of an asymmetric device at various current densities (2-20 $A g^{-1}$), (c) specific capacitance of the device as a function of applied current density, (d) cycling stability of the asymmetric device under continuous charge/discharge at a scan rate of 50 $mV s^{-1}$, inset of Figure 6(d) shows CVs before (1) and after 2500 cycles (2), (e) Nyquist plots of the device before and after cycling, inset of Figure 6(e) shows cell response in the high frequency region, and (f) the Ragone plot of the asymmetric device.

To access the feasibility of using the new electrode material for actual device performance, energy density and power density (the Ragone plot) are the real device parameters. A Ragone plot derived from constant-current charge/discharge characteristics, along with the other asymmetric supercapacitors made from activated carbon for comparison is shown in Figure 6(f). The asymmetric device made from activated carbon//T-Ag₆Mo₁₀O₃₃, using a discharge

current density of 2 A g^{-1} (corresponding to a power density of 1.51 kW kg^{-1}), and an energy density of 22.1 Wh kg^{-1} is obtained. Even at a high power density of 15.1 kW kg^{-1} (corresponding to a discharge current of 20 A g^{-1}), the device still possesses an energy density of 9.1 Wh kg^{-1} , an indication of its high performance ability. The energy and power density performance of activated carbon//T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ device is found better than that of the other transition metal molybdates, such as AC// $\text{NiMoO}_4\text{-CoMoO}_4$,^[19] AC// $\beta\text{-NiMoO}_4\text{-CoMoO}_4$,^[32] and AC//Mo doped MnO_2 ,^[60] AC//Ni-Co oxide,^[61] etc., representing a significant improvement over the current state-of-the-art of molybdenum oxide based supercapacitors. Based on the results discussed here, the spectacular performance of T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ can be ascribed to the followings: (a) mixed crystal-chemistry, i.e., electronic as well as ionic conduction of silver molybdates, (b) favorable arrangement of Ag and Mo atoms, i.e., chain of Ag^+ ions between two MoO_6 octahedra in tetragonal silver molybdate and (c) co-existence of surface and intercalation redox reactions due to the layered structure of T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$. In conclusion, the present work exploits the mixed crystal-chemistry of electronic and ionic conduction of metal molybdates in offering an alternative pseudocapacitive electrode material. The layered structured T- $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ electrode showed co-existence of surface and intercalation redox reactions. A prototypical asymmetric device delivered an energy density of 22.1 Wh kg^{-1} at a power density of 1.51 kW kg^{-1} (corresponding to an applied current density of 2 A g^{-1}). The improvement in the energy density without compromising the power density indicates that the new pseudocapacitive electrode material may be attractive for a wide range of applications.

Experimental section

Chemical used: Ammonium heptamolybdate tetrahydrate $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$, Silver nitrate (AgNO_3) and DI water, were used as purchased.

Synthesis of $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods: In this typical synthesis procedure, 877 mg of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was mixed in 20 ml of DI water. Another solution of 425 mg of AgNO_3 in 20 ml of DI water was prepared separately and drop wise added into the above solution. A dilute solution of HNO_3 (1M) was used to adjust the pH (~ 2) of the resultant solution. The as-formed greenish-yellow solution was then transferred to 50 ml capacity Teflon lined autoclave for hydrothermal reactions at 140 °C for 12 hours. A yellowish precipitate was centrifuged and washed with ethanol and DI water several times and dried at 70 °C. To obtain $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods, the as obtained yellowish precipitate was annealed at 455 °C in air atmosphere for 3 hours. The as-prepared powder sample was used for further characterizations.

Electrode preparation for electrochemical characterization: The working electrode was prepared by mixing the as-prepared $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods powder (85 %), carbon black (10 %) and PVDF (polyvinylidene fluoride) (5 %) into a 5 ml vial containing 500 μl of NMP (N-methyl-2-pyrrolidone), under magnetic stirring to make slurry. 20 μl of this slurry was coated onto a current collector (graphite-paper, 1 cm^2) and dried in a laboratory oven at 100 °C. The loading mass of active material was measured to be ~ 2 mg for all three samples. Three electrode testing (half-cell) was done in an aqueous solution of KOH (2 M) in a potential window of -0.4 V to 0.85 V vs. Ag/AgCl. The full cell was fabricated using activated carbon and $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods as positive and negative electrodes, respectively, and separated using an Advantec filter paper. The mass of the active electrodes was optimized to a 1.1:1 (AC: $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods) ratio.

Material characterizations: The sample was characterized using powder X-ray diffractometry (Shimadzu XRD 6000, Cu K_α radiation $\lambda = 1.54$ Å, power; 2 kW) at a scan rate of 1°min^{-1} in the 2 theta range of 10° - 55° . Field Emission Scanning Electron Microscopy (FESEM; JEOL, JSM 7600F thermal FEG, JSM 6340F cold cathode FEG) and Transmission Electron Microscopy (TEM; JEOL, JEM 2010 and JEM 2100F) were used to evaluate the microscopy

morphology of samples. The IR spectroscopy (Perkin Elmer, Model Spectrum GX) was used to extract the information about the functional groups present in $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods. The XPS experiments were performed with a Thermo Scientific ESCALAB 250Xi spectrometer, using monochromated 1486.6 eV Al-K_α radiation with a spot width of 500 μm and a flood gun for charge compensation. The base pressure of the XPS systems was in the range of 10^{-10} mbar. All the peaks were fitted using a Shirley background and Voigt line shapes (Lorentzian-Gaussian). Electrochemical measurements were carried out using AutoLab PGSTAT 30 potentiostat. A three-electrode cell configuration was used for half-cell testing in which active material ($\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanorods) coated graphite paper (1 cm^2), platinum sheet and saturated Ag/AgCl electrode were employed as working, counter and reference electrode, respectively, in an aqueous electrolyte (2 M KOH). Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with 10 mV amplitude in a frequency range from 100 kHz-10 mHz at open circuit potential (OCP).

Supporting information

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

Acknowledgments

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Mixed-metal molybdates are interesting host materials for ion insertion electrodes due to their versatile crystal-chemistry which confers a highway for the conduction of electrons as well as ions. Silver decamolybdate in triclinic crystal structure ($\text{T-Ag}_6\text{Mo}_{10}\text{O}_{33}$) consists of layers of MoO_6 octahedra separated by the array of silver ions are able to store a high level of charges.

Key words

silver molybdate nanorods; supercapacitors; asymmetric device; crystal chemistry

V. Kumar, V. Bhavanasi, K. Parida, P. S. Lee*

*E-mail: pslee@ntu.edu.sg

S. Matz, D. Hoogestraat, K. Al-Shamery

Design of Mixed-metal Silver Decamolybdate nanostructures for high specific Energies at high Power density