Hexagonal-molybdenum trioxide (h-MoO$_3$) as an electrode material for rechargeable aqueous aluminium ion batteries

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Abstract: Aqueous aluminium ion batteries are at an early development stage and there is a need to discover new electrode materials for the fabrication of high energy density devices. To address this issue, we investigate MoO$_3$ nanowires as a possible electrode material for use in rechargeable Al ion batteries that can operate in aqueous conditions. We present a hexagonal structure of MoO$_3$ microrods as an Al-ion intercalation host material and show its first-time use as a potential electrode for an aqueous Al ion battery system. This yields a discharge capacity of ~300 mAh$^{-1}$ for 150 cycles and ~90% retention after 400 cycles at a current density of 3 Ag$^{-1}$. The utilization of this sort of material and aqueous electrolytes guarantees both the safety and the simple recycling of spent batteries.

Introduction

The establishment of renewable energy sources at scale such as wind and solar farms is gaining momentum due to the ever-increasing energy needs of the modern world. Another significant driver is the detrimental environmental impacts of fossil fuels. Therefore, to ensure this trend continues there is an urgent need to develop better energy storage mechanisms.[1] Since these sources are intermittent, suitable storage systems are required. There are two emerging solutions to this problem, namely battery storage or storing energy in the form of a fuel such as green hydrogen. In addition to energy storage the reduction in vehicle emissions is also a realisable goal through the advent of electric vehicles powered either by batteries or fuel cells. For electric vehicles, batteries are required which are low-cost, have high energy density, are highly stable and are safe to use.[2] At present for both storage and electric vehicles Lithium ion batteries dominate, however there some reports regarding safety and emerging geopolitical restrictions around the availability of Li and Co which are used in many commercial Li ion batteries.[3] Therefore, there is a significant research effort is required in developing alternative battery systems to overcome these shortcomings. A potential solution for sustainable battery technology is to use aqueous systems rather than the currently employed organic electrolyte systems and replace Li with cheaper alternatives. This will help to reduce the cost, simplify the production process and facilitate more widespread recycling of batteries which is difficult at present with Li ion batteries due to safety issues.[4]

Moreover, aluminium is the most abundant metal in the Earth’s crust at around 8 wt%. One third of the current demand for aluminium is met by recycling while the energy spent in the production of aluminium metal is three times lower compared with the production of lithium.[5] Therefore, there has been considerable interest in developing Al ion batteries as an alternative technology.[6] Considering sustainability, safety and environmental impact, aqueous batteries have been identified as being ideally suited for the future. In recent times, there have been several reports on aqueous battery systems. Aqueous lithium-ion batteries[7] were one of the first to be proposed which was then followed by sodium-ion batteries.[8] However, progress was hampered due to the high efficiency of organic based Li ion batteries and the large ionic radius of sodium ions which inhibited performance. Therefore, aluminium has been proposed as a suitable alternative due to its high earth abundance which makes it cheaper than other metal-based batteries. Due to aluminium being a trivalent ion its volumetric capacity is exceptionally high with a value of 8046 mAh/ml which makes it highly attractive for battery applications.[9]

Compared to other multivalent ion systems such as aqueous magnesium ion batteries[10] very few reports have been published on aqueous aluminium ion batteries (AAIB) irrespective of its high volumetric capacity. However a recent study has indicated that this is a promising battery technology.[11] Aluminium batteries are considered to be a promising technology as it offers 4 times higher volumetric capacity compared to Lithium with comparable gravimetric capacity. This would result in a further reduction in size of several electronic devices as the battery requires less space. Therefore, with the same volume of battery an electric vehicle could have 2 to 4 times the range in comparison to commercial batteries.[3] Even though Aluminium has a high volumetric capacity and is safe to use as an anode in aqueous electrolytes, unlike Lithium, it is prone to corrosion and results in instability and large capacity fade.[12] Even so, Jayaprakash et al reported an aluminium anode with a vanadium oxide-based cathode in an aluminium ion battery (AIB), however this was not an aqueous system but used an ionic liquid electrolyte where a chloroaluminate redox species was the charge carrier ion.[13] Due to the highly acidic nature of the liquid-liquid-AICls mixture the oxide layer on the surface of aluminium dissolves which enables the stripping of aluminium, however there are some significant problems with corrosion of the current collectors. Following this study, pyrolytic graphite was employed with chloroaluminate systems for ultrafast AIBs.[14] Subsequently, Reed et al studied the potential instabilities caused by the chloroaluminate electrolyte to stainless steel current collectors which required the use of expensive metals like platinum or palladium to replace stainless steel to ensure stability which drastically increases the

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cost of battery. In comparison to chloroaluminate systems, the use of an aqueous electrolyte has the advantage of being less corrosive, while also facilitating better kinetics during charging, which enhances the performance and in principle offers a way to deliver stable and cheap rechargeable batteries.\(^{[16]}\)

Therefore, given the continued difficulties with Al metal as an anode material such as hydrogen evolution, electrode stability and maintaining an oxide free surface in an aqueous electrolyte attention has been focused on the development of a suitable alternative anode for AAIBs which can reversibly intercalate Al-ions within the stability limit of an aqueous electrolyte. One strategy is to use metal oxide anodes that can accommodate Al ions into their structure. TiO\(_2\) is one of the most investigated anode materials for AAIBs. The first AAlB half-cell was proposed by Liu et al using AlCl\(_3\) as the Al\(^{3+}\) ion source.\(^{[17]}\) Following this study, a few reports were published utilizing TiO\(_2\) as an anode material.\(^{[18]}\) Subsequently, a full cell was reported using a TiO\(_2\) anode and a copper hexacyanoferrate cathode with Al\(_2\)(SO\(_4\))\(_3\) as the electrolyte.\(^{[19]}\) Recently Zhao et al reported surface modified Aluminum as an anode with a MnO\(_2\) cathode in an aqueous AlCl\(_3\) electrolyte.\(^{[20]}\) To date only TiO\(_2\),\(^{[19]}\) V\(_2\)O\(_5\),\(^{[20]}\) CuHCF\(^{[16]}\), Spinel MnO\(_2\),\(^{[21]}\) Cryptomelane\(^{[22]}\) and MoO\(_3\)\(^{[23]}\) have been studied as electrode materials for AAIBs. For a successful AAlB the primary consideration is to find appropriate Al-ion intercalating cathodes and anodes, where the latter is a significant challenge. Our recent work reported on the use of potassium rich cryptomelane as a suitable cathode material for the reversible intercalation of Al\(^{3+}\) ions where it was found that the K\(^+\) ions in the structure were beneficial for intercalation of the Al\(^{3+}\) ions via replacement reaction.\(^{[22]}\) Therefore it was postulated that the presence of host ions with a larger ionic radius than aluminium ions within a metal oxide structure could be a generic approach for enabling more efficient Al-ion intercalation.

MoO\(_3\) electrodes are less explored but orthorhombic MoO\(_3\) has indicated that Al\(^{3+}\) ion insertion is possible into this metal oxide.\(^{[23-24]}\) Here, we prepared molybdenum trioxide with the hexagonal crystal structure (h-MoO\(_3\)) via a simple hydrothermal route and investigated it as an electrode material for an AAlB. The h-MoO\(_3\) phase is formed by the zigzag chains of MoO\(_6\) octahedra that are linked together at the corner along the c-axis of crystal.\(^{[25]}\) The advantages of using this phase rather than the previously explored orthorhombic phase is the incorporation of alkali or ammonium ions into the tunnels which dictates their dimensions and has implications for the electrochemical intercalation of Al\(^{3+}\) ions as we reported earlier for potassium rich cryptomelane (MnO\(_2\)) which showed enhanced performance compared to MnO\(_2\) without the presence of ammonium ions in the tunnels.\(^{[22]}\) It is demonstrated that the Al\(^{3+}\) ions are intercalated/deintercalated into the lattice structures of h-MoO\(_3\) and show promising behaviour as an electrode material for an AAlB.

**Results and Discussion**

The general composition of h-MoO\(_3\) is \((\text{A})_x\text{MoO}_3\cdot(\text{H}_2\text{O})_y\) where A is an alkali or ammonium ion, and x and y depends on the method of preparation. The connectivity between the chains through the adjacent oxygen results in the formation of hexagonal tunnels with a radius ranging from ~1.5 - 1.6 Å when containing an ammonium ion as schematically represented in the scheme 1.\(^{[25]}\)

In principle this should accommodate the insertion of Al\(^{3+}\) ions which have an ionic radius of 0.51 Å.\(^{[22]}\) Previous work on the insertion of multivalent ions into metal oxides indicated that it is the non-hydrated ion that is inserted.\(^{[26]}\) Figure S1a shows the X-ray diffraction (XRD) pattern of this material coated on stainless steel, which confirms its crystalline structure. The Rietveld refinement (Figure S1b) identified peaks that match the standard pattern of the pure hexagonal phase of NH\(_2\)(MoO\(_3\))\(_2\) (PDF 00-039-0035) with a minor component attributed to the monoclinic phase of Mo\(_2\)O\(_4\) (PDF 01-081-1264).

![Scheme 1: Schematic showing the hexagonal tunnels with ammonium ions occupying the space.](image)

A detailed morphological analysis was carried out using scanning electron microscopy as shown in Figure 1a and b which indicates the formation of hexagonal rods and confirms the synthesis of h-MoO\(_3\). The synthesized powder shows relatively uniform hexagonal rods with lengths ranging from 35-75 µm (Figure S2) and diameters ranging from 1-10 µm. A cross section image of the rod is also included in the inset of Figure 1a which shows the hexagonal arrangement of the MoO\(_3\) material. Figure 1(c-f) shows the EDX (Energy-dispersive X-ray spectroscopy) mapping of the electrode material and confirms the presence of molybdenum and oxygen in the microrods. In principle, this hexagonal architecture could enhance the electrochemical activity due to the high surface area of such structures thereby enabling Al ion intercalation.
Figure 1. (a) and (b) SEM images of prepared h-MoO$_3$, SEM elemental mapping h-MoO$_3$. (c) Mapping area, (d) Mapped image, (e) Molybdenum (f) Oxygen.

To confirm the reversible intercalation/de-intercalation of Al ions into h-MoO$_3$, cyclic voltammograms were carried out in 1 M AlCl$_3$ and are shown in Figure 2. The electrodes were prepared by coating the slurry prepared with h-MoO$_3$, activated carbon and PVDF binder onto the stainless steel. The prepared electrodes have an electrical resistivity of ~140 $\Omega$ cm as determined by electrochemical impedance spectroscopy. The cyclic voltammetry profiles were obtained at different scan rates of 100 mVs$^{-1}$, 50 mVs$^{-1}$ and 20 mVs$^{-1}$ in a voltage window from 0.2 V to -0.8 V where broad redox peaks were observed in the CV scan that are attributed to Al-ion insertion/extraction. For the cathodic scan there is no evidence of a sharp increase in current in the potential window studied indicating that the aluminium ion insertion reaction was preferred over the hydrogen evolution reaction. The relationship between peak current and scan rate describes the nature of the electrochemical reaction happening at the electrode and whether it is under solid phase diffusion control or a surface confined charge transfer process. In this case the peak current varied linearly with the square root of the scan rate indicating a solid phase diffusion reaction at the electrode interface which indicates that aluminium ion intercalation is the dominant reaction in h-MoO$_3$ rods.

Figure 2. CV diagram at scanning rates of 20, 10 and 5 mVs$^{-1}$. The inset is the linear fit of the peak current versus the square root of the scan rate.

The h-MoO$_3$ powders were dispersed in ethanol and drop casted on to a glassy carbon electrode and subjected to 100 cyclic voltammetric cycles to conduct ex-situ SEM experiments to determine the structural changes that occur when h-MoO$_3$ is intercalated with Al$^{3+}$ ions. The electrodes were washed copiously to remove any surface bound electrolyte and then investigated by SEM and EDX analysis. The structural change in the electrode after 100 potential cycles over the potential range of 0.2 to -0.65 V is shown in Figure S3. The morphology changed and showed a swelling of the electrode material. Furthermore, the composition of the electrode after Al ion insertion was analysed by SEM-EDX (Figure 3). As seen in Figure 1 the pure h-MoO$_3$ did not show any presence of aluminium as expected whereas a clear signal for aluminium is seen in the cycled electrode (Figure 3d). To confirm that this surface changes is not due to the electrolyte, microscopic images were obtained of the pristine powder dipped in AlCl$_3$ electrolyte for 24 hrs as shown in Figure S4. The elemental mapping experiments (Figure 3) show the uniform distribution of aluminium throughout the sample. Based on the above analysis and CV measurements, it is reasonable to conclude that electrochemical insertion of aluminium ions into the hexagonal MoO$_3$ rods is successful in an AlCl$_3$ aqueous solution.
To confirm if this is a bulk process as indicated by the cyclic voltammetry data\[\text{[4a]}\], \textit{ex situ} XRD analysis of the electrodes was also carried out to study any structural changes that occur upon reversible aluminium intercalation. The comparison of the XRD patterns of freshly prepared, Al-inserted and Al-extracted h-MoO\textsubscript{3} is shown in Figure 4a. The samples maintain their crystal structure upon application of a potential cycle as observed in the comparative data which substantiates the structural stability of the electrode. However, there is an effect seen upon intercalation of Al ions where there is a decrease in intensity in the h-MoO\textsubscript{3} peak at $2\theta = 16.75^\circ$ (Figure 4b). This peak then increases in intensity when Al ions are removed from the h-MoO\textsubscript{3} structure. Interestingly, a new peak is observed at a $2\theta$ value of 16.11\(^\circ\) after Al ion intercalation which again decreases in intensity after Al ion extraction. This newly formed peak cannot be attributed to a new phase of h-MoO\textsubscript{3} but possibly corresponds to the formation of y-Al\textsubscript{2}O\textsubscript{3} (04-016-7505). It is known for ZnO anodes that have been investigated for Li ion batteries that Li\textsubscript{2}O can be formed during Li ion storage before the alloying process to form Li\textsubscript{x}Zn (x ≤ 1).\[\text{[27]}\] Therefore, this phenomenon could also be occurring during the course of the process before the Al ions are intercalated into the h-MoO\textsubscript{3} structure. In addition, there is also evidence of a small change in the lattice parameters due to the slight shift observed for some peaks as shown in Figure 4c during the discharge process. This is attributed to the insertion of Al\textsuperscript{3+} ions which in principle should result in a change in the lattice structure of the host material. This is substantiated by the return of the peak to its original position upon Al\textsuperscript{3+} ion extraction (Figure 4c). The calculated lattice parameters for the fresh and reduced electrodes from the refined structures are provided in the supplementary information in Table S1.

To further understand the intercalation chemistry, XPS experiments were carried out for freshly prepared h-MoO\textsubscript{3} and after Al ion intercalation. It must be emphasised that the samples were analysed after 120 s of ion beam etching to avoid any surface contamination and to eliminate the effect of any residual electrolyte that may be present even after washing the samples. In addition, in this experiment a gas cluster beam is used for etching which uses a weakly bound cluster of Ar gas atoms which can still remove material but spreads the energy and single etching which uses a weakly bound cluster of Ar gas atoms which can still remove material but spreads the energy and single charge across the whole cluster. This vastly decreases the damage zone in the remaining surface, as there is significantly less energy imparted into the material by the cluster impact. This results in XPS spectra that accurately represent the real surface chemistry. Figure 5a shows the survey spectra of both the fresh and intercalated electrodes where a peak corresponding to aluminium is observed in the latter. Figure 5d shows the high...
resolution Al 2p spectrum of the intercalated electrode which can be deconvoluted into two peaks, one at ~74.7 corresponding to Al\(^{3+}\) which is consistent with previous work where Al\(^{3+}\) ions are inserted into TiO\(_2\)\(^{[17]}\) and one at ~76 eV corresponding to the presence of aluminium oxide,\(^{[28]}\) which is consistent with the XPS results. In the survey spectrum, peaks for F 1s at 686.8 eV and C 1s at 284.8 eV are also observed which indicates the presence of the PVDF binder and activated carbon. The Mo 3d core level spectrum for fresh h-MoO\(_2\) (Figure 5b) can be deconvoluted into 4 peaks that corresponds to the typical doublet of spin-orbit splitting of both Mo\(^{3+}\) and Mo\(^{4+}\). From the deconvoluted spectrum it is seen that most of the contribution is from Mo\(^{6+}\) (78.87%) with Mo 3d\(_{5/2}\) peak at 232.75 eV and the remaining 21.13% from Mo\(^{5+}\) with a peak at 231.98 eV. Figure 5c shows the Mo 3d spectrum after aluminium ion insertion. The peak obtained was deconvoluted into doublets corresponding to Mo\(^{4+}\), Mo\(^{5+}\) and Mo\(^{6+}\).\(^{[29]}\) Upon aluminium ion insertion a peak at 235.05 eV was observed which corresponds to Mo\(^{5+}\) interaction with a trivalent cation like Fe\(^{3+}\) or Al\(^{3+}\).\(^{[30]}\) In this case Al\(^{3+}\) interaction leads to a peak shift to 234.05 eV, due to conversion of Mo\(^{6+}\) also occurred resulting in an increase in the atomic percentage of Mo\(^{5+}\) from 21.13% to 70.15%. Subsequently Mo\(^{4+}\) also emerged which results from the reduction of Mo\(^{5+}\). From XPS analysis the reduced electrode’s composition can be calculated as Al\(_{0.15}\)MoO\(_2\). Even though XPS is a surface technique these results strongly indicate that Aluminum ions are intercalating into h-MoO\(_2\) given the extent of prior sample etching. It can also be seen from the XPS data that some Al remains in the sample after potential cycling (Figure S5) and is consistent with the XRD data (Figure 4b).

Figure 6a shows the charge discharge curves of h-MoO\(_2\) electrodes with potential vs an Ag/AgCl reference electrode at a current density of 2 A g\(^{-1}\). This 3-electrode charge-discharge curve of the h-MoO\(_2\) anode shows a plateau at ~0.4 V which indicates the insertion of aluminium ions into the lattice structures and is coherent with the CV curves (Figure 2). An initial discharge capacity of 39.3 mAh g\(^{-1}\) was obtained (Figure 6a) which increased to 314 mAh g\(^{-1}\) on the 67\(^{th}\) cycle (Figure 6b) and then a stable discharge capacity of ~300 mAh g\(^{-1}\) was obtained for up to 150 cycles. This trend of capacity increment can be attributed to the electrode activation due to pore opening which can occur in metal oxide systems and also due to reduced electrolyte electrode intercalation.\(^{[31]}\) Figure 6c shows the coulombic efficiency vs cycle number which is maintained at ~89 % after this electrode activation process. A gradual reduction of specific charge capacity was then observed and reached a value of ~265 mAh g\(^{-1}\) after 400 cycles (Figure 6d).

This high stability and capacity retention compared to previous reports\(^{[23–24]}\) can be attributed to the hexagonal crystal structure that facilitates ion intercalation without significant distortion to the lattice structure. This is consistent with previous studies where improved stability for pseudocapacitive and Li ion battery applications was also observed in hexagonal MoO\(_3\).\(^{[32]}\) It should be noted that in all the charge/discharge experiments a deep discharge to -1 V was unable to be reached at low current density. A typical discharge profile obtained at such a low current density of 0.1 A g\(^{-1}\) (Figure S6) shows a plateau at -0.5 V and a further plateau at -0.68V but shows an unusually high capacity of ~7000 mAh g\(^{-1}\), the origin of which is unknown. This behaviour is similar to a previous report of orthorhombic - MoO\(_3\) but in that case the electrolyte used was Al(NO\(_3\))\(_3\) which was determined to be
unsuitable for this application and indicated that AlCl₃ was a far more suitable electrolyte for Al ion intercalation,[33]

![Figure 6. Galvanostatic charge/discharge results of h-MoO₃ in 1 M AlCl₃ with Ag/AgCl reference electrode (a) 1st, 50th, 100th, 200th, 300th, and 400th at 2 Ag⁻¹. (b) Shows a charge/discharge curve of h-MoO₃ at the 67th cycle at which the highest capacity is obtained at 3 Ag⁻¹. (c) Coulombic efficiency vs no of cycles. (d) Specific charge capacity and discharge capacity vs Number of cycles.](image)

The electrode was then tested at various charging/discharging rates which was varied from 1 to 5 A g⁻¹ (Figure 7a). For a freshly prepared electrode the performance was initially poor as reflected by the low capacity values. However for an electrode that was cycled at 3 A g⁻¹ for 50 cycles the performance was significantly improved as shown in Figure 7b. This is consistent with the data in Figure 6a which shows that the electrode needs to be cycled several times to activate the material. The variable rate data also shows that upon a return to a lower rate of 1 Ag⁻¹ that the initial capacity is retained at 475 mAhg⁻¹.

![Figure 7. Rate performance of the prepared electrodes of h-MoO₃ in 1M AlCl₃ with Ag/AgCl reference electrode at different current densities from 1 Ag⁻¹, 3 Ag⁻¹, 4 Ag⁻¹, 5 Ag⁻¹. (a) Rate performance of the fresh electrode. (b) Rate performance of the electrode after 50 cycles.](image)

Conclusions

In summary, the formation of hexagonal MoO₃ can be achieved by a simple hydrothermal synthesis route. The electrochemical insertion/extraction of Aluminum-ion into hexagonal MoO₃ microrods in 1 M AlCl₃ aqueous solution and its feasible application as anode was demonstrated. This potential anode for an aqueous Al ion system yields a discharge capacity of ~300 mAhg⁻¹ for 150 cycles and ~90% retention after 400 cycles at a current density of 3 Ag⁻¹ which demonstrates the promising commercial viability of rechargeable AlIBs. This work provides additional significant information on the development of intercalating materials that contain guest species to promote the reversible intercalation of multivalent ions for aqueous rechargeable batteries.

Experimental Section

The electrode materials were prepared using a simple hydrothermal method. For a typical synthesis, 1 M (NH₄)₂MoO₄·4H₂O was dissolved into 30 ml of deionized water. Following 20 minutes of stirring, this solution was added to 30 ml of ethanol along with 2 g of polyethylene glycol (PEG). To this milky white solution 2 ml of HNO₃ was added under stirring conditions to keep the pH between 4-5. This solution was kept stirring for a further 30 minutes and was then transferred to a Teflon-lined stainless-steel autoclave (100 mL capacity) and heated at 140 °C for 24 h. The resultant product was transferred to a centrifuge tube and washed with deionized water and ethanol several times. The resultant powder was dried at 70°C for 6 h in an oven. The obtained dark blue powder was used for further characterization. This blue colour has been seen previously for nanosized MoO₃.[33]

Scanning electron microscopy images were obtained using a Zeiss Sigma electron microscope with a gold sputtered layer on the samples, which were adhered to carbon tape. Samples mounted on a stainless steel substrate (MTI Corp) were used for XRD analysis. A Rigaku SmartLab diffractometer (Cu source, 40 kV 40 mA) was employed to obtain Powder X-ray diffraction patterns in parallel beam (PB) geometry (which virtually eliminates well-known instrument error functions,[34] which contribute to asymmetric peak broadening, such as rough or non-flat samples, axial divergence, and sample transparency) with an incident slit of 0.8 mm and receiving slit of 20 mm with a HyPix 3000 detector. XRD patterns were obtained over a range of 2-80° with 20 at a step size of 0.01°. Rietveld refinement was undertaken with TOPAS v.6. The electrochemical measurements were carried out using a Biologic VSP3 potentiostat in a typical 3 electrode configuration where the working electrode was the sample coated on stainless steel, a graphite rod was used as the counter electrode (rod, L 150 mm, diam. 3 mm) and a Ag/AgCl was used as a reference electrode (Ionode, Australia). The stainless-steel substrates were cut into 1 cm x 2 cm pieces and washed in acetone to remove any residual impurities. The slurry for the electrode was prepared by mixing h-MoO₃ powder, Polyvinylidene fluoride and activated carbon in N-Methyl-2-pyrrolidone at a ratio of 7:1:5:1.5. This slurry was stirred for 1 hour to ensure uniform mixing and then coated onto the stainless steel to obtain a thin film. These thin film coated electrodes were dried in a vacuum oven for 4 hours at 140°C. A Kratos XPS was used to conduct the XPS analysis of the sample. Each sample was etched for 120 seconds using Argon clusters at 30 eV to etch a few nanometres of the electrode surface while avoiding damage of the sample. The electrodes named AI-inserted and Al-extracted were prepared using a single linear sweep and a full potential cycle respectively, on a fresh electrode, where the voltage ranges used were the same as those shown in Figure 2.
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