Investigation of polyoxometalate-(poly)pyrrole heterogeneous nanostructures as cathodes for rechargeable magnesium-ion batteries

Hakeem K. Henry, a Sang Bok Lee a

a Department of Chemistry and Biochemistry, University of Maryland, MD, U.S.

Polyoxometalate (POM) anionic clusters are explored as new host materials for Mg$^{2+}$ ion storage. Pairing of these redox-active molecules with a poly(pyrrole) conductive polymer allows the POM molecules to partake in fast electron-transfer reactions which are not observed in the absence of the polymer.

With the evolution of advanced portable electronics and electric vehicles, it is expected that current state-of-the-art lithium-ion batteries (LIBs) will not be able to meet the growing energy demands. In the last decade, multivalent-ion (Mg$^{2+}$, Ca$^{2+}$, Al$^{3+}$) battery systems have gained interest due to their high energy density and resource availability. [1] Magnesium in particular is a promising alternative for beyond-lithium energy storage systems because of its high volumetric capacity (3833 mAh/cm$^3$) compared to lithium (2062 mAh/cm$^3$). Magnesium is also much more abundant, lower in cost, environmentally benign, and intrinsically safer as it does not form dendritic structures which would allow the utilization of a Mg metal anode. [2] Currently, there are no commercially available cathodes for magnesium-ion batteries primarily because Mg$^{2+}$ ions do not readily insert into conventional layered metal oxides that have been used for lithium without the addition of water to the electrolyte. [3, 4] The primary challenge facing cathode development is overcoming the strong coulombic interaction that occurs between the host material and the divalent Mg-ion that results in sluggish insertion kinetics causing low capacity, poor coulombic efficiency, and short cycle life. [5]

In 2004, Aurbach’s work on Chevrel Phase (CP) Mo$_6$S$_8$ cathodes for Mg-ion storage successfully demonstrated that Mg ions could reversibly insert into the host material efficiently for more than 2000 cycles with only a 15% fade in capacity. [2] The CP cathode had an initial discharge capacity of 130 mAh g$^{-1}$ and an operating voltage of 1.2 V vs. Mg/Mg$^{2+}$. [2, 7, 8] This work sparked a resurgence in research efforts aimed at the development of viable cathode materials for rechargeable magnesium-ion batteries. One of the most important properties for the rational design of host materials for multivalent ion storage is the ability of that material to effectively redistribute the incoming charge density of the inserting ion. Much of the success associated with the CP Mo$_6$S$_8$ cathode was due to the intrinsic ability of the 6 Mo atoms in the Mo$_6$ polyhedra to function together as a single transition metal ion. By doing so, the incoming charge density of the Mg$^{2+}$ ion is delocalized throughout all 6 Mo atoms, thus causing little to no change in the crystal structure of the material. [5] Similar delocalization of electron density behavior has been observed in the metal oxygen clusters, polyoxometalates. [9]
Fig. 1  (a) Molecular structure of Keggin phosphomolybdate α-PMo$_{12}$O$_{40}^{3-}$ (PMo$_{12}$) polyoxometalate consisting of 12 Mo atoms, 4 inert O atoms associated with the phosphate center, 24 bridging O atoms and 12 terminal O atoms. [10] (b) Schematic depicting the PMo$_{12}$ complex formation with poly(pyrrole).

Polyoxometalates (POMs) are a diverse class of inorganic molecules made up of metal oxygen clusters of early transition metals. [11, 12] To date, thousands of different POMs have been synthesized, isolated, and characterized. However, the most widely studied and commercially available POM is the Keggin structure which follows the formula: [XM$_{12}$O$_{40}$]$^{n-}$ where X is the heteroatom (P or Si) and M is the addenda atom (Mo, W, V, or Nb). [11] Known mostly for their ability to readily accept electrons and form highly stable reduced states, POMs have traditionally been used as co-catalysts and strong oxidizing agents for organic materials. [11, 13, 14] In recent years, POMs have also found applications as energy storage materials ranging from ternary supercapacitors to cathodes in molecular cluster batteries for Li. [15-18] To date, no work has been done to apply this molecular cathode material to Mg systems. The promising aspect of using POMs for energy storage materials lies in their unique redox chemistry. More specifically, in the Keggin phosphomolybdate anion (PMO$_{12}$O$_{40}^{3-}$) shown in Fig. 1a, each of the 12 Mo atoms can theoretically undergo a 2-electron reduction from Mo(VI) to Mo(IV) for a total of 24 electrons transferred per POM molecule, giving this particular POM (PMo$_{12}$), a high theoretical capacity of 352 mAh g$^{-1}$. [19]

While PMo$_{12}$ appears to be an ideal host material for electrochemical energy storage due to its high theoretical capacity as well as its ability to redistribute the incoming charge density via electron delocalization among all 12 Mo atoms; the two primary drawbacks that must first be remedied are its (1) high solubility in both aqueous and organic solutions and its (2) low electronic conductivity between individual POM molecules. This prevents POMs from being used as standalone cathode materials for
energy storage applications. Traditionally, any applications of POMs for electrochemical energy storage first require the addition of conductive substrates such as reduced graphene oxide sheets, carbon nanotubes, and other conductive supports. [20] In order to use these molecules as cathode materials in this work, we used a one-pot co-electrodeposition synthesis method to integrate the POM molecules into the matrix of a conductive organic polymer (COP) substrate, poly(pyrrrole) (PPy) in this study. [21, 22] Fig. 1b shows PPy-COP complex formation via the coulombic interactions between the two species.

By doing so, we simultaneously addressed both issues by using the conductive polymer to electrically wire each of the POM molecules together (enabling fast electron transfer between individual POM molecules), allowing them all to partake in the electrochemical reaction while also encapsulating them within the strongly insoluble polymer matrix, therefore reducing the solubility of the POM active material. [23] In theory, the conductive polymer can also function as an integrated current collector which will serve to reduce ohmic drops (polarization) during electron transfer. While POMs have been used previously for lithium-ion batteries; to date, there have been no attempts made to apply this molecules’ interesting redox chemistry towards magnesium-ion systems. In this work, we report a proof-of-concept study in which POM molecules are used as the active material in a heterogeneous cathode for Mg$^{2+}$ ion storage. Herein, we demonstrate the application of POM-COP nanostructures as a potential cathode material for rechargeable magnesium-ion batteries (RMBs). The focus of this work was not on the overall performance of the cathode, but instead to exemplify the technique of using nanocomposite materials to achieve a synergistic effect as a blueprint for the rational design of multivalent ion batteries.

Using chronoamperometry to apply a constant voltage of 0.8 V vs. Ag/AgCl, the pyrrole monomer was electrochemically polymerized and deposited within the pores of the alumina template along with the PMO$_{12}$ molecules. After removal of the template, the free-standing nanowires left behind served as the cathode material, as depicted in Fig. 2.

![Schematic of the co-electrodeposition synthesis method of PMO$_{12}$-PPy nanowire cathode using an anodized alumina hard template. The AAO porous template (left) is used to deposit the cathode material (middle) followed by the removal of the template, leaving the free-standing nanowires (right) remaining.](image-url)
Separately, both PMO\textsubscript{12} and PPy are unable to serve as functional cathodes for Mg\textsuperscript{2+} ion storage. PPy by itself has no redox activity in non-aqueous Mg electrolyte, as shown later in Fig. 5b; PMO\textsubscript{12} salts have little to no electronic conductivity and cannot form insoluble films in solution. However, the synergistic effect achieved by pairing the high capacity PMO\textsubscript{12} active material with the high electronically conductive organic polymer allows for the enhancement of the electrochemical performance of the hybrid cathode.

![Fig. 3](image)

**Fig. 3**  SEM images of top (a) and side (b) views of fabricated nanowires. (c,d) TEM image, (e,f) STEM image, of PMO\textsubscript{12}-PPy nanowires.

The “wiring” effect achieved by the integration of PMO\textsubscript{12} into the conductive polymer matrix allows for fast electron transfer reactions to take place between all of the PMO\textsubscript{12} molecules and the current collector. The presence of the PPy conductive polymer should not only suppress the dissolution process of the PMO\textsubscript{12} active material but also function as an integrated current collector which serves to improve electron transport pathways which should improve the power performance of this cathode.
The SEM characterization of the hybrid cathode shows the successful electrochemical synthesis of the polymer nanowires embedded with the PMo$_{12}$ active material (Fig. 3a,b). The TEM (Fig. 3c,d) and STEM (Fig. 3e,f) images show the heavy atom Mo clusters present in the nanowires in a dark and bright contrast, respectively. The clusters appear to be well dispersed throughout the nanowire. The XPS survey spectra (Fig. 4a,b) also confirms the presence of the Mo-based POM as well as the carbon and nitrogen signals from the poly(pyrrole) nanowires.

Fig. 4 XPS (a) survey spectra and (b) Mo 3d spectra of the PMo$_{12}$-PPy nanowire cathode.

Fig. 5 (a,b) Cyclic voltammetry, (c) galvanostatic charge-discharge plots for the 1st (blue), 50th (red), and 100th (black) cycle, and (d) coulombic efficiency curves. CVs were performed in 0.1 M Mg(ClO$_4$)$_2$/PC electrolyte and cycled at a scan rate of 5 mV/s.
From the cyclic voltammograms in Fig. 5a, we can see clear oxidation and reduction peaks of the PMo12-PPy cathode when cycled in magnesium electrolyte at 2.4 and 2.1 V vs. Mg/Mg$^{2+}$, respectively. The redox peaks are highly reversible and show no significant shifting after several cycles at a scan rate of 5 mV/s. The electrochemical properties of the cathode are indicative that the PMo$_{12}$-PPy is stable over the 1.6 V potential window and is capable of reacting with Mg$^{2+}$ ions and forming oxidized and reduced states reversibly. For the charge-discharge studies in Fig. 5c, galvanostatic cycling with potential limits (GCPL) was used to cycle the cathodes at a rate of 1C. Current densities for the galvanostatic charge-discharge cycling were calculated using the theoretical capacity of PMo$_{12}$ assuming a 24 electron-transfer reaction. Specific capacity values were calculated based on the mass of the PMo$_{12}$ active material present. This mass was determined using an electrochemical quartz crystal microbalance (EQCM) measurement shown in S1 of the supplemental information. From this cycling data we can see that a high capacity of 242 mAh g$^{-1}$ was achieved on the first discharge cycle (nearly 70% of theoretical value) with 145 mAh g$^{-1}$ remaining after 50 cycles. After 100 cycles, approximately 50% of the initial discharge capacity still remained (Fig. 5d). A consistent coulombic efficiency greater than 80% was also observed for the duration of the cycling.

Conclusions

In this work we have successfully demonstrated the application of polyoxometalate anionic clusters as molecular cathodes for magnesium-ion batteries. The SEM, TEM, and STEM studies indicate the successful fabrication of the polymer nanowires with the POM molecules embedded throughout the conductive matrix. The XPS analysis survey spectra confirmed the Mo signal in the phosphomolybdate anion. The synergistic effect between the conductive polymer and the POM molecules allowed for good electron transport and high ionic mobility while also suppressing the dissolution of the active material. The electrochemical testing showed a reversible redox couple indicative of the reversible oxidation and reduction of the POM active material. The hybrid cathode achieved a high specific capacity of 246 mAh g$^{-1}$ (with respect to the mass of PMo$_{12}$) which is nearly 70% of the theoretical value. Despite the capacity fade, the molecular cathode still retained 50% of the initial capacity after 100 cycles. The results of this study demonstrate the potential of polyoxometalate molecular cathodes as high capacity host materials for multivalent ion storage. The structural diversity and tunability of these molecules make them a promising new class of cathode materials for rechargeable magnesium-ion batteries.

It is important to reiterate that the aim of this work was not to focus on the performance of this cathode but instead to showcase the fundamental chemistry that allows for the storage of magnesium ions in order to advance the field of rechargeable magnesium-ion batteries and other multi-valent ion systems. The ability of host materials to receive and redistribute the charge density of the incoming ion without degradation of its structure is critical for the future of multi-valent ion batteries because of the increased amount of charge associated with ions. This work demonstrates the potential of these polyoxometalate inorganic molecules for Mg$^{2+}$ ion storage by pairing them with the conductive polymer poly(pyrrole) via a synergistic effect that allows fast electron transfer in the high electronically conductive
polymer combined with the high redox-activity of the POM active material. Although the electrochemical performance, specifically the cycle life, was not high compared to other Mg-cathodes, this material can still be used as a model system to study in order to answer more fundamental questions about the insertion reaction mechanism of monovalent versus multivalent ion systems.

Conflicts of interest
There are no conflicts of interest to declare.

Acknowledgements
We acknowledge the support of the Maryland Nanocenter, its Fablab, and its AIMLab. This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DESC0001160.

Notes and references
7. Thole, F.; Wan, L. W. F.; Prendergast, D., Re-examining the Chevrel phase Mo6S8 cathode for Mg intercalation from an electronic structure perspective. Physical Chemistry Chemical Physics 2015, 17 (35), 22548-22551.


