



# Molybdenum polyoxometalates as active species for energy storage in non-aqueous media



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## ABSTRACT

The Keggin-type polyoxometalate  $\text{Li}_3\text{PMo}_{12}\text{O}_{40}$  was evaluated for energy storage applications in non-aqueous media. In acetonitrile, using a static H-cell, high coulombic efficiency ( $\sim 90\%$ ) and stable ( $>500$  h) charge and discharge results were obtained. Different separators taking advantage of charge and size-based differentiation were compared for this system. Celgard<sup>®</sup> 2325, Nafion<sup>®</sup> 117 and aramid nanofiber-based membranes (ANF) were examined. Both Li-exchanged Nafion<sup>®</sup> 117 and ANF membranes enabled stable charge/discharge cycles with high coulombic efficiency for this non-aqueous polyoxometalate system. The ANF membrane, which separates based on size, permitted operation at higher current densities than the Nafion<sup>®</sup> 117 ion-exchange membrane.

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## 1. Introduction

The availability of cheap, reliable energy sources is essential in today's society, with ever-increasing demand as developing nations continue their economic progress. Renewable energy has seen growing interest from developed nations dependent on fossil fuel supply and concerns about the climate impacts of greenhouse gas emissions. Solar and wind power have become commercially viable and competitive with fossil fuels [1,2]. The supply of renewable energy is estimated to grow from 13% of total U.S. electricity generation in 2015 to approximately double that percentage in 2040 according to the U.S. Energy Information Administration Reference Case [3].

Large-scale integration of renewable energy sources presents new challenges, as most cannot produce energy on demand. One of the largest hurdles to large-scale implementation is therefore energy storage and delivery. Pumped hydroelectric is the most popular and widely used among the existing energy storage methods [4]. Among battery technologies, redox flow batteries (RFBs) have gained interest over the past several decades, as their design allows for flexible layouts and they can be scaled to meet different grid needs [5]. Energy is stored in electrolytes contained in tanks for catholyte and anolyte; the electrolytes circulate during both charge and discharge, greatly increasing the capacity compared to static systems. The separator or ion-exchange

membrane (IEM) divides the cell and separates the two electrolytes while permitting charge carriers to pass between them. RFBs are very flexible with respect to size and location, since the reactants, product and active species are stored in the electrolyte. It has been suggested that the capacity scale ratio of redox flow batteries to portable device batteries could be up to 10000 [6]. One of key advantages of RFBs is the ability to decouple energy and power density [7,8], which enhances the design flexibility of these devices.

The choice of active species is critical to RFB performance. Researchers have investigated a wide range of active species for use in RFBs; examples include all-vanadium and hydrogen-bromine RFBs [9]. In the present study, we explore the use of polyoxometalates (POMs) as the active species. These materials have versatile, tunable structures and compositions; they can undergo multi-electron redox reactions and are generally air/water stable. Polyoxometalates make up a large class of early transition metal oxide clusters, with heteropolyanions of the Keggin ( $\text{XM}_{12}\text{O}_{40}^{n-}$ ) and Dawson ( $\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$ ) structures among the most widely investigated [10]. The X component is usually P, Si, or B and the M is usually Mo, W or V. POMs have been studied as catalysts for several decades, and have been widely used in other fields such as energy, biomedical, and optical applications [11].

In energy applications, POMs have been mostly studied for use in fuel cells, supercapacitors, and as electrode components [12,13]. One of the appealing features is their stable multi-electron redox reactions. Sonoyama et al. investigated the potassium salt,  $\text{K}_3\text{PMo}_{12}\text{O}_{40}$ , as a lithium battery cathode component. Lithium ions were presumed to be intercalated into bulk  $\text{K}_3\text{PMo}_{12}\text{O}_{40}$  layers

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during discharge [14]. Wang et al. previously reported that  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  incorporated into electrodes can undergo 24 electron transfers during charge/discharge cycles [15]. Such results suggest a huge potential for the use of POMs in energy storage applications. While some research investigating POM RFBs has appeared in recent years [16–18], surprisingly little attention has been dedicated to this topic. Pratt and Anderson examined several different POMs in either aqueous or non-aqueous media, with  $\text{SiV}_3\text{W}_9\text{O}_{40}^{7-}$  in the aqueous phase showing 95% coulombic efficiency in charge/discharge cycling. The POMs in aqueous systems generally exhibited coulombic efficiencies of 50%–95% in charge/discharge tests. However, the use of POMs in non-aqueous systems for RFB applications has not been discussed in detail. The present work examines the performance of POMs in acetonitrile. It builds on previous studies [19,20] of the electrochemical properties of polyoxometalates in acetonitrile.

Non-aqueous RFBs offer both advantages and disadvantages relative to aqueous systems. Water has a relatively narrow window for electrochemical processes, 1.5 V for practical purposes, while acetonitrile has a potential window of 5 V, potentially increasing the energy density. Reactions that occur outside the voltage window within which water is stable can therefore be made accessible in organic solvents. However, there are also disadvantages for non-aqueous RFBs, among these are higher solvent cost, higher viscosities, lower conductivities, and lower current densities compared to aqueous systems. In order to improve the low conductivities in non-aqueous systems, support electrolyte was used to increase the conductivities. Therefore, the cost of support electrolyte is also an issue for RFBs. Further, the solubilities of active materials in non-aqueous media are typically lower than those in water. In the present work, lithium was chosen as the counter ion in order to prevent  $\text{H}_2$  generation during charge and discharge. Further, the lithium salt of phosphomolybdic acid has the highest solubility in acetonitrile (0.8 M) among the all the group IA and IIA salts of this compound.

Membrane performance may also differ between aqueous and non-aqueous media. High ionic conductivity, high ion selectivity, good chemical stability, good mechanical stability and long lifetime are all key properties for membranes [21]. Depending on the specific system one may choose ion-exchange membranes nano-porous membranes. Examples evaluated in this work included  $\text{Li}^+$ -exchanged Nafion<sup>®</sup>117 and a nanoporous aramid nanofiber based membrane (ANF) previously reported by Yang et al. [22]. The ANF membranes were constructed by layer-by-layer assembly from a stable dispersion of high-aspect-ratio aramid nanofibers (ANFs) with diameters between 3 and 30 nm [22]. Additional information about the properties of these materials is given below.

## 2. Experimental methods

All standard potentials and diffusivities were measured by cyclic voltammetry (CV) with an Autolab PGSTAT302N Potentiostat and Nova software. The three electrode cyclic voltammetry experiments were performed with a 3 mm glassy carbon working electrode (BASi),  $\text{Ag}/\text{Ag}^+$  (BASi) as the reference electrode and a platinum wire (BASi) as the counter electrode. The working electrodes were all polished, washed in an ultrasonic bath to ensure a clean surface, and dried in air before the experiment.  $\text{Li}_3\text{PMo}_{12}\text{O}_{40}$  was obtained from Nippon Inorganic Colour & Chemical Co., Ltd. The support LiTf (Lithium trifluoromethanesulfonate, 99.995%) was obtained from Sigma-Aldrich and solvent ACN (acetonitrile, 99.9%) from Fisher Scientific. Working solutions were bubbled with nitrogen for 10 min before the CV, and the experiments were run in the air at room temperature.

Electrochemical impedance spectroscopy (EIS) was performed in a two-electrode configuration with an Autolab PGSTAT302N Potentiostat in a static H-cell (Adams & Chittenden Scientific Glass.) Each side of the half H-cell was filled with 5 mL 0.1 M LiTf in ACN. The H-cell design has been previously presented in [23]. The two electrodes (graphite plates with an area of 1 cm<sup>2</sup>, GraphiteStore) were calcined at 550 °C in nitrogen to remove moisture prior to use.

Attenuated total reflectance (ATR) FTIR (FT/IR-4100 Jasco) spectra of electrolyte solutions were measured at wavelengths between 600 cm<sup>−1</sup> to 4000 cm<sup>−1</sup>. These were used to detect changes in polyoxometalate characteristics before and after electrochemical experiments.

Crossover tests were performed in the H-cell and the membranes were placed between the electrolyte solution on one side and pure acetonitrile on the other. Both were stirred with micro stir bars, and the initially pure acetonitrile side was sampled over time using a NanoPhotometer<sup>®</sup>P300.

Charge/Discharge (CD) experiments were performed in the static H-cell with a Maccor Series 4000 battery tester. The working electrodes were the same graphite electrodes used in EIS experiments. Each side of the H-cell was filled with 5 mL of the tested solution, and electrodes were soaked in the solution. The electrodes were calcined prior to CD experiments. CD experiments were monitored with  $\text{Ag}/\text{Ag}^+$  reference electrodes. Both sides of the H-cell contained a micro stir bar to minimize mass transport effects while the cell was being charged or discharged. The separators used were Nafion<sup>®</sup> 117 (Fuel Cell Store), Celgard<sup>®</sup>2325 (Celgard), and an aramid nanofiber based membrane (ANF) provided by the Kotov group at the University of Michigan [24].

Membranes were soaked in acetonitrile containing the supporting electrolyte (LiTf) for more than 24 h prior to each test. The Nafion 117 membrane was exchanged with lithium prior to use, following the procedure adopted from [25].

Redox Flow Battery experiments were performed with a Gen 1 Flow Cell set [26] which was made with 316 stainless steel connected with Tygon tubing (Saint-Gobain, 1.6 mm inner diameter). A 1.28 nm thick ANF membrane with 4.63 cm<sup>2</sup> active area was used as separator; two pieces of Goretex tape (0.01 inch thick, Gallagher Fluid Seals) were placed on the bare portions of the stainless steel housing between the cathode and anode for electrical isolation, and the pumps (Masterflex L/S Digital Drive) provided a 14 mL/min flow rate. Electrodes were cut from 6 mm thick carbon felt (GFA6, SGL Group) and the charge/discharge experiment was performed with a Maccor Series 4000 battery tester. The cell was assembled outside the glovebox, and then operated in the glovebox. The two sides were filled with 15 mL of a solution of 0.01 M  $\text{Li}_3\text{PMo}_{12}\text{O}_{40}$  with 0.1 M LiTf in acetonitrile which had previously undergone bulk electrolysis to produce an open circuit potential of −0.4 E/V  $\text{Ag}/\text{Ag}^+$ . Before the charge/discharge experiment, the pretreated POM solution was pumped through the system for 1 h in order to soak the electrode and membrane. During charge/discharge experiments, the current was fixed at 0.9 mA (~0.2 mA/cm<sup>2</sup>). The cutoff range was set as 0.05 V to 0.8 V and 50% state of charge in order to protect the bulk solution.

## 3. Results and discussion

### 3.1. Membrane selection

Membrane selection was the first step in the experimental design, as membrane properties can have a large influence on the charge/discharge results. A good membrane or separator will selectively allow charge carriers to pass freely while preventing transport of other ions that would result in mixing and loss of performance. Such a selection generally involves a tradeoff, as

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