***$M_x\text{Mn}_8\text{O}_{16}$ ($M = \text{Ag or K}$) as Promising Cathode
Materials for Secondary Mg Based Batteries:
the Role of the cation M***

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M_xMn₈O₁₆ (M = Ag or K) as Promising Cathode Materials for Secondary Mg Based Batteries: the Role of the cation M

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Ag_xMn₈O₁₆ (Ag-OMS-2) and K_xMn₈O₁₆ (K-OMS-2) were investigated as high voltage cathode materials for Mg based batteries. Both M_xMn₈O₁₆ materials delivered high initial capacities (> 180 mAh/g), and K_xMn₈O₁₆ showed high cycle stability with a reversible capacity of > 170 mAh/g after 20 cycles.

Mg based batteries may ultimately be viable alternatives for lithium-ion batteries, with important advantages of low cost and high earth abundance of magnesium, thus research associated with Mg batteries has been a recent focus.¹ However, there are still challenges associated with Mg battery technology which need to be addressed. A notable limitation associated with Mg based batteries is a scarcity of cathode materials which provide high power, capacity, and cycle life.^{1c} Specifically, the strong polarization of the small divalent Mg²⁺ ion may require shielding or some other approach to mitigate the typically slow Mg²⁺ ion diffusion.^{1d} Chevrel phase materials provide faster than typical Mg-ion diffusion,^{1a, 2} however, the discharge voltage of ~1.2 V (vs. Mg/Mg²⁺) coupled with modest capacity leads to low energy density. Other studies include V₂O₅³, Mg_xV₂O₅⁴, and MnO₂⁵ as Mg battery cathode materials. In particular, manganese dioxides with various polymorphs (α , β , γ and δ) have been investigated as cathode materials because of their environmental friendliness and high earth abundance of manganese, but issues associated with capacity fade have been reported. As an example, one study reported the initial capacity of α -MnO₂ as 310 mAh/g, but the capacity of α -MnO₂ decreased to ~0 mAh/g after 20 cycles.^{5a} In general, high initial discharge capacities for α -MnO₂ were demonstrated in several reports,^{5b, 5e} but significant overpotential was observed (capacities reported to <1.8 V vs. Mg/Mg²⁺) attributed to sluggish

Mg²⁺ ion diffusion.^{5a, 5b, 5e}

The addition of water to the magnesium based electrolyte has been shown to act as a shielding molecule to improve Mg²⁺ ion diffusion and reduce polarization,^{3b, 6} where the H₂O can facilitate the insertion / de-insertion of Mg²⁺ by forming a solvation shell around Mg²⁺, reducing the electrostatic interactions between Mg²⁺ and the counter ions.^{5c, 5d} One of the earliest demonstrations of this concept was insertion of Mg²⁺ ions into V₂O₅ in 1993,^{3b} where the delivered capacity of V₂O₅ in 1 M Mg(ClO₄)₂/acetonitrile dramatically increased from ~25 mAh/g to 170 mAh/g after the addition of 1 M water. In recent years, some researchers revisited the shielding effect of water in Mg based batteries utilizing layered MnO₂ as cathode material.^{5c, 5d} In water containing electrolytes, δ -MnO₂ (birnessite), a layered material, showed a strong correlation between capacity and water content, where higher water concentrations contributed to larger capacities with delivered capacities of 57, 81, 113, 170 and 228 mAh/g in the first cycle, for electrolytes containing 0, 0.5, 2, 5 and 10 M of water, respectively.^{5d} The AC impedance measurements demonstrated that water could also lower the interfacial resistance.^{5d}

Herein, we report the electrochemistry of silver and potassium containing α -MnO₂ materials, specifically Ag_xMn₈O₁₆ and K_xMn₈O₁₆, utilizing a non-reactive, environmentally friendly glyme based electrolyte, in the presence and absence of added water. These materials are synthetic analogues of cryptomelane type 2 × 2 tunneled manganese dioxides also known as octahedral molecular sieves 2 (OMS-2).⁷ This is the first investigation of the shielding effect in tunnelled manganese oxide materials, and there appear to be no prior reports demonstrating the Mg²⁺ ion insertion / de-insertion of an α -MnO₂ structured cathode material with capacity, cycle life and low polarization numbers comparable to our study. As-prepared materials were characterized by XRD and all the peaks of Ag_xMn₈O₁₆ and K_xMn₈O₁₆ can be assigned to tetragonal Ag_{1.8}Mn₈O₁₆ (PDF # 01-077-1987) and tetragonal K_{1.33}Mn₈O₁₆ (PDF # 01-077-1796), respectively, **Figure 1**. The insets in **Figure 1** show the structures of silver and potassium containing α -MnO₂ with tetragonal symmetry viewed along the c-axis. The crystal structures of Ag_xMn₈O₁₆ and K_xMn₈O₁₆ consist of 2 × 2 tunnels, which were formed by the interconnection of edge sharing MnO₆ octahedra,

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Figure 1. X-ray powder diffraction patterns of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ (a) and $\text{K}_x\text{Mn}_8\text{O}_{16}$ (b). Inset: crystal structure of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ (a) and $\text{K}_x\text{Mn}_8\text{O}_{16}$ (b), purple: MnO_6 octahedra, red: O, grey: Ag, blue: K.

with Ag^+ and K^+ ions, respectively, positioned in the centers of the tunnels.⁷ Based on the XRD reference patterns, the Ag^+ and K^+ ions are located in the centers of the tunnels, where the unit cell parameters a and b of $\text{K}_x\text{Mn}_8\text{O}_{16}$ (9.87 Å) are slightly larger than $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ (9.72 Å), suggesting larger tunnel dimensions. TGA data for both materials showed similar weight loss profiles with a minor weight loss below 400°C (attributed to physically adsorbed and structural water) and a major step-wise weight loss between 500–800°C (attributed to thermal decomposition of MnO_2). The loss between 500 – 600 °C was attributed to thermal decomposition of MnO_2 to Mn_2O_3 and the loss between 700 – 800 °C was attributed to thermal decomposition of Mn_2O_3 to Mn_3O_4 . Based on previous reports,⁸ the oxygen contents were calculated from the weight losses between 400 and 850°C. Therefore, we assign the formulas of $\text{Ag}_{1.22}\text{Mn}_8\text{O}_{15.6} \cdot 2.3\text{H}_2\text{O}$ to $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ and $\text{K}_{0.81}\text{Mn}_8\text{O}_{14.5} \cdot 2.7\text{H}_2\text{O}$ to $\text{K}_x\text{Mn}_8\text{O}_{16}$. Lower oxygen content of $\text{K}_x\text{Mn}_8\text{O}_{16}$ implies that the material has more oxygen deficiencies (oxygen vacancies), which may create additional a-b plane diffusion pathways for the guest ions.^{8b}

Figure 2. Cyclic voltammetry data of (a) $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ and (b) $\text{K}_x\text{Mn}_8\text{O}_{16}$ in anhydrous electrolyte (black) and water containing electrolyte (red).

The electrochemical activity of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ and $\text{K}_x\text{Mn}_8\text{O}_{16}$ was evaluated by slow scan voltammetry, **Figure 2**. The materials showed anodic and cathodic peaks in both water containing and anhydrous glyme based electrolytes indicating Mg^{2+} insertion / de-insertion processes, specifically 0.5 M magnesium bis(trifluoromethylsulfonylimide) ($\text{Mg}(\text{TFSI})_2$) in acetonitrile (CH_3CN) / dipropylene glycol dimethyl ether (0.5 M) with and without 3 M water, respectively. For $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ (**Figure 2a**), the cathodic peaks were higher in water containing electrolyte compared to non-aqueous electrolyte. The first reduction peak of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ in anhydrous electrolyte was broad and the following (2nd and 3rd) reduction peaks had higher current at more positive voltages. The oxidation peak potential shifted by -30 mV between each of cycles

1-2 and cycles 2-3. The structural water in $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ ($\text{Ag}_{1.22}\text{Mn}_8\text{O}_{16} \cdot 2.3\text{H}_2\text{O}$) may promote the extraction process of Mg^{2+} . For $\text{K}_x\text{Mn}_8\text{O}_{16}$, for the oxidative peak, a +20 mV shift in peak potential was observed between cycles 1 and 3 in the anhydrous electrolyte (**Figure 2b**). This electrochemical behavior may be related to the presence of additional oxygen defects in $\text{K}_x\text{Mn}_8\text{O}_{16}$ which could offer additional Mg^{2+} ion diffusion pathways.^{8b, 9}

The voltages of redox peaks and the peak separations (ΔE) are listed to show differences in polarization with different electrolytes, **Table 1**. Notably, ΔE values in anhydrous electrolytes were larger than those in water containing electrolytes for both materials, further demonstrating the improved Mg ion diffusion in the presence of water molecules. Furthermore, $\text{K}_x\text{Mn}_8\text{O}_{16}$ showed similar reduction peak voltages as $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ but lower oxidation peak voltages in the water containing electrolyte, indicating less overpotential for the Mg^{2+} de-insertion process in $\text{K}_x\text{Mn}_8\text{O}_{16}$. In the anhydrous electrolyte, $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ displayed a reduction peak at -0.66 V, more negative than that of $\text{K}_x\text{Mn}_8\text{O}_{16}$ (-0.39 V) for cycle 1, and $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ displayed similar reduction peak voltages to $\text{K}_x\text{Mn}_8\text{O}_{16}$ in the subsequent cycles.

Table 1. Cathodic and anodic peak positions of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ and $\text{K}_x\text{Mn}_8\text{O}_{16}$.

	Anhydrous electrolyte			Water containing electrolyte		
$\text{Ag}_x\text{Mn}_8\text{O}_{16}$	E_{pc}/V	E_{pa}/V	$\Delta E/V$	E_{pc}/V	E_{pa}/V	$\Delta E/V$
1 st cycle	-0.66	0.77	1.43	-0.26	0.50	0.76
2 nd cycle	-0.34	0.74	1.08	-0.20	0.53	0.73
3 rd cycle	-0.22	0.71	0.94	-0.19	0.61	0.80
	Anhydrous electrolyte			Water containing electrolyte		
$\text{K}_x\text{Mn}_8\text{O}_{16}$	E_{pc}/V	E_{pa}/V	$\Delta E/V$	E_{pc}/V	E_{pa}/V	$\Delta E/V$
1 st cycle	-0.39	0.59	0.98	-0.18	0.35	0.53
2 nd cycle	-0.24	0.58	0.82	-0.18	0.39	0.57
3 rd cycle	-0.18	0.61	0.79	-0.17	0.48	0.65

In order to examine the potential application of these materials in rechargeable Mg based batteries, galvanostatic discharge/charge tests were performed at a current density of 50 mA/g in water containing electrolyte, **Figure 3**. For $\text{Ag}_x\text{Mn}_8\text{O}_{16}$, a flat voltage plateau occurred at around -0.18 V versus Ag/Ag^+ (~2.8 V, vs. Mg/Mg^{2+}) in the first cycle and it slightly increased to -0.13 V (~2.9 V, vs. Mg/Mg^{2+}) in the second cycle (**Figure 3a**). The delivered capacities were 178 mAh/g in the first and 190 mAh/g in the second cycle, comparable to its performance in Li based batteries.^{8b, 10} For $\text{K}_x\text{Mn}_8\text{O}_{16}$, the voltage plateau appeared at a slightly higher voltage (~0.0 V, vs. Ag/Ag^+ , ~3.0 V, vs. Mg/Mg^{2+}) than $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ (**Figure 3a**), consistent with the cyclic voltammetry results, **Table 1**. The capacities in the 1st and 2nd cycles were 251 and 233 mAh/g, respectively. The initial capacity of $\text{K}_x\text{Mn}_8\text{O}_{16}$ was approximately ~40% higher than the capacity of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$.

The cells were tested for 20 cycles to evaluate the cycle stability, **Figure 3b**. For $\text{Ag}_x\text{Mn}_8\text{O}_{16}$, the capacity retention was 47% with a capacity of 83 mAh/g in the 20th cycle. The cycle performance of $\text{K}_x\text{Mn}_8\text{O}_{16}$ was significantly better where after 20 cycles, the capacity was 189 mAh/g, corresponding to 75% capacity

retention. Although these materials delivered different initial gravimetric capacities, 6.2 electron equivalents per formula unit were transferred for $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ while 7.0 electron equivalents for $\text{K}_x\text{Mn}_8\text{O}_{16}$, indicating similar amounts of magnesiation for both materials. However, the capacity for $\text{K}_x\text{Mn}_8\text{O}_{16}$ was maintained around 170 mAh/g after the 3rd cycle, which here is attributed to the presence of stabilizing K^+ . This may be associated with the larger ionic radius radii of K^+ (1.38 Å) compared to Ag^+ (1.15 Å) and the stabilizing effect of the K^+ ion in the tunnel.

Figure 3. (a) 1st and 2nd Discharge/charge curves of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ (dashed line) and $\text{K}_x\text{Mn}_8\text{O}_{16}$ (solid line) at a current density of 50 mA/g, (b) cycling performance at 50 mA/g, (c) discharge/charge curves of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ (dashed line) and $\text{K}_x\text{Mn}_8\text{O}_{16}$ (solid line) at current densities of 100 mA/g (cycle 10 – red, cycle 30 – purple), 200 mA/g (cycle 20 – black), and (d) cycling performance at 100 (cycles 1-10, 21-30) and 200 mA/g (cycles 11-20).

Figure 4. Transmission electron microscope (TEM) images of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ (a) before and (b) after cycling and $\text{K}_x\text{Mn}_8\text{O}_{16}$ (c) before and (d) after cycling. Insets: selected area electron diffraction (SAED) patterns.

Rate capabilities of these materials were analyzed using current densities of 100 mA/g and 200 mA/g, **Figures 3c and 3d**. The capacities decreased to 106 and 72 mAh/g at a current density of 100 mA/g for $\text{K}_x\text{Mn}_8\text{O}_{16}$ and $\text{Ag}_x\text{Mn}_8\text{O}_{16}$, respectively, and the capacities further decreased to 59 mAh/g and 25 mAh/g at 200 mA/g, suggesting sluggish diffusion of Mg^{2+} or $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$. In comparison of the capacities at 100 mA/g and 200 mA/g, the capacity of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ decreased by 65% at the higher rate while that of $\text{K}_x\text{Mn}_8\text{O}_{16}$ only decreased by 44%, implying that Mg^{2+} ion movement is more facile in $\text{K}_x\text{Mn}_8\text{O}_{16}$ than $\text{Ag}_x\text{Mn}_8\text{O}_{16}$.

XRD was recorded for the samples after cycling. Both materials became amorphous where only the most intense tunnel related diffraction peak (121) could be identified. The number of electron equivalents per mole of $\text{M}_x\text{Mn}_8\text{O}_{16}$ was calculated for the reduction peaks as ~ 5 for both $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ and $\text{K}_x\text{Mn}_8\text{O}_{16}$. A previous theoretical analysis of the reduction of $\alpha\text{-MnO}_2$ indicated that it could be reduced to 4 electron equivalents per Mn_8O_{16} unit via lithiation without decomposition of the structure.¹¹ Beyond 4 electron equivalents, magnesiation of $\alpha\text{-MnO}_2$ was shown to result in formation of an amorphous shell and crystalline core.¹² The observation was supported by a computational study, indicating that conversion of $\alpha\text{-MnO}_2$ to amorphous magnesium and manganese oxides should be the preferred reaction type during discharge in the Mg battery.¹³

Therefore, morphological and phase changes before and after cycling were investigated by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies, **Figure 4**. As-prepared $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ and $\text{K}_x\text{Mn}_8\text{O}_{16}$ showed rod-like morphologies with lengths of 100 – 200 nm and 20 – 50 nm, respectively. After cycling, the nanorod morphologies were maintained and there were minor changes in the lengths of the nanorods, indicating that the Mg^{2+} insertion / de-insertion process has little effect on particle morphologies and sizes. However, SAED patterns presented apparent changes in the intensity of diffraction rings for the materials after cycling. Before cycling, the (130), (121) and (141) planes of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ can be accurately indexed, and four intense diffraction rings of $\text{K}_x\text{Mn}_8\text{O}_{16}$ can be assigned to (130), (121), (031) and (141) planes. Most of the diffraction patterns of $\text{K}_x\text{Mn}_8\text{O}_{16}$ faded after cycling and only the (121) plane was observed. For $\text{Ag}_x\text{Mn}_8\text{O}_{16}$, the (121) plane was clearly identified after cycling while the diffraction intensity of other crystal planes decreased. This result is in accordance with the bulk XRD data where only the tunnel related diffraction peak (121) could be identified, **Figure S1**. These data indicate amorphization of both the Ag^+ and K^+ containing Mn_8O_{16} materials upon electrochemical cycling, consistent with the prior reports of amorphization upon magnesiation of $\text{K-}\alpha\text{-MnO}_2$.¹²

Figure 5. X-ray photoelectron spectra (XPS) of O 1s (a and b) and Mn 2p (c and d) before and after cycling.

X-ray photoelectron spectra (XPS) were utilized to analyze surface chemical composition and Mn oxidation state, **Figure 5**. Peaks were standardized for XPS using C 1s. The O 1s spectral region data was deconvoluted and assigned to three chemical states, lattice oxygen (O_{lattice}), surface oxygen species (O_{surface}), and surface adsorbed oxygen species (O_{adsorbed}).¹⁴ Lattice oxygen (O_{lattice}), as expected, is the primary oxygen species in the as-prepared $M_xMn_8O_{16}$ materials. However, upon battery cycling the amount of lattice oxygen in both $M_xMn_8O_{16}$ materials drastically decreased and the amount of surface oxygen species increased, consistent with the observed amorphization via XRD (**Figure S1**) and SAED (**Figure 4**). Moreover, the peak contribution from physisorbed water (O_{adsorbed}) increased after cycling. This implies that water in the electrolyte may participate in the magnesiation/demagnesiation processes. Another notable change was observed at Mn 2p ($2p_{1/2}$ and $2p_{3/2}$) regions, where both peaks became broader and shifted to lower binding energies after cycling for both materials (**Figure 5c** and **5d**). Such a change demonstrates that the insertion of Mg^{2+} ions results in reduction of Mn where the oxidation state of Mn cannot be fully recovered after charging, which may lead to the capacity fading. Specific O_{lattice} , O_{surface} and O_{adsorbed} binding energies and relative areas, and Mn 2p binding energies are listed in **Table S1**.

In conclusion, $Ag_xMn_8O_{16}$ and $K_xMn_8O_{16}$ were prepared via low temperature synthetic methods. Smaller polarization in water containing environmentally friendly glyme based electrolyte for both materials was evidenced by cyclic voltammetry, illustrating the “shielding effect” of water molecules. Constant current cycling tests showed high initial capacities for both of these materials (>

180 mAh/g). Notably, $K_xMn_8O_{16}$ exhibited a reversible capacity of > 170 mAh/g with a flat voltage plateau at ~0 V vs. Ag/Ag^+ for 20 cycles. This is the highest capacity and best cycle stability reported for $M_xMn_8O_{16}$ structured cathode materials in Mg based batteries. This study indicates that an α - MnO_2 structured material prepared under low temperature conditions with a suitable stabilizing ion (K^+) is a cathode material worthy of further study for use in rechargeable Mg based batteries.

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