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Crystallite Size Effects and the
Notable Role of Electrolyte Water Content**

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Magnesium-Ion Battery-Relevant Electrochemistry of MgMn_2O_4 : Crystallite Size Effects and the Notable Role of Electrolyte Water Content

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MgMn_2O_4 nanoparticles with crystallite sizes of 11 (MMO-1) and 31 nm (MMO-2) were synthesized and their magnesium-ion battery-relevant electrochemistry was investigated. MMO-1 delivered an initial capacity of 220 mAh/g (678 mWh/g). Electrolyte water content had a profound effect on cycle retention.

Magnesium-ion (Mg^{2+}) batteries (MIB) offer the opportunity for high volumetric capacity due to the dicationic nature of Mg^{2+} (3832 mAh/cm³ of Mg). However, the bivalency of Mg^{2+} with its small cation size results in very strong Mg^{2+} - anion electrostatic attractions within the cathode lattice, and slow Mg^{2+} diffusion and exchange.^{1, 2} Thus, an important challenge is identification of cathodes capable of faster Mg^{2+} (de)insertion,³ and electrolytes to facilitate Mg^{2+} (de)solvation.

Chevreton phase materials which employ sulfide anions, such as $\text{Mg}_x\text{Mo}_3\text{S}_4$, have been previously reported as cathodes for MIB,^{4,6} capable of providing 2000 cycles at 100% depth of discharge with a capacity fade <15%.⁴ While the weaker Mg^{2+} - sulfide electrostatic attractions facilitate Mg^{2+} (de)insertion, the working voltage for these materials of approximately 1.5 V (vs Mg^{2+}/Mg), may be considered low for some applications.

Metal oxides have also been studied as MIB cathode materials.⁷⁻⁹ Although the oxide anions will contribute to a higher working voltage relative to sulfide-containing materials, there will also be strong Mg^{2+} - oxide electrostatic attractions which may kinetically impede Mg^{2+} de-insertion with metal oxide materials. To address this issue, water added to the electrolyte remains in the Mg^{2+} coordination sphere both in solution and when Mg^{2+} insertion occurs. Water bonded to Mg^{2+} is claimed to “shield” the Mg^{2+} upon, thus reducing the

Mg^{2+} - oxide electrostatic attraction.¹⁰⁻¹² The preceding voltage and cycle life hypotheses concerning Mg^{2+} battery-relevant electrochemistry were consistent in principle to our previous study of vanadium oxide xerogels ($\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$).^{13, 14}

In addition to vanadium oxides, manganese oxides are another promising family of MIB cathode materials. Manganese oxides are a structurally rich class of materials; providing layered, tunneled, or spinel structured materials.¹⁵⁻¹⁷ In the presence of water, α - MnO_2 structured silver hollandite or potassium cryptomelane ($\text{M}_x\text{Mn}_8\text{O}_{16}$, M = Ag or K) can deliver ~180 mAh/g capacity where Mg^{2+} ion (de)insertion was demonstrated in $\text{K}_x\text{Mn}_8\text{O}_{16}$ and $\text{Ag}_x\text{Mn}_8\text{O}_{16}$.¹⁸ When cycled in anhydrous organo-aluminate electrolyte, K- α - MnO_2 showed high initial capacity of 300 mAh/g but significant fade to 150 mAh/g at the 2nd cycle, with additional capacity loss upon subsequent cycling.¹⁹ Scanning tunneling electron microscope (STEM) and X-ray absorption spectroscopy (XAS) detected formation of an amorphous layer (MgO and Mn_2O_3) on the α - MnO_2 surface after magnesiation, indicating a conversion reaction rather than an insertion process,²⁰ consistent with their theoretical predictions.²¹ In layered birnessite, water in the electrolyte also plays an important role: an irreversible structural conversion to spinel was observed upon Mg^{2+} insertion into $\text{MnO}_2 \cdot 0.94\text{H}_2\text{O}$ in dry electrolyte, yet the (de)insertion of Mg^{2+} in an electrolyte containing water was reversible with retention of the layered structure.^{11, 22, 23} Water was also shown to improve the electrochemistry of electrodeposited amorphous MnO_2 nanorods, proportional to the concentration of water in electrolyte.¹⁰

Spinel magnesium manganese oxide (MgMn_2O_4) has a tetragonal structure different from the typical cubic structure of spinels, due to distortion induced by the strong Jahn-Teller effect of Mn^{3+} .²⁴⁻²⁶ A cation migration is often observed in MgMn_2O_4 , in which Mg^{2+} and Mn^{3+} exchange positions due to their similar ionic radii (0.63 Å for tetrahedral Mg^{2+} and 0.72 Å for octahedral Mn^{3+} , respectively).²⁷ The exchange triggers a structural change from tetragonal to cubic, termed an “inversion reaction”²⁸⁻³¹ and is most common under high temperature and high pressure conditions.^{29, 31}

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LiMn_2O_4 is a successful cathode material in lithium ion batteries, where the nano-sized material exhibits excellent rate capability.^{32, 33} LiMn_2O_4 has also been applied in a hybrid battery with Mg metal anode, the initial discharge capacity is over 100 mAh/g in both 0.5 M $\text{Mg}(\text{TFSI})_2$ -LiTFSI/diglyme and 0.25 M $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ based electrolyte systems, ex-situ XRD and XAS demonstrate the LiMn_2O_4 is stable during cycling.³⁴ Thus, the analogue structure MgMn_2O_4 , has been of interest as a potential cathode material for MIB.^{35, 36} LiMn_2O_4 can be converted to MgMn_2O_4 in aqueous Mg^{2+} electrolyte, and the resultant MgMn_2O_4 delivered ~40 mAh/g capacity in aqueous electrolyte.³⁷ Chemically synthesized MgMn_2O_4 was also studied in aqueous Mg^{2+} electrolyte, the initial capacity was ~160 mAh/g.³⁶ Unlike the situation in aqueous electrolyte, investigations of MgMn_2O_4 in non-aqueous Mg^{2+} electrolyte have been limited. For a three electrode system utilizing a Pt reference, a V_2O_5 electrode, and an MgMn_2O_4 electrode in an electrolyte of 0.5 M $\text{Mg}(\text{ClO}_4)_2$ in EC : DEC (50 : 50), a discharge capacity of 120 mAh/g can be delivered.³⁶ Another example was studied in an electrolyte of 0.2 M $\text{Mg}(\text{CH}_3\text{COO})_2$ / 0.1 M AlCl_3 in PC, 102 mAh/g capacity can be observed.³⁸

Our previous studies have demonstrated strong correlations between crystallite size and electrochemical performance in manganese oxides. We present here the first systematic study of MgMn_2O_4 as a cathode material in MIB. The materials were synthesized by a modified Pechini method, and annealing temperature was used to control crystallite size of the products. The electrochemistry of 11 nm **MMO-1** and 31 nm **MMO-2** was studied in magnesium based electrolyte with and without added water in the electrolyte. Higher capacity was delivered by the smaller crystallite sized material and capacity retention increased in the presence of water. While hydrous electrolytes may be impractical for batteries with Mg metal anodes, it is anticipated that such electrolytes may be viable in Mg-ion batteries with alternative anodes, such as Mg_3Bi_2 .³⁹

The as-synthesized MgMn_2O_4 samples were characterized by synchrotron X-ray powder diffraction (XPD). **Fig. 1** shows the Rietveld refinement of XPD diffraction patterns. Both **MMO-1** and **MMO-2** can be fitted to tetragonal spinel MgMn_2O_4 structure with space group of $I41/amd$. Both samples show reasonable R_{wp} values: **MMO-1** (9.30 %) and **MMO-2** (7.42 %). The fitted crystal structure parameters and atom arrangements are shown in **Table S1** and **Table S2**. In the tetragonal structure, Mg^{2+} is in the tetragonal site and Mn^{3+} occupies the octahedral site. A minor structural inversion has been reported from the rearrangement of tetragonal Mn^{3+} and octahedral Mg^{2+} .²⁸ In our case, very low inversion was observed (0.07 % for **MMO-1** and 0.70% for **MMO-2**). **MMO-1** (annealed at 400°C) displayed significant diffraction peak broadening, while **MMO-2** (annealed at 550°C) showed sharper and more intense peaks. The crystallite size values calculated from Rietveld refinement were 13 nm for **MMO-1** and 42 nm for **MMO-2**. Using the Scherrer equation and the (101) peak at 18.15° to calculate crystallite size of the samples gave values of 11 nm for **MMO-1** and 31 nm for **MMO-2**, which are used to describe the materials throughout this

manuscript. Transmission electron microscopy (TEM) images of **MMO-1** and **MMO-2**, **Fig. 2**, indicate the **MMO-1** nanoparticles were ~ 10 nm size, while the **MMO-2** particles

were in 20-50 nm range consistent with crystallite size values estimated from diffraction.

Fig. 1 Synchrotron X-ray powder diffraction (XPD) and Rietveld analysis of as-synthesized MgMn_2O_4 samples: (a) **MMO-1**, (b) **MMO-2**.

Fig. 2 TEM images of (a) **MMO-1** and (b) **MMO-2**.

The Mg / Mn ratio of each sample was evaluated using inductively coupled plasma-optical emission spectroscopy (ICP-OES) yielding a formula of MgMn_2O_4 for both **MMO-1** and **MMO-2**. Thermogravimetric analysis (TGA) of the precursor, **Fig. S1**, showed 70% weight loss upon heating to 580 °C. A rapid weight loss occurred at 220-350 °C with minor weight loss between 350-580 °C. The synthesized **MMO-1** lost 5.8% and **MMO-2** lost 1.8% weight upon heating to 800°C,

consistent with $\text{MgMn}_2\text{O}_4 \cdot 0.7\text{H}_2\text{O}$ and $\text{MgMn}_2\text{O}_4 \cdot 0.2\text{H}_2\text{O}$, respectively. The BET surface area for **MMO-1** was 73 m^2/g , and **MMO-2** was 24 m^2/g .

The electrochemistry of as-synthesized MgMn_2O_4 samples (3.9 mg/cm^2 mass loading on electrodes) was studied in two Mg^{2+} electrolytes: 0.5 M $\text{Mg}(\text{TFSI})_2$ in acetonitrile/0.5 M dipropylene glycol dimethyl ether (anhydrous) and 0.5 M $\text{Mg}(\text{TFSI})_2$ + 3 M H_2O in acetonitrile/0.5 M dipropylene glycol dimethyl ether (hydrous). The cyclic voltammetry (CV) curves of **MMO-1** and **MMO-2** in both electrolytes are shown in **Fig. 3**. In the anhydrous electrolyte, **MMO-1** has redox potentials of 0 V (E_{pc}) / 0.7 V (E_{pa}), corresponding to the redox of $\text{Mn}^{3+} / \text{Mn}^{4+}$. **MMO-2** has similar E_{pc} and a slightly higher E_{pa} of 0.8 V, **Fig. 3a**. The peak current of 11 nm **MMO-1** is ~ 4 times higher than that of the 31 nm **MMO-2**, which indicates that the crystallite size has a significant influence on the Mg^{2+} (de)insertion into the MgMn_2O_4 structure. It is notable that no significant decrease in peak current was observed on either sample over 4 CV cycles, suggesting reasonable reversibility of the material. In the electrolyte containing 3 M H_2O , the E_{pc} of **MMO-1** shifts to -0.1 V and no E_{pa} can be observed. **MMO-2** displays 0.07 V (E_{pc}) / 0.6 V (E_{pa}). The crystallite size affects electrochemistry in the hydrous electrolyte where **MMO-1** has ~3 times higher peak current than **MMO-2**, and the Mg^{2+}

(de)insertion is reversible without significant change in current over 4 cycles.

Galvanostatic charge-discharge testing was used and the initial charge-discharge voltage curves in both anhydrous and hydrous electrolytes at 0.1 C are shown in **Fig. 4a**, displaying a sloping voltage profile with an average working potential of 0.02 V vs Ag^+/Ag (3.07 V vs Mg^{2+}/Mg). **MMO-1** delivered 220 mAh/g capacity (0.81 Mg^{2+} insertion) at 1st discharge in both electrolytes, however, **MMO-2** delivered only 70 mAh/g (0.26 Mg^{2+} insertion). **Fig. 4b** displays the cycling results of **MMO-1** and **MMO-2**. Although the discharge capacity at the initial cycles was similar in both electrolytes, the MgMn_2O_4 samples showed more significant capacity decrease with cycling in dry electrolyte. **MMO-1** decreased in delivered capacity from the 1st cycle to the 40th cycle, where the final capacity retention was 28% (63 mAh/g of 220 mAh/g), **MMO-2** lost 42% capacity in the same electrolyte (41 mAh/g of 71 mAh/g). The reversibility of MgMn_2O_4 was significantly improved by the addition of water, **MMO-1** delivered 162 mAh/g at the 40th cycle, corresponding to 74% capacity retention, while no significant capacity decrease was observed for **MMO-2**.

Notably, the energy density of **MMO-1** could reach 678 mWh/g, significantly higher than the energy density of Chevrel phase materials (~ 130 mWh/g)⁴ or magnesium vanadium oxide xerogels (420 mWh/g).¹⁴ The high energy delivery of **MMO-1** results from the high working voltage and high capacity, making the MgMn_2O_4 a promising MIB cathode material. Rate capability was studied in hydrous and anhydrous electrolytes (**Fig. 4c**): at 0.5, 1.0, and 2.0C, **MMO-1** delivered 93, 70, and 50% of its 0.1 C capacity, respectively, and its capacity fully recovered over the last five 0.1C cycles in hydrous electrolyte, while in anhydrous electrolyte only 40, 28, and 16% of its 0.1 C capacity was delivered at 0.5 C, 1.0 C, and 2.0 C, respectively and only 63% capacity was recovered at last five 0.1 C cycles in anhydrous electrolyte. At the higher rates of 0.5, 1.0, and 2.0C **MMO-2** delivered 63, 51, and 27% of its capacity at 0.1 C, where 70% capacity was retained over the last five 0.1 C cycles in hydrous electrolyte, and the capacity retention in anhydrous electrolyte was slightly lower at each rate affirming the crucial role of water in reversibility and rate capability.

Fig. 3 Cyclic voltammetry test of **MMO-1** (11 nm) and **MMO-2** (31 nm) in a) 0.5 M $\text{Mg}(\text{TFSI})_2$ in acetonitrile/0.5 M dipropylene glycol dimethyl ether, b) 0.5 M $\text{Mg}(\text{TFSI})_2$ + 3 M H_2O in acetonitrile/0.5 M dipropylene glycol dimethyl ether electrolyte. Scan rate: 0.1 mV/s.

The higher discharge capacity and better rate capability of **MMO-1** can be attributed to its smaller crystallite size and higher surface area where the ion diffusion path for Mg^{2+} is shorter. The polarization was lower compared to the 31 nm **MMO-2**,²³ making Mg^{2+} diffusion more facile in **MMO-1**. Water

additive in the electrolyte improved the reversibility of Mg^{2+} (de)insertion into the structure. It has been demonstrated that water facilitates the dissociation of Mg^{2+} from TFSI^- , resulting in higher free Mg^{2+} in electrolyte, and water can also reduce the Mg^{2+} de-solvation energy, which facilitates the subtraction of Mg^{2+} from MgMn_2O_4 structure in charge process.^{40, 41} Mn dissolution is thought to be a crucial drawback in spinel LiMn_2O_4 ,^{42, 43} and MgMn_2O_4 is considered to have the same problem, since all the Mn sites are in +3 oxidation state. 3.2 % Mn dissolution was reported from LiMn_2O_4 in LiPF_6 electrolyte.⁴² In this case, no measurable dissolution of Mn^{n+} could be detected in either **MMO-1** and **MMO-2** after soaking in both hydrous and anhydrous Mg^{2+} electrolyte for 10 days, possibly due to the absence of free LiF in our electrolyte.

Fig. 4 (a) 1st cycle voltage curve (b) cycle no. vs. discharge capacity and (c) rate capability of **MMO-1** and **MMO-2** in 0.5 M $\text{Mg}(\text{TFSI})_2$ in acetonitrile/0.5 M dipropylene glycol dimethyl ether with or without water. (d) X-ray diffraction of **MMO-1** electrodes: (i) as-prepared; after (ii) 1st charge and (iii) 1st discharge in hydrous electrolyte; after (iv) 1st charge and (v) 1st discharge in anhydrous electrolyte. *graphite, #Al foil Since Mg^{2+} has high charge density, its insertion can result in significant structural changes or decomposition of the cathode lattice. For example amorphous MgO and Mn_2O_3 were observed in the Mg^{2+} inserted α - MnO_2 structure.²⁰ In order to study the structural stability of MgMn_2O_4 , the electrodes of **MMO-1** were recollected after 1st charge, 1st discharge in hydrous and anhydrous electrolyte, and then tested on XRD, **Fig. 4c**. **MMO-1** kept the spinel structure after the 1st charge in hydrous electrolyte & discharge in both electrolytes, where no obvious peak shift or peak intensity decrease was observed. However, after the 1st charge in anhydrous electrolyte two new peaks at 24° and 48° appeared, indicating less structural stability. Our previous study showed that hollandite structure is more stable upon Mg^{2+} (de)insertion in hydrous electrolyte,¹⁸ similar to the results here. The electrodes after 40 cycles were collected and XRD results are in **Fig. S2**, where the electrode from hydrous electrolyte still shows all characteristic diffraction peaks with slightly lower intensity compared to the as-prepared electrode, while that from anhydrous electrolyte has lower intensity, yet maintains the parent phase indicating a stable structure.

Spinel MgMn_2O_4 was successfully synthesized and the crystallite size was controlled by adjusting annealing temperature. The 11 nm **MMO-1** delivered 220 mAh/g capacity in both hydrous and anhydrous electrolyte, ~3 times higher than the 31 nm **MMO-2**. Water addition to the electrolyte was found to play an important role in the reversibility of cathode: the capacity retention of **MMO-1** can be improved from 28 % to 74 % in the presence of water. It is worth noting that the spinel structure was stable in Mg^{2+} electrolyte after cycling, most notably in the water containing electrolyte. This manuscript reports a systematic study of spinel MgMn_2O_4 in organic Mg^{2+} electrolyte, where both crystallite size and water content are shown to be important factors influencing the electrochemistry.

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