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Synthetic Control of Manganese Birnessite: Impact of Crystallite Size on Li, Na, and Mg based Electrochemistry

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Abstract

The synthesis and characterization of Mg-birnessite (Mg_xMnO_2) with different crystallite sizes, prepared through low temperature precipitation and ion exchange was demonstrated. The influence of crystallite size on electrochemical performance of Mg-birnessite was studied for the first time, where material with smaller crystallite size was demonstrated to have enhanced capacity and rate capability in Li ion, Na ion, and Mg ion based electrolytes. Cation diffusion using GITT type testing demonstrated the ion diffusion coefficient of Mg^{2+} was ~10X lower compared with Li^+ and Na^+ . This work illustrates that tuning of inorganic materials properties can lead to significant enhancement of electrochemical performance in lithium, sodium as well as magnesium based batteries for materials such as Mg-birnessite and provides a deliberate approach to improve electrochemical performance.

Keywords magnesium birnessite; manganese oxide; sol gel; lithium ion battery; sodium ion battery; magnesium ion battery

1. Introduction

Rechargeable Li-ion batteries (LIB) are one of the most commercially successful energy storage devices whose use has seen significant expansion over the past two decades. The research and subsequent commercialization of generations of Li-ion batteries have promoted the development of new electronic devices, medical devices and electric vehicles. Despite the success of Li-ion batteries, several factors may impede even broader implementation, including safety concerns, high cost, and the natural scarcity of Li. Recently, significant effort has been devoted to the research & development of alternatives to lithium battery systems, including sodium and magnesium based systems.

Sodium based batteries are considered a promising alternative to LIB.(1, 2) Sodium is among the most abundant elements on earth with a more uniform distribution than lithium. Beyond the low cost and natural abundance, Na^+ typically has lower de-solvation energy than Li^+ , which is benefit for the ion diffusion kinetics. In addition to sodium ion batteries, magnesium ion batteries are also promising battery systems. Magnesium based batteries are another promising alternative to LIB due as magnesium is abundant in the earth's crust, and the non-dendritic deposition at the magnesium surface makes Mg a safer anode alternative to Li.(3-5) However, the development of magnesium based batteries has been hampered by several challenges, including the slow kinetics associated with Mg^{2+} (de)insertion into a host lattice. The slow kinetics have been attributed to the high polarization and charge density of Mg^{2+} .(6, 7) Introducing small amounts of strong dipole molecules can facilitate Mg^{2+} diffusion and insertion

kinetics, which has been termed the “shielding effect”.(8) It has been postulated that water is more effective at solvating small, highly charged ions than organic molecules of the electrolyte, as the water molecules hinder the ion pairing of Mg^{2+} with counter anions, thus reducing the electrostatic interaction between Mg^{2+} and the host lattice.(9) Another possible advantage of water in the electrolyte is that the de-solvation energy of Mg^{2+} is lower in aqueous environment, in other words, the charge transfer process is facilitated by water molecules.(9) The shielding effect was first demonstrated in V_2O_5 .(8, 10) and was recently reported for amorphous MnO_2 nanowires.(11) Additionally, a recent report described the structural rearrangement of pristine birnessite (no interlayer cations) upon hydrated Mg^{2+} insertion.(12) A reversible phase transition during discharge/charge process was observed while the (002) interlayer water maintained its arrangement, further stabilizing the host lattice. The water molecules in electrolyte facilitated Mg^{2+} kinetics through shielding and by reducing the interfacial resistance.(12)

Manganese oxide materials are desirable cathode materials due to their low cost and environmentally benign character. Specifically, 2-D layered birnessite ($\text{R}_y\text{MnO}_2 \cdot x\text{H}_2\text{O}$, R = monovalent or divalent metal ions) materials are conceptually appealing because of their excellent ion-exchange properties,(13, 14) and can be prepared via aqueous(15, 16) and nonaqueous(15) sol gel synthesis routes. Edge-sharing MnO_6 octahedra constitute the MnO_2 layers where the interlayer spacing of 7 Å is occupied by metal ions and water molecules.(17) Previous electrochemical studies demonstrated the insertion/de-insertion capability of birnessite in Li^+ ,(18-21) Na^+ ,(22, 23) Mg^{2+} electrolytes.(12, 24) Our previous studies revealed strong correlations between crystallite size and electrochemical performance with notable improvements in delivered capacity by smaller crystallite size materials for both silver hollandite ($\text{Ag}_x\text{Mn}_8\text{O}_{16}$)(25) and magnetite (Fe_3O_4). (26) Conductivity can be also enhanced on smaller

crystallite size materials by reduced bandgap, originating from higher numbers of surface defects.(26) Under intermittent pulsatile discharge, magnetite achieved a ~30% capacity enhancement with a 35% decrease in crystallite size. Additionally, smaller crystallites were demonstrated to have more evenly distributed and uniform discharge by Transmission X-ray Microscopy combined with X-ray absorption near edge spectroscopy (TXM-XANES). (27) The smaller silver hollandite crystallites also showed better performance at different discharge rates where the discharge capacity was 40% higher than larger crystallites from 1C to 8C rates.(25) However, the crystallite size effect in rechargeable sodium and magnesium batteries has not yet been reported. To our knowledge, this is the first investigation of the crystallite size effect for reversible sodium and magnesium electrochemistry.

Herein, we designed a study of a Mg cation containing birnessite based with different crystallite sizes synthesized through a room temperature precipitation and ion exchange reaction, and characterized to determine structure and magnesium content. Electrochemical behavior was determined using cyclic voltammetry and galvanostatic testing in lithium ion, sodium ion and magnesium ion based electrolytes, where the influence of crystallite size on electrochemical activity of Mg-birnessite was evaluated. Additionally, the role of electrolyte solvent and of added water in the electrolyte in conjunction with crystallite size was studied for the magnesium based system. The cation diffusion coefficient in different electrolyte system was evaluated via Galvanostatic intermittent titration technique (GITT). The data affirm the impact of material crystallite size on the resultant electrochemistry.

2. Experimental section

2.1. Synthesis

Mg-birnessite was synthesized using modifications to a previously reported method.⁽¹⁴⁾ Briefly, sodium hydroxide aqueous solution, manganese (II) nitrate, and sodium persulfate powder were used as the starting materials for the reaction. The as-synthesized Na-birnessite (Na_xMnO_2) (~0.7 g) was used to prepare Mg-birnessite (Mg_yMnO_2) through ion-exchange with 1 M aqueous magnesium nitrate for 24 h. The sample with smaller crystallite size was denoted as **MgB-1**, and the larger crystallite size sample as **MgB-2**. The concentrations of the reactants were adjusted to yield products of different crystallite size: 0.056 M Mn^{2+} , 1 M NaOH, 0.138 M $\text{Na}_2\text{S}_2\text{O}_8$ for **MgB-1**; 0.222 M Mn^{2+} , 4 M NaOH, 0.55 M $\text{Na}_2\text{S}_2\text{O}_8$ for **MgB-2**.

2.2. Characterization

X-ray powder diffraction (XRD) data was collected using a Rigaku Smart Lab diffractometer with Cu-K α radiation. The crystallite size was calculated by applying the Scherrer equation⁽²⁸⁾ to the FWHM of the (001) peak. An instrumental broadening correction was applied using a LaB₆ standard. Simultaneous thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) data was measured using a TA instrument SDT Q600. Material composition was determined through inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Thermofisher iCAP 6300 series instrument. SEM images were collected with a JEOL JSM-6010PLUS in secondary electron imaging mode. N₂ adsorption-desorption measurements were performed using a Quantachrome Nova 4200e instrument and a multipoint BET (Brunauer, Emmett, and Teller) method was used for calculating the surface area.

2.3. Electrochemical testing

Electrodes were prepared using Mg-birnessite, carbon and PVDF binder coated onto aluminum foil. Cyclic voltammetry (CV) of the Mg-birnessite samples was conducted inside an argon-filled glovebox using a three electrode system: the working electrode contained Mg-

birnessite, and the counter and reference electrodes were lithium metal. A scan rate of 0.5 mV/s over a voltage window of 2.0 to 4.1V was used. The electrolyte was 1.0 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (v/v 30/70). Galvanostatic cycling data used coin-type cells with lithium anodes tested between voltage limits of 2.0 V and 3.8 V at rates of 0.2 C, 1.0 C, and 2.0 C (1 C = 170 mA/g).

Galvanostatic cycling tests in Na⁺ electrolyte were conducted in 1.0 M NaPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (v/v 50/50) using coin type cells, sodium metal was used as anode. The voltage window was 1.6 V to 3.3 V, at rates of 0.1 C, 0.5 C, and 1.0 C.

For CV testing in Mg²⁺ electrolyte, the working electrode contained Mg-birnessite, a carbon counter electrode was used along with a silver/silver nitrate reference electrode. The electrolyte was 0.4 M magnesium (II) bis-(trifluoromethane sulfonyl) imide (Mg(TFSI)₂)/0.5 M dipropylene glycol dimethyl ether (dipro-glyme) in acetonitrile. A scan rate of 0.5 mV/s was used with a voltage window of 1.2 to -0.8V. The water content in the electrolyte was adjusted by adding water and measuring the content using a Karl Fischer Titrator. Galvanostatic cycling data in magnesium electrolyte was tested using voltage limits of -0.8 and 0.9 V. Rates of 0.2 C, 0.5 C, 1.0 C, and 2.0 C were used for charge and discharge.

Galvanostatic intermittent titration technique (GITT) measurement were conducted at 0.2 C in Li⁺ and Mg²⁺ electrolytes (same as galvanostatic cycling tests), at 0.1 C in Na⁺ electrolyte (same as galvanostatic cycling tests) by applying a galvanostatic step of 10 min for Li⁺ and Mg²⁺ test and 20 min for Na⁺ test, and a relaxation time of 4h for the Li⁺ test, 8h for the Mg²⁺ test, 2h for the Na⁺ test.

3. Results and discussion

3.1. Synthesis and characterization

The as-synthesized Mg-birnessite materials were characterized by X-ray powder diffraction (XRD). The XRD patterns shown in **Figure 1a** matched closely with the monoclinic phase (space group C 2/m) Mg-birnessite (ICSD 68917). Mg-birnessite has a layered structure comprised of edge-shared MnO_6 octahedra with Mg^{2+} ions and water molecules between the layers, as shown in **Figure 1b**. Specifically, Mg-birnessite is a type B birnessite with the following lattice parameters: $a = 5.050 \text{ \AA}$, $b = 2.846 \text{ \AA}$, $c = 7.054 \text{ \AA}$, $\beta = 96.63^\circ$,⁽²⁹⁾ while Na-birnessite is a type A birnessite with the following lattice parameters: $a = 5.174 \text{ \AA}$, $b = 2.850 \text{ \AA}$, $c = 7.336 \text{ \AA}$, $\beta = 103.18^\circ$,⁽³⁰⁾ consistent with the higher charge density of Mg^{2+} ($0.72 \text{ \AA}$) relative to Na^+ ($1.02 \text{ \AA}$).^(31, 32) As a type B birnessite, Mg^{2+} is located between the interlayer hydrates and the MnO_6 layer in Mg-birnessite, while the cations share the same layer with the water molecule in type A birnessites such as Na-birnessite.⁽¹³⁾ In Mg-birnessite, Mg^{2+} coordinates octahedrally with three oxygen atoms from the MnO_6 layer and three oxygen atoms from water molecules, where the Mg-O bond lengths range from $1.879 \text{ \AA}$ to $2.387 \text{ \AA}$, as shown in **Figure 1b**.⁽²⁹⁾ The MnO_6 octahedron has 4 Mn-O bond lengths of $1.926 \text{ \AA}$ and 2 Mn-O bond lengths of $1.952 \text{ \AA}$, reflecting that Mn^{3+} has a high spin d^4 electron configuration, where the Jahn-Teller effect can be observed in the MnO_6 units. Two strong diffraction peaks at 12.3° (001) and 24.8° (002), **Figure 1a**, indicating highly ordered layers along the c axis, while the remaining peaks were lower intensity and broad, suggesting that the as-synthesized samples were nanocrystalline. The (001) peak was used to determine the interlayer spacing of $7.2 \text{ \AA}$ and the crystallite sizes of 9 nm (**MgB-1**) and 23 nm (**MgB-2**).

The chemical composition of as-synthesized Mg-birnessite samples was determined through a combination of TGA/DSC and ICP-OES analysis. A typical TGA/DSC curve of **MgB-**

1 is shown in **Figure 2**. Due to its high charge density and hydration enthalpy (~2000 kJ/mol),(17) Mg^{2+} can strongly retain the interlayer hydrates, which results in a broader temperature range for Mg-birnessite water loss from room temperature to 250°C, while the water loss process in Na-birnessite ends at 150°C. Based on the TGA results, the water comprised 14.8% of the total sample mass, where the surface water amount was estimated as 2.8% based on the mass loss at the temperature corresponding to the strong first DSC peak below 100°C. The Mg and Na content of the as-synthesized Mg-birnessite samples was determined by ICP-OES. Thus, from the TGA and ICP-OES results, the chemical formula of $\text{Mg}_{0.15}\text{Na}_{0.02}\text{MnO}_2 \cdot 0.7\text{H}_2\text{O}$ was assigned to **MgB-1**, $\text{Mg}_{0.14}\text{Na}_{0.04}\text{MnO}_2 \cdot 0.7\text{H}_2\text{O}$ was assigned to **MgB-2**. Scanning electron microscopy images of Mg-birnessite samples showed a morphology consisting of agglomerates of sub-micron sized particles, with granular morphology, with no significant morphology differences between the two samples, shown in **Figure 3**. The BET surface area for **MgB-1** is 66 m^2/g , which is slightly larger than the value for **MgB-2**, 58 m^2/g .

3.2. Lithium based electrochemistry

The electrochemical properties of the as-synthesized Mg-birnessite samples were studied in Li^+ containing electrolyte. The cyclic voltammetry of the 9 nm **MgB-1** showed a major redox couple at ~2.60V/3.30V, which can be assigned to the $\text{Mn}^{4+}/\text{Mn}^{3+}$ couple, **Figure 4a**.(33) Similar to prior reports for K-birnessite, two shoulder peaks can be observed at around 3.00 and 3.80 V.(18, 34) **MgB-2** with a 23 nm crystallite size showed ~40% lower current on both cathodic and anodic peaks. The discharge/charge cycling performance of **MgB-1** and **MgB-2** was studied. **MgB-1** delivered 197 mAh/g initial capacity at 0.2 C (1.16 Li^+ insertion), 128 mAh/g at 1.0 C (0.75 Li^+ insertion), and 98 mAh/g at 2.0 C (0.58 Li^+ insertion), while the values

for **MgB-2** are 154 mAh/g at 0.2 C (0.91 Li⁺ insertion), 97 mAh/g at 1.0 C (0.57 Li⁺ insertion), and 63 mAh/g at 2.0 C (0.37 Li⁺ insertion). Both the CV results as well as the galvanostatic discharge results affirm the improved delivered capacity from **MgB-1**, the smaller crystallite sized material.

The AC impedance results are shown in **Figure 4d**, the typical shape of the curves is a semi-circle in high frequency range, which corresponds to the electrolyte resistance and charge transfer resistance, and a straight line with slope in low frequency range, which is the characteristic shape for ion diffusion in a solid. The initial impedance from as-prepared cells was similar between **MgB-1** and **MgB-2**. The impedance of both materials increased after the cycling test. The smaller crystallite size **MgB-1** with larger surface area and shorter ion diffusion pathways displays ~25% improvement in discharge capacity at each rate, and lower impedance compared to the larger sized material **MgB-2** in lithium ion based electrolyte.

3.3. Sodium based electrochemistry

The electrochemical properties of the as-synthesized Mg-birnessite samples were studied in Na⁺ containing electrolyte. The discharge/charge cycling performance of **MgB-1** and **MgB-2** is shown in **Figure 5** where **MgB-1** delivered 165 mAh/g initial discharge capacity at 0.1 C, corresponding to 0.97 Na⁺ insertion, the value of **MgB-2** was 142 mAh/g (0.84 Na⁺ insertion), **Figure 5b**. **MgB-1** showed ~20% higher capacity than **MgB-2** at 0.2 C, ~25% higher capacity at 0.5 C, and ~18% higher capacity at 1.0 C. Notably, the smaller crystallite size material samples provided improved electrochemistry in a sodium based system.

Figure 5c compares the impedance data of **MgB-1** and **MgB-2** before and after cycling. The higher initial impedance of as-prepared cells has been assigned to charge transfer resistance.(23) Interestingly, the impedance became smaller after cycling, likely to the removal

of a passivation layer. **MgB-1** showed lower impedance at both stages than **MgB-2**, which agrees with the better performance of **MgB-1** in the cycling test. The results indicate that Na^+ insertion can be facilitated by the smaller crystallite size of the **MgB-1** material, especially at high rates. The cycling performance and rate capability demonstrated that Mg-birnessite may be a promising cathode material for sodium ion batteries.

3.4. Magnesium based electrochemistry

The electrolyte used for the magnesium ion battery test was 0.4 M $\text{Mg}(\text{TFSI})_2$ in acetonitrile with addition of 2.4 M water and 0.5 M dipropylene glycol dimethyl ether (dipro-glyme). It has been demonstrated that water facilitate the solvation of Mg^{2+} and reduce the repulsion from cathode lattice. (11, 12) Glycol ether based compounds have been used as additives or solvents in organic electrolyte systems.(35, 36) Their flexible backbone and polydentate properties can facilitate the solvation of Mg^{2+} , yet long chain polyethers can also limit the mobility of Mg^{2+} . Thus, we identified a novel solvent, dipropylene glycol dimethyl ether (dipro-glyme) with three oxygen donor atoms as an additive for the electrolyte with the motivation of facilitating Mg ion solvation with no negative impact on performance. The electrochemical performance of **MgB-1** was studied by cyclic voltammetry in electrolytes using $\text{Mg}(\text{TFSI})_2$ in an acetonitrile electrolyte system with and without dipro-glyme, **Figure 6**. The CV conducted in anhydrous conditions demonstrated low peak currents, **Figure 6a**. These data indicate that the interlayer water alone is not sufficient for reversible electrochemistry. However, in the presence of added water at a molar ratio of $\text{Mg}^{2+}/\text{water} = 1/6$, the cathodic and anodic peaks were clearly visible, **Figure 6b**. Notably, even though the water content was the same in both electrolyte solutions, the sample containing the ether based solvent showed higher peak

currents than the sample in acetonitrile alone. The anodic peak in the electrolyte without dipro-glyme is significantly lower than in the electrolyte containing the dipro-glyme. It is clear that the addition of dipro-glyme assists the solvation of Mg^{2+} and facilitated de-insertion from the Mg-birnessite structure.(35) This finding motivated a more detailed study of the water content in acetonitrile based electrolyte and electrolyte containing ether functionality.

After optimization of the magnesium electrolyte system, the crystallite size effect was studied. **Figure 7** compares the CV curves between **MgB-1** and **MgB-2** in 0.4 M $\text{Mg}(\text{TFSI})_2$ / acetonitrile and 0.5 M dipro-glyme with water present, **MgB-1** had higher peak current than **MgB-2** on both cathodic and anodic peak, the reversibility was also enhanced by the smaller crystallite size of **MgB-1**. The current retention of the 2nd cathodic peak of **MgB-1** in $\text{Mg}^{2+}/\text{water} = 1/6$ electrolyte was 91%, yet the number for **MgB-2** was 71%. The CV results at a scan rate of 0.5 mV s^{-1} illustrated that the Mg^{2+} insertion/de-insertion kinetics are more limited by the larger crystallite. Galvanostatic cycling data was collected in 0.4 M $\text{Mg}(\text{TFSI})_2$ / acetonitrile and 0.5 M dipro-glyme with $\text{Mg}^{2+}/\text{water} = 1/6$ at rates of 0.2 C, 0.5 C, 1.0 C, and 2.0 C to evaluate the capacity and reversibility of Mg-birnessite samples, **Figure 8**. In the 1st discharge curve of **MgB-1**, a plateau can be observed at $\sim 0.2 - 0 \text{ V}$ versus Ag^+/Ag , corresponding to $\sim 3.1 - 2.9 \text{ V}$ versus Mg^{2+}/Mg . The **MgB-1** showed 1st discharge capacity of 136 mAh/g at 0.2 C, corresponding to 0.4 Mg^{2+} insertion, while the initial capacity of **MgB-2** was 80 mAh/g. The capacity in this sample increased over following cycles to 125 mAh/g. The crystallite size effect can be clearly observed at 0.5 C, **MgB-1** has $\sim 60 \text{ mAh/g}$ capacity, which is 25% higher than **MgB-2**. At rate higher than 0.5C, the influence of crystallite size was not observed, as both material showed very low specific capacity. After cycling at 0.2 C, 0.5, 1.0 C, and 2.0 C, the cells were again tested at 0.2 C, where the **MgB-1** delivered 92 mAh/g capacity,

~30% percent higher than **MgB-2**. These results provide the first evidence of a crystallite size effect in Mg^{2+} containing electrolyte, where the shorter diffusion pathway and higher surface area in smaller crystallite size material can improve the sluggish kinetics of Mg^{2+} diffusion, resulting in enhanced capacity and reversibility. Thus, targeting small crystallite size materials could be a general strategy in the design of cathode materials for MIB.

3.5. Cation diffusion study

To evaluate cation diffusion coefficients in different battery systems, galvanostatic intermittent titration technique (GITT) type tests were performed in Li^+ , Na^+ , and Mg^{2+} based electrolytes. The cells were discharged in galvanostatic mode at a constant current for a fixed time interval followed by an open-circuit rest for a period of time to allow the cell voltage to relax to its steady-state value (E_s). **Figure 9a-c** show the GITT results in Li^+ , Na^+ , Mg^{2+} electrolyte, respectively. When the relationship between cell potential and $s^{1/2}$ is a straight line, the diffusion coefficient can be calculated via the equation:(37)

$$D_{\text{Li}^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2$$

Where V_M is the molar volume of the compound, M_B is the relative formula mass, and S is the area between the electrolyte and the active material, ΔE_s and ΔE_τ are shown in **c** figure in each electrolyte. **Figure 9d** shows the calculated diffusion coefficient values (D_+) of **MgB-1** in the different electrolyte systems (**MgB-2** has similar values). The D_{Li^+} and D_{Na^+} values were in the $\sim 10^{-11}$ - 10^{-13} cm^2/s range, and decreased with the depth of discharge (DOD). $D_{\text{Mg}^{2+}}$ showed values of $\sim 10^{-12}$ - 10^{-14} cm^2/s range with a similar trend with decreasing values with discharge. The Mg^{2+} diffusion in Mg-birnessite material was ~10 times lower than Li^+ and Na^+ diffusion,

the average values of the diffusion coefficients in different electrolyte are: $1.4 \times 10^{-11} \text{ cm}^2/\text{s}$ of D_{Li^+} , $1.1 \times 10^{-11} \text{ cm}^2/\text{s}$ of D_{Na^+} , $1.2 \times 10^{-12} \text{ cm}^2/\text{s}$ of $\text{D}_{\text{Mg}^{2+}}$.

The ionic radius of Li^+ is $0.76 \text{ \AA}$, while Na^+ is $1.02 \text{ \AA}$, and Mg^{2+} is $0.72 \text{ \AA}$. Considering the divalency of Mg^{2+} , the ion surface charge density is in the order of $\text{Mg}^{2+} \gg \text{Li}^+ > \text{Na}^+$.⁽²⁾ More solvent molecules are needed to stabilize the strong charge density of Mg^{2+} during solvation process, resulting in a high de-solvation energy, which is directly related with ion diffusion kinetics in the solid.⁽²⁾ Previous theoretical analysis of cation de-solvation energy in different solvent has demonstrated the de-solvation order of the three cations: Mg^{2+} has 490 kJ/mol de-solvation energy in acetonitrile, Li^+ has 211.3 kJ/mol and 207.7 kJ/mol de-solvation energy in EC and DEC, Na^+ has 151.9 kJ/mol and 147.5 kJ/mol de-solvation energy in EC and DEC.⁽³⁸⁾ Thus, the high de-solvation energy of Mg^{2+} limited the ion diffusion kinetics even when shielded by water molecules. The high charge density of Mg^{2+} also generates higher repulsion in the lattice structure of cathode material than Li^+ and Na^+ . The cation diffusion study shown here illustrated that the Mg^{2+} diffusion is still sluggish even when shielded by additive molecules, especially when it is compared with Li^+ and Na^+ diffusion.

4. Summary

Mg-birnessite with different crystallite sizes was successfully synthesized using a room temperature, aqueous-based strategy. The materials have a layered structure, with an interlayer spacing of $7.2 \text{ \AA}$ as indicated by the $[001]$ peak in the XRD pattern. The Mg-birnessite structure was selected to benefit from the “pillar effect” of Mg^{2+} in the structure and provide structural stability during electrochemical reduction and oxidation. The influence of crystallite size on electrochemical performance of Mg-birnessite was studied for the first time, where material with

smaller crystallite size was demonstrated to have enhanced capacity and rate capability in Li ion, Na ion, and Mg ion based electrolytes. The cation diffusion study conducted using GITT method demonstrated the ion diffusion coefficient of Mg^{2+} was ~10X lower compared with Li^+ and Na^+ . Thus, the Mg-birnessite synthesized through a low temperature precipitation / ion exchange method allowing crystallite size control indicated beneficial effect on the electrochemistry material Li^+ , Na^+ , and Mg^{2+} based electrolyte system.

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Figure 1. a) X-ray powder diffraction patterns of as-synthesized Mg-birnessite samples. b) Crystal structure of Mg-birnessite along b-axis. Pink octahedra with red balls are edge-shared MnO_6 units; yellow balls are Mg^{2+} ; blue balls are water molecules. The coordination environments of Mn and Mg are also shown.

Figure 2. TGA/DSC curve of **MgB-1**. The pink shaded region indicates the water loss range.

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Graphical Abstract Text

Synthesis of Mg-birnessite(Mg_xMnO_2) with different crystallite sizes via low temperature precipitation and ion exchange was demonstrated. The influence of crystallite size on electrochemistry of Mg-birnessite was studied for the first time. Material with smaller crystallite size showed enhanced capacity and rate capability in Li^+ , Na^+ , and Mg^{2+} based electrolytes.

ACCEPTED MANUSCRIPT

Highlights

- Mg_xMnO_2 prepared via low temperature precipitation and ion exchange
- First electrochemical study of Mg_xMnO_2 as a function of crystallite size
- Battery performance was studied in Li^+ , Na^+ , and Mg^{2+} based electrolytes
- Small crystallite size showed enhanced capacity and rate capability
- Mg^{2+} ion diffusion coefficient was $\sim 10\times$ lower than that of Li^+ and Na^+