Synthesis and Electrochemical Study of $\text{Mg}_{1.5}\text{MnO}_3$: A Defect Spinel Cathode for Rechargeable Magnesium Battery

Partha Saha^{1,2}, Prashanth H. Jampani¹, DaeHo Hong¹, Bharat Gattu³, James A. Poston², Ayyakkannu Manivannan², Moni Kanchan Datta^{1,2}, and Prashant N. Kumta^{1,2,3,4,5,6}

¹Department of Bioengineering, Swanson School of Engineering, University of Pittsburgh, PA 15261

²US Department of Energy, National Energy Technology Laboratory, Morgantown, WV 26507, USA

³Mechanical Engineering and Materials Science, Swanson School of Engineering, University of Pittsburgh, PA 15261

⁴Chemical and Petroleum Engineering, Swanson School of Engineering, University of Pittsburgh, PA 15261

⁵School of Dental Medicine, University of Pittsburgh, PA 15261

⁶Center for Complex Engineered Multifunctional Materials, University of Pittsburgh, Pittsburgh, PA 15261, USA

Abstract

$\text{Mg}_{1.5}\text{MnO}_3$, a defect oxide spinel (space group: $Fd3m$; unit cell: 0.833294nm) of particle size ~100nm derived by the Pechini route was tested as a cathode for rechargeable magnesium battery. Cyclic voltammetry illustrates a reversible reaction occurring in the 0.3-2.0V potential window versus magnesium. The spinel however exhibits a low capacity of ~12.4 mAhg⁻¹ up to 20 cycle when cycled at a current rate of ~C/27. X-ray photoelectron spectroscopy surface probe of magnesiated/de-magnesiated electrodes confirms the oxidation state change of Mn during intercalation/de-intercalation of Mg-ion from the $\text{Mg}_{1.5}\text{MnO}_3$ electrode. The low capacity of $\text{Mg}_{1.5}\text{MnO}_3$ electrode mainly stem from the kinetic limitation of Mg-ion removal from the defect oxide spinel as the electrochemical impedance spectroscopy results of electrodes show that charge transfer resistance, R_c increases in de-magnesiated state.

Keywords: Magnesium; Defect Oxide Spinel; Nanocrystalline Materials; Electrochemistry, X-ray Photoelectron Spectroscopy

1. Introduction

Magnesium based rechargeable batteries are proposed as alternatives to lithium-ion batteries particularly for electrical energy storage (EES) technologies due to the global abundance Mg (~13.9% Mg compared to ~0.0007% of Li in the earth's crust), low cost (~\$2,700/ton for Mg compared to \$64,000/ton for Li), and potentially, better safety characteristics [1, 2]. The divalent magnesium (Mg^{2+}) also affords the ability to generate almost two-fold increase in volumetric capacity compared to lithium (3832 mAh/cc for Mg vs. 2062 mAh/cc for Li). Moreover, the similarity of the ionic radius of Mg^{2+} (86 pm) to Li^+ (90 pm) renders the notion of intercalation based cathodes potentially attractive, if made realizable for magnesium. However, the attainment of suitable and efficient reversible intercalation electrodes similar to lithium is limited for magnesium owing to the strong polarization and kinetic barriers [2, 3]. Thus, there is a paucity in the choice of cathodes due to the difficulty associated with the electrochemical insertion of Mg^{2+} into various inorganic compounds [2, 4].

Aurbach *et al.* [1] first demonstrated a rechargeable magnesium battery using Mg anode and the Chevrel phase ($\text{Mg}_x\text{Mo}_6\text{S}_8$) cathode utilizing 0.25 molar $\text{Mg}(\text{AlCl}_2\text{EtBu})_2/\text{tetrahydrofuran}$ (THF) organic electrolyte offering a practical energy density of $\sim 60 \text{ Wh kg}^{-1}$ over an impressive ~ 3000 cycles. Since then, several intercalation cathodes, for example, $\text{Mg}_x\text{M}_y\text{SiO}_4$ ($\text{M} = \text{Mn, Fe, Co, } x+y=2$) [5-7], MgCo_2O_4 , $\text{Mg}_{0.67}\text{Ni}_{1.33}\text{O}_2$ [8], TiS_2 [9], MoS_2 [10-13], CuMo_6S_8 [14], $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ [15], V_yO_x , MoO_3 [16-19], as well as conversion cathodes such as sulfur [20] have been proposed. Unfortunately, with the exception of the Chevrel phase (Mo_6T_8 , $\text{T} = \text{S, Se}$) family and sulfur, the specific capacity of all the other cathodes are considerably low and below the expected theoretical limits either due to mismatch of Mg anodes with the electrolytes causing surface passivation and poor cycling performance or

the low diffusivity of Mg-ions in the inorganic compounds and other transport related limitations rendering it difficult for intercalation reactions to occur.

Recently, Zhang *et al.* [21] showed that α -MnO₂ is a promising Mg battery cathode capable of delivering specific capacity $\sim 280 \text{mAhg}^{-1}$ during the 1st discharge. However, there is rapid capacity fade during cycling due to the partial collapse of the α -MnO₂ tunnel structure associated with Mg²⁺ intercalation/de-intercalation combined with the Jahn-Teller instability of the MnO₆ octahedra [22]. Therefore, there is a need to develop transition metal oxide (TMO) based ‘cyclable and stable’ cathodes, wherein the reversible intercalation/de-intercalation of magnesium ions can occur over many cycles. In this regard, a recent paper reported the synthesis of nanocrystalline MgMnO₃ cubic defect spinel [23-25]. A similar defect spinel system was also reported wherein the tetrahedral sites occupied by the divalent ions were partially substituted (one-third) with univalent ion exploring its potential for Li-ion systems [26]. Defect spinel type structures in the Li-Mn-O system [27] are well known Li-ion cathodes with excellent capacity retention over several cycles due to the presence of oxygen defects. Although known however, Mg-Mn-O based defect spinels have never been explored for secondary Mg batteries. The defect chemistry in this system enables Mn ions to assume variable oxidation states, while compensating the b-sites vacancies allowing the possible reversible redox reactions of Mg²⁺/Mn³⁺ and Mg²⁺/Mn⁴⁺ electrochemical couples to occur. Hence we herein report for the first time the electrochemical response of Mg_{1.5}MnO₃ cubic defect spinel cathode for cycling of Mg ions as a possible electrode system rechargeable Mg batteries.

2. Methods

Materials preparation - Mg_{1.5}MnO₃ powder was prepared via the Pechini’s route by mixing stoichiometric amounts of Mg(NO₃)₂ (Aldrich, 99.99%) and Mn(NO₃)₂ (Aldrich, 50wt%

1 in dilute HNO_3) in de-ionized water along with citric acid (CA) (Aldrich, 99.5%) employed as
2 the complexing agent. The obtained solution mixture was heated to 40°C before the addition of
3 ethylene glycol (EG) (Aldrich, 99.5%). The molar ratio of M:CA:EG was maintained at 1:1.7:2.0
4 where M is the sum of all the metal ions (Mg and Mn). The temperature of the mixture was
5 further raised to 60°C to evaporate water until only ~ 50 mL of the solution remained. At this
6 point, the solution was transferred into a heating mantle and pre-heated to 70°C and subsequently
7 to 120°C . Due to the exothermic reaction nature, the temperature increased rapidly releasing NO_2
8 gas until the reaction is completed with no further release of the NO_2 gas. The resultant
9 compound was dried overnight in an oven and calcined at $\sim 923\text{K}$ for 2h in air to yield a
10 completely crystalline oxide spinel phase. The calcined powder was subjected to X-ray
11 diffraction (XRD) using Philips XPERT PRO system employing CuK_α radiation ($\lambda = 0.15406$
12 nm). The crystal structure was determined by Rietveld refinement using a computer program
13 (“Calculate XRD Power Pattern”, part of the JADE software). Particle size of the spinel oxide
14 was determined from SEM (JEOL JSM-6610LV scanning electron microscope operating at 20
15 kV), bright field and HRTEM images captured using the transmission electron microscope
16 (JEOL JEM 2000FX) (TEM) operating at 200 kV.

17 *Electrochemical measurements* - Electrode for electrochemical testing was prepared by
18 mixing 80 wt% $\text{Mg}_{1.5}\text{MnO}_3$ (-325 mesh powder), 10 wt% super-P, and 10 wt% polyvinylidene
19 fluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidinone (NMP) and then coated onto a graphite
20 foil followed by drying at $\sim 100^\circ\text{C}$ for 24h under vacuum. Cyclic Voltammogram (CV) was
21 performed at a scan rate of $\sim 0.1 \text{ mVs}^{-1}$ using an electrochemical workstation (VersaSTAT 3,
22 Princeton Applied Research) in a 2016 coin cell employing Mg foil as reference and counter, and
23 studied electrode as working electrode, separated by Celgard[®] separator soaked in 0.4 molar

(PhMgCl)-AlCl₃/THF electrolyte. All the electrochemical cells were assembled inside an argon-filled MBraun Inc. glove box (< 0.1 ppm each of O₂ and H₂O at room temperature). Galvanostatic charge-discharge measurements were conducted at ambient temperature in a 2016 coin cell in the voltage range of 0.3-1.5V at constant current rates of 7mA/g with a minute rest time between each charge/discharge cycle in an Arbin battery measurement system. In addition to charge-discharge testing, electrochemical impedance spectroscopy (EIS) was performed to obtain a fundamental understanding of the charge storage mechanisms occurring on pristine and cycled electrodes. EIS was performed on the Versastat 3 (Princeton Applied Research Inc.) over a frequency range of 0.01Hz-100KHz. An A.C. amplitude of 5 mV was used and the spectra were obtained before cycling and following the 1st and 2nd charge and discharge cycles. Electrode potential was stabilized after charge/discharge and EIS was performed in order to understand the charge storage behavior upon cycling. The effect of cycling on charge transfer parameters was also analyzed by performing equivalent circuit modeling using Z-View (Scribner Associates, Inc.; version 3.3).

X-ray photoelectron spectroscopy (XPS) analysis - XPS was used to investigate the valence states of manganese and oxygen ions during the galvanostatic cycling of Mg_{1.5}MnO₃ electrodes. In order to do this, electrodes at magnesiated/de-magnesiated state was analyzed by XPS using a Physical Electronics (PHI) model 32-096 X-ray source control and a 22-040 power supply interfaced to a model 04-548 X-ray source with an Omni Focus III spherical capacitance analyzer. The system is routinely operated within the pressure range of 10⁻⁸ to 10⁻⁹ Torr. The XPS instrument was calibrated utilizing the photoemission lines, E_b of Cu 2p_{3/2}-932.7 eV, E_b of Au 4f_{7/2}-84 eV and E_b of Ag 3d_{5/2}-368.3eV for a magnesium anode. The reported intensities

were experimentally determined by peak areas divided by the instrumental sensitivity factors. Charge correction was achieved by referencing the adventitious C 1s peak to 284.8 eV.

3. Results and Discussion

Figure 1a shows the XRD pattern of calcined powder of $\text{Mg}_{1.5}\text{MnO}_3$ along with the simulated and difference plot derived from Rietveld refinement of the experimental data. The structural parameters was fitted to a non-perovskite cubic defect spinel structure in the space group $Fd3m$ (227) as the starting model similar to that reported for MgMnO_3 defect spinel structure [23]. The simulated XRD pattern gives the best fit (weighted R profile- $R_{\text{wp}}=7.17\%$, R expected- $R_{\text{exp}} = 5.54\%$, goodness of fit- $\chi^2 = 1.67$) of a cubic defect spinel with a lattice parameter $a = 0.8332\text{nm}$, unit cell volume $= 579.4 \times 10^{-3} \text{ nm}^3$ and density $\rho = 3.89 \text{ g/cm}^3$. Figure 1b shows the crystal structure of $\text{Mg}_{1.5}\text{MnO}_3$ (2×2 sub cells) cubic defect spinel obtained from the refined crystallographic data of the structure. The unit cell of $\text{Mg}_{1.5}\text{MnO}_3$ consists of 16 octahedral sub-lattice sites partially occupied by Mg^{2+} ions and the remaining $\text{Mg}^{2+}/\text{Mn}^{3+}$ ions are distributed in the 8b tetrahedral sub-lattice sites and the charge accordingly compensated by the O^{2-} ion vacancies in the 32-sites. The structural parameters obtained from the Rietveld refinement of $\text{Mg}_{1.5}\text{MnO}_3$ are listed in the inset of Figure 1a. Scanning electron micrograph of $\text{Mg}_{1.5}\text{MnO}_3$ powder is shown in Figure 2a. It can be seen that the particles are agglomerated and in the nanometer to submicron size range. The bright field TEM image (Figure 2b) of $\text{Mg}_{1.5}\text{MnO}_3$ powder shows the particle size to be in the $\sim 100\text{nm}$ size range. Figure 2c shows a HRTEM image of a single $\text{Mg}_{1.5}\text{MnO}_3$ particle. Fast Fourier transform (FFT) selected area diffraction pattern, shown in the inset of Figure 2c, was used to calculate the lattice spacing of

the nanocrystalline particle. The lattice fringe spacing was found to be $\sim 0.49\text{nm}$ corresponding to the inter-planar d-spacing of $\{111\}$ planes of $\text{Mg}_{1.5}\text{MnO}_3$.

The electrochemically active nature of the $\text{Mg}_{1.5}\text{MnO}_3$ electrode was verified by conducting cyclic voltammetry. Accordingly, CV was performed between 0.3V - 2.0V employing a sweep rate of $\sim 0.1\text{ mVs}^{-1}$ in a 2016 coin cell configuration. Figure 3 illustrates the CV comprising two cathodic (magnesium) peaks at $\sim 0.54\text{V}$ and $\sim 0.87\text{V}$, and two anodic (demagnesium) reactions occurring at $\sim 0.72\text{V}$ and $\sim 1.13\text{V}$, respectively. From the CV, it is clearly evident that the Mg-ion insertion/extraction process is a two-step redox reaction, similar to the other reported cathodes [5, 28]. Figure 4a shows the capacity and Coulombic efficiency versus cycle number plot conducted at a current rate of $\sim 7\text{mA g}^{-1}$ ($\sim \text{C}/27$ rate based on the calculated theoretical capacity $\sim 190\text{ mAh g}^{-1}$ assuming 0.5Mg-ion removal and cycling). The capacity however, in the present study was observed to be limited to only $\sim 12.4\text{ mAh g}^{-1}$ corresponding to the reversible removal of ~ 0.032 of $\text{Mg}^{2+}/\text{Mg}_{1.5}\text{MnO}_3$ formula unit, albeit yielding a 99.9% Coulombic efficiency. Figure 4b shows the typical cell voltage versus specific capacity plot for the $\text{Mg}_{1.5}\text{MnO}_3$ electrode cycled at a constant current rate of $\sim 7\text{mA g}^{-1}$ between 0.3 - 1.5V for the 1st, 2nd, and 19th cycles. It is clearly visible from the Figure 4b that two reaction plateaus are present during the charge-discharge cycle which appears as peaks in the dQ/dV versus voltage plot as shown in Figure 4c. Importantly, the voltage plateaus are maintained throughout the cycling, as the voltage profile for 1st, 2nd, and 19th cycle clearly overlap indicating no capacity fade behavior. The differential capacity plot for the 1st, 2nd and 19th cycle, shown in Figure 4c indicates reversible magnesium/de-magnesium reactions occurring during the charge-discharge cycles. In the 1st cycle two demagnesium peaks are observed at $\sim 0.65\text{V}$ and $\sim 1.10\text{V}$ whereas the magnesium peaks are observed at $\sim 0.55\text{V}$ and $\sim 0.87\text{V}$, respectively. These

1 results indicate signature characteristics seen in the differential capacity plot in agreement with
2 that observed in the CV plot discussed above (see Figure 3).

3 In order to track the possible structural changes occurring during galvanostatic cycling,
4 *ex-situ* XRD patterns of the pristine, magnesiated and de-magnesiated electrodes were acquired.
5 The 2016 coin cells were disassembled inside the glove box and the electrodes were washed with
6 copious amount of anhydrous tetrahydrofuran followed by drying under vacuum. Figure 5 shows
7 the XRD patterns of the electrodes at various stages of magnesiation and de-magnesiation. The
8 XRD pattern of the pristine electrode shows diffraction peaks corresponding to the defect oxide
9 spinel of $\text{Mg}_{1.5}\text{MnO}_3$ structure (*Fd3m* space group) along with the presence of carbon evidenced
10 by the presence of strong XRD peaks collected on the current collector (26.6° , 54.8° 2θ values).
11 Similarly, the electrode in the magnesiated ($\sim 1.5\text{V}$) and de-magnesiated ($\sim 0.3\text{V}$) state shows no
12 signs of peak shifts or appearance of new Bragg's diffraction lines suggesting that the spinel
13 structure is very much retained primarily due to partial Mg^{2+} intercalation/de-intercalation from
14 the $\text{Mg}_{1.5}\text{MnO}_3$ electrode. Any subtle changes in the crystal structure likely due to the partial
15 number of Mg^{2+} reversibly cycling are however beyond the detection limit of X-ray diffraction
16 and hence are not visible in the X-ray scans. The limitation of *ex-situ* XRD for detecting the
17 structural changes of $\text{Mg}_{1.5}\text{MnO}_3$ electrode during cycling thus prompted us to examine the
18 surface of the electrodes by XPS analysis.

19 XPS was carried out on the $\text{Mg}_{1.5}\text{MnO}_3$ electrode to study the possible structural changes
20 during demagnesiation and magnesiation reactions which was also reported in our previous
21 review paper [29]. Figure 6 shows the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ doublet XPS spectra of de-
22 magnesiated (charge state), magnesiated (discharge state) $\text{Mg}_{1.5}\text{MnO}_3$ electrode after 10 cycle
23 and demagnesiated $\text{Mg}_{1.5}\text{MnO}_3$ electrode after 100 cycle. The XPS spectra clearly show the

shifts in the binding energy of $2p_{3/2}$ and $2p_{1/2}$ doublet of charged and discharged electrodes. During charge, Mg^{2+} ion extraction occurs from the $Mg_{1.5}MnO_3$ electrode leading to an increase in the binding energy of Mn $2p_{3/2}$ (~643.3eV) and Mn $2p_{1/2}$ peaks (~654.8eV), indicating an oxidation of Mn^{3+} ion to Mn^{4+} ion caused by the removal of Mg^{2+} [30]. On the other hand, $Mg_{1.5}MnO_3$ electrode in the magnesiated state shows Mn $2p_{3/2}$ (~642.8eV) and Mn $2p_{1/2}$ peaks (~654.5eV) at slightly lower binding energies indicating a reduction of Mn^{4+} ion to form Mn^{3+} ion. Similarly, the demagnesiated $Mg_{1.5}MnO_3$ electrode after 100 cycles also shows the Mn $2p_{3/2}$ (~643.5eV) and Mn $2p_{1/2}$ peaks (~655.2eV) at higher binding energies due to the oxidation of Mn^{3+} ion to Mn^{4+} ion during the removal of Mg^{2+} from the $Mg_{1.5-x}MnO_3$ electrode. ~~Figure 6b shows the Mn 3p XPS spectra, where the de-magnesiated electrode after 10 and 100 cycle shows broad fairly symmetric peaks at binding energies ~51eV and ~50.5eV, respectively, which correspond closely to the mixed valence state of Mn^{2+}/Mn^{3+} , and the magnesiated electrode after 10 cycle shows a peak close to binding energy ~50.2 eV. Again, the shifts in the peak position and associated binding energy during the charge/discharge processes suggest that Mg^{2+} extraction/insertion is a reversible phenomenon associated by a change in the redox center of Mn^{3+}/Mn^{4+} ion. Similarly, the surface level Mn 3s and O 1s XPS spectra shown in Fig. 6c and 6d, respectively, illustrate the change in the peak positions and binding energy during charge/discharge state suggesting the reversible reaction processes of Mg^{2+} in the $Mg_{1.5}MnO_3$ electrode although the peak positions of Mn 3s spectra observed at ~89-90eV may overlap with the satellite peaks of Mn 3p spectra.~~ Overall the XPS study of the de-magnesiated and magnesiated $Mg_{1.5}MnO_3$ electrode does provide an explanation that Mg^{2+} ion extraction/insertion indeed occurs in the defect oxide spinel and is clearly associated with change in the valence

states of $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions. The XPS data thus show credence to the cyclability of Mg^{2+} indicating the electrochemical active nature of the system despite the low capacity values.

The exact reasons corresponding to the cycling of only 6.4% of Mg^{2+} as opposed to the expected reversible cycling of all of the 0.5Mg-ion ($\sim 100\%$ of Mg^{2+}) causing Mn to attain the desired +4 oxidation state is indicative of the possibility of charge transfer limitations and barriers due to the mixed presence of Mg^{2+} -ions in the tetrahedral and octahedral sites thereby contributing to an insurmountable activation energy barrier. In order to understand the above phenomenon, electrochemical impedance spectroscopy (EIS) was used to probe the changes in the electrode character subsequent to the 1st and 2nd cycle charge/discharge cycles. Figure 7 depicts the Nyquist plots of the electrode at various stages of cycling. A distinct difference is observed between the charge and discharge states of the electrode confirming the expeditious initial and subsequent magnesiation reactions into the $\text{Mg}_{1.5}\text{MnO}_3$ electrode. The demagnesiation reaction or the charged state however, appears to be difficult indicating significant resistance to charge transfer.

This trend is clearly observed by examining the value of R_e and R_i shown in Table 1. R_e , the electrode resistance is a measure of the ease of charge transfer across the electrochemical interface, while R_i , the interfacial resistance is a result of the solid electrolyte interphase (SEI)-type layer formation [31-34]. The circuit shown in Figure 7 was used for modeling of the equivalent circuit to obtain the values of these resistances given in Table 1. The Randall's circuit shown in Figure 7 (inset) considers a number of electrochemical phenomena including series resistance (R_s), charge and electron transfer kinetics (CPE_e and R_e), coupling of a chemical and an electrochemical process- Gerischer impedance (GE), Mg-ion trapping in the host (CPE_i and R_i), diffusion characteristics and associated ion-trapping (W_o , R_{trap} , CPE_{trap}). The model was

selected since it has previously been reported to be an exact representation of the magnesiation/demagnesiation phenomena [35], and correspondingly has been used to understand the charge storage behavior in the Chevrel phase electrodes [33]. It can be observed that the charge-transfer resistance, R_e increases in both cycles post demagnesiation (charge) while the interfacial resistance, R_i follows the opposite trend. Such a behavior is indicative of a difficulty in both insertion and extraction of Mg-ion in the $Mg_{1.5}MnO_3$ electrode. Demagnesiation (charge) is kinetically limited, while magnesiation(discharge) is limited by the resistance provided by the formation of a SEI-type layer. This type of behavior could be attributed to one or more of various phenomena occurring, either the poor intrinsic electronic conductivity of the defect spinel structure itself, or the difficulty in removal of the Mg-ions from the 8b tetrahedral sites due to Mg^{2+}/Mn^{3+} cation mixing as is known in analogous Li transition metal oxide cathodes such as $LiNiO_2$ [36]. Additionally, the limitation in cycling of the Mg^{2+} could also be attributed to higher voltages needed for the complete removal of Mg which is also likely restricted by the low voltage window of the non-aqueous electrolyte used for the electrochemical cycling, an area requiring further scrutiny [37]. Nevertheless, the reversible nature of Mg^{2+} cycling is to be noted indicating the electrochemically nature of the system for cycling of Mg^{2+} .

4. Conclusion

Preliminary electrochemical characterization of nanocrystalline ($\sim 100nm$) $Mg_{1.5}MnO_3$ cubic defect spinel derived by the Pechini method suggests that the oxide is electrochemically active wherein Mg^{2+} extraction/ insertion occurs via a 2-step reaction within the 0.3-1.5V potential window (*versus* Mg reference electrode). XPS surface probe of magnesiated and demagnesiated electrodes suggest a possible change in Mn^{3+}/Mn^{4+} valence state during the Mg-ion extraction/insertion from $Mg_{1.5}MnO_3$ electrode. EIS shows that the charge transfer resistance

(R_e) increases after the charged state whereas interfacial resistance (R_i) increases post discharge suggesting that demagnesian is kinetically limited whereas the magnesian is limited due to the formation of SEI-type layer on the electrode surface. Although the reversible capacity ($\sim 12.4 \text{ mAhg}^{-1}$) is low, the capacity retention up to 20 cycles with Coulombic efficiency $\sim 99.9\%$ further supports the electrochemically active nature of this intriguing oxide warranting further in-depth study.

Acknowledgements

The authors gratefully acknowledge the financial support as part of the Department of Energy's National Energy Technology Laboratory's program DOE-NETL) (contract number DE-FE0004000). PNK also acknowledge the Edward R. Weidlein Chair Professorship funds and the Center for Complex Engineered Multifunctional Materials (CCEMM) for partial support of this research.

Indemnification

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Figure Captions

Figure 1 (a) Observed and simulated powder XRD pattern of $\text{Mg}_{1.5}\text{MnO}_3$ with the Miller indices observed lines. Relevant refined parameters based on the fit are listed in the figure, (b) crystal structure of $\text{Mg}_{1.5}\text{MnO}_3$ cubic defect spinel (2×2 sub cells); Mg atoms are shown in red; Mn atoms are indicated in blue; and O atoms are displayed in green,

Figure 2 (a) SEM, (b) Bright field TEM, and (c) HRTEM image showing lattice fringes and FFT SAD pattern (inset) of $\text{Mg}_{1.5}\text{MnO}_3$.

Figure 3 Cyclic voltammogram (scan rate $\sim 0.1 \text{ mVs}^{-1}$) of $\text{Mg}_{1.5}\text{MnO}_3$ electrode cycled in the potential window of 0.3V-1.5V.

Figure 4 (a) Specific charge-discharge capacity and Coulombic efficiency vs. cycle number curves of $\text{Mg}_{1.5}\text{MnO}_3$ electrode cycled at a constant current of $\sim 7 \text{ mA g}^{-1}$ in the potential window 0.3V-1.5V, (b) voltage versus capacity plot (1^{st} , 2^{nd} , and 19^{th} cycle) of the electrode comprising $\text{Mg}_{1.5}\text{MnO}_3$ at constant current rate of $\sim 7 \text{ mA g}^{-1}$ and (c) differential capacity vs. cell potential curves obtained after the 1^{st} , 2^{nd} , and 19^{th} cycle.

Figure 5 *Ex-situ* XRD patterns of the pristine, magnesiated, and de-magnesiated $\text{Mg}_{1.5}\text{MnO}_3$ electrode.

Figure 6 (a) The XPS spectra of Mn $2p_{3/2}$ and $2p_{1/2}$ doublet of the $\text{Mg}_{1.5}\text{MnO}_3$ electrodes at de-magnesiated and magnesiated state, (b) Mn 3p, (c) Mn 3s, and (d) O 1s spectra (reprinted with permission from Ref. 29, Copyright (2014), Elsevier).

Figure 7 Nyquist plots of the $\text{Mg}_{1.5}\text{MnO}_3$ electrode during different stages of galvanostatic cycle. Curves corresponding to the state of pristine electrode and that of the same, subsequent to the 1^{st} and 2^{nd} magnesiation and de-magnesiation steps are plotted herein.

Table Caption

Table 1 Charge-transfer parameters obtained by Randle's equivalent circuit modeling of the curves in Figure 7 using the circuit model shown in Figure 7 (inset).

References

- [1] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature*, 407 (2000) 724-727.
- [2] P. Novák, R. Imhof, O. Haas, *Electrochimica Acta*, 45 (1999) 351-367.
- [3] E. Levi, Y. Gofer, D. Aurbach, *Chemistry of Materials*, 22 (2010) 860-868.
- [4] P.G. Bruce, F. Krok, J. Nowinski, V.C. Gibson, K. Tavakkoli, *Journal of Materials Chemistry*, 1 (1991) 705-706.
- [5] Z. Feng, J. Yang, Y. NuLi, J. Wang, *Journal of Power Sources*, 184 (2008) 604-609.
- [6] Y. Li, Y. Nuli, J. Yang, T. Yiliner, J. Wang, *Chinese Science Bulletin*, 56 (2011) 386-390.
- [7] Y. NuLi, Y. Zheng, Y. Wang, J. Yang, J. Wang, *Journal of Materials Chemistry*, 21 (2011) 12437-12443.
- [8] T. Ichitsubo, T. Adachi, S. Yagi, T. Doi, *Journal of Materials Chemistry*, 21 (2011) 11764-11772.
- [9] Z.-L. Tao, L.-N. Xu, X.-L. Gou, J. Chen, H.-T. Yuan, *Chemical Communications*, (2004) 2080-2081.
- [10] L.-F. Jiao, Y. Liu, Q. Wu, Y. Zhao, K. Cao, H. Liu, Y. Wang, H. Yuan, *Nanoscale*, (2013).
- [11] X.-L. Li, Y.-D. Li, *The Journal of Physical Chemistry B*, 108 (2004) 13893-13900.
- [12] Y. Liang, R. Feng, S. Yang, H. Ma, J. Liang, J. Chen, *Advanced Materials*, 23 (2011) 640-643.
- [13] Y. Liu, L. Jiao, Q. Wu, J. Du, Y. Zhao, Y. Si, Y. Wang, H. Yuan, *Journal of Materials Chemistry A*, 1 (2013) 5822-5826.
- [14] A. Mitelman, M.D. Levi, E. Lancry, E. Levi, D. Aurbach, *Chemical Communications*, (2007) 4212-4214.
- [15] K. Makino, Y. Katayama, T. Miura, T. Kishi, *Journal of Power Sources*, 99 (2001) 66-69.
- [16] P. Novák, W. Scheifele, O. Haas, *Journal of Power Sources*, 54 (1995) 479-482.
- [17] V. Shklover, T. Haibach, F. Ried, R. Nesper, P. Novák, *Journal of Solid State Chemistry*, 123 (1996) 317-323.
- [18] M.E. Spahr, P. Novák, O. Haas, R. Nesper, *Journal of Power Sources*, 54 (1995) 346-351.
- [19] G. Gershtinsky, H.D. Yoo, Y. Gofer, D. Aurbach, *Langmuir*, (2013).
- [20] H.S. Kim, T.S. Arthur, G.D. Allred, J. Zajicek, J.G. Newman, A.E. Rodnyansky, A.G. Oliver, W.C. Boggess, J. Muldoon, *Nat Commun*, 2 (2011) 427.
- [21] R. Zhang, X. Yu, K.-W. Nam, C. Ling, T.S. Arthur, W. Song, A.M. Knapp, S.N. Ehrlich, X.-Q. Yang, M. Matsui, *Electrochemistry Communications*, 23 (2012) 110-113.
- [22] A. Yamada, M. Tanaka, K. Tanaka, K. Sekai, *Journal of Power Sources*, 81-82 (1999) 73-78.
- [23] M.S. Seehra, V. Singh, S. Thota, B. Prasad, J. Kumar, *Applied Physics Letters*, 97 (2010) 112507-112503.
- [24] H. Toussaint, *Revue de Chimie Minérale*, 141 (1964) 141-195.
- [25] P. Saha, M.K. Datta, A. Manivannan, P.N. Kumta, *Meeting Abstracts*, MA2012-02 (2012) 353.
- [26] V. Singh, M.S. Seehra, A. Manivannan, P.N. Kumta, *Journal of Applied Physics*, 111 (2012) 07E302-303.
- [27] Y. Xia, H. Wang, Q. Zhang, H. Nakamura, H. Noguchi, M. Yoshio, *Journal of Power Sources*, 166 (2007) 485-491.
- [28] Y. NuLi, J. Yang, Y. Li, J. Wang, *Chemical Communications*, 46 (2010) 3794-3796.
- [29] P. Saha, M.K. Datta, O.I. Velikokhatnyi, A. Manivannan, D. Alman, P.N. Kumta, *Progress in Materials Science*, 66 (2014) 1-86.
- [30] H.W. Nesbitt, D. Banerjee, *American Mineralogist*, 83 (1998) 305-315.
- [31] S. Yang, H. Song, H. Yi, W. Liu, H. Zhang, X. Chen, *Electrochimica Acta*, 55 (2009) 521-527.
- [32] R. Epur, P.J. Hanumantha, M.K. Datta, D. Hong, B. Gattu, P.N. Kumta, *Journal of Materials Chemistry A*, 3 (2015) 11117-11129.
- [33] P. Saha, P.H. Jampani, M.K. Datta, C.U. Okoli, A. Manivannan, P.N. Kumta, *Journal of The Electrochemical Society*, 161 (2014) A593-A598.

- 1 [34] P. Saha, P.H. Jampani, M.K. Datta, D. Hong, C.U. Okoli, A. Manivannan, P.N. Kumta, The Journal of
2 Physical Chemistry C, 119 (2015) 5771-5782.
- 3 [35] M.D. Levi, H. Gizbar, E. Lancry, Y. Gofer, E. Levi, D. Aurbach, Journal of Electroanalytical Chemistry,
4 569 (2004) 211-223.
- 5 [36] C.-C. Chang, N. Scarr, P.N. Kumta, Solid State Ionics, 112 (1998) 329-344.
- 6 [37] J. Muldoon, C.B. Bucur, A.G. Oliver, T. Sugimoto, M. Matsui, H.S. Kim, G.D. Allred, J. Zajicek, Y.
7 Kotani, Energy & Environmental Science, 5 (2012) 5941-5950.

8

9

Table 1 Charge-transfer parameters obtained by Randle's equivalent circuit modeling of the curves in **Figure 7** using the circuit model shown in **Figure 7** (inset).

State	R_s $\Omega\text{-cm}^2$	CPE_e		R_e ($\times 10^3$) $\Omega\text{-cm}^2$	CPE_i		$R_i(\times 10^3)$ $\Omega\text{-cm}^2$	GE		W_o			R_{trap} $\Omega\text{-cm}^2$	CPE_{trap}	
		$T(\times 10^{-5})$	P		$T(\times 10^{-5})$	P		$T(\times 10^{-3})$	P	R	T	P		$T(\times 10^{-3})$	P
Before cycling	9.96	1.65	1.07	7.82	2.76	0.67	12.77	620.34	0.11	36.90	1	1	2.43	3.03	0.63
After 1 st discharge	10.85	10.00	1.05	2.49	2.07	0.73	5.95	1.16	4267	3.39	1	1	1.90E-06	9.29	0.59
After 1 st charge	10.05	4.73	0.74	23.03	3.44	0.71	0.60	1.31	0.37	73.66	1	1	1.83E-03	25.16	0.18
After 2 nd discharge	10.42	2.31	0.72	0.45	3.42	0.81	4.98	63.99	2.51	4.33	1	1	1.32E-01	0.21	1.61
After 2 nd charge	10.01	5.61	0.74	31.72	0.56	0.90	0.18	0.55	27.14	31.81	1	1	35.32	7.66	1.49E-11

Graphicsl Abstract

$\text{Mg}_{1.5}\text{MnO}_3$, a defect oxide spinel derived by the Pechini route, was tested as cathode for rechargeable magnesium battery. TEM and XRD analyses of $\text{Mg}_{1.5}\text{MnO}_3$ shows the formation of $\sim 100\text{nm}$ sized nano particles in the cubic defect spinel structure (space group: $Fd3m$; unit cell: 0.833294nm). Cyclic voltammetry illustrates a reversible reaction occurring between $0.3\text{-}1.5\text{V}$ versus magnesium. Galvanostatic cycling of the $\text{Mg}_{1.5}\text{MnO}_3$ cathode exhibits a low capacity of $\sim 12.4\text{ mAh/g}$ up to 20 cycle with $\sim 99.9\%$ Coulombic efficiency when cycled at a current rate of $\sim C/27$. XPS (X-ray photoelectron spectroscopy) surface probe of magnesiated/de-magnesiated electrodes confirm a change in the redox center of Mn-ions during intercalation/de-intercalation of Mg-ion from the $\text{Mg}_{1.5}\text{MnO}_3$ electrode. The low capacity of $\text{Mg}_{1.5}\text{MnO}_3$ electrode mainly stem from the kinetic limitation of Mg-ion removal from the defect oxide spinel as the electrochemical impedance spectroscopy results of electrodes after 1st and 2nd cycle show that charge transfer resistance, R_e , increases post charge state whereas interfacial resistance, R_i , increases after discharge state, respectively.

Figure 1a.

(b)

Figure 1b.

Figure 2a.

Figure 2b.

Figure 2c.

Figure 3.

Figure 4a.

Figure 4b.

Figure 4c.

Figure 5.

Figure 6.

Figure 7.