Electronic Supplementary Material (ESI) for

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

Jiefu Yin[1], Alexander B. Brady[1], Esther S. Takeuchi[1,2,3]*, Amy C. Marschilok[1,2]*, Kenneth J. Takeuchi[1,2]*

1. Department of Chemistry, Stony Brook University, Stony Brook, NY 11794
2. Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY 11794
3. Energy Sciences Directorate, Brookhaven National Laboratory, Upton, NY 11973

*corresponding authors: (E.S.T) esther.takeuchi@stonybrook.edu, (A.C.M.) amy.marschilok@stonybrook.edu, (K.J.T.) kenneth.takeuchi.1@stonybrook.edu

Experimental

Synthesis and characterization

$MgMn_2O_4$ was synthesized via a modified Pechini method. $Mg(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ were added to a mixture of 5 mL H_2O and 5 mL ethylene glycol, citric acid was then added into the solution, yielding concentrations of 0.5 M Mg^{2+}, 1 M Mn^{2+}, and 3 M citric acid. The solution was heated to 70 °C for 24 h, the resulting brown polymer was annealed at 200 °C for 12h. The annealed solid was grounded and then annealed at 400 or 550°C for 10 h.

Material was initially characterized by X-ray powder diffraction (XRD) using a Rigaku SmartLab XRD, with Cu Kα radiation and Bragg-Brentano focusing geometry. The as-prepared material

was also characterized by synchrotron X-ray powder diffraction (XPD) at the XPD 1 beamline in NSLS-II. The beam was calibrated to a wavelength of 0.18321 Å. The two dimensional data was integrated to simulate a one-dimensional pattern using the Fit2D software,[1] Rietveld refinement was carried out using GSAS II.[2] X-ray powder diffraction (XRD) of electrodes was measured using a Rigaku SmartLab XRD, with Cu Kα radiation and Bragg-Brentano focusing geometry.[3] Crystallite size was also determined using the Scherrer equation.[3] Simultaneous thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) was performed using a TA Instruments Q600. Elemental composition was measured via inductively coupled plasma-optical emission spectrometry (ICP-OES) with a Thermo Scientific ICAP ICP-OES. Transmission electron microscopy (TEM) images were collected by a transmission electron microscope (JEOL JEM 1400) equipped with a Gatan CCD camera.

Electrochemical test

The cathode was prepared by casting a slurry of 85% $MgMn_2O_4$, 5% super P carbon, 5% graphite, and 5% Polyvinylidene fluoride (PVDF) on Al foil. Typical active material loading is 3.9 mg/cm^2. All electrochemical tests in Mg^{2+} containing electrolyte were conducted in an Argon filled glovebox at room temperature. A three electrode system was used, with $Ag/AgNO_3$ reference and carbon auxiliary electrodes. 0.5 M magnesium bis(trifluoromethylsulfonylimide) ($Mg(TFSI)_2$) /0.5 M dipropylene glycol dimethyl ether (dipro-glyme) in acetonitrile was used as electrolyte, 3 M water was added in some cases. Cyclic voltammetry data was collected between voltage limits of −1.0 and +1.1 V using a scan rate of 0.1 mV/s. Galvanostatic cycling was tested at 0.1 C (1 C = 270 mAh/g) rate for both discharge and charge, between voltage limits of −1.0 ~ +1.0 V or −1.0 ~

+0.9 V versus Ag^+/Ag. Rate capability was examined at 0.1 C, 0.5 C, 1C, 2C, and 0.1 C, with a constant charge rate of 0.1 C. Electrodes were re-collected from the cell after testing and washed with acetonitrile before additional characterization. Mn dissolution tests were conducted on samples prepared by soaking 25 mg $MgMn_2O_4$ powder in 2 mL electrolyte for 10 days, the mixture was then filtered, and the electrolyte was measured using ICP-OES.

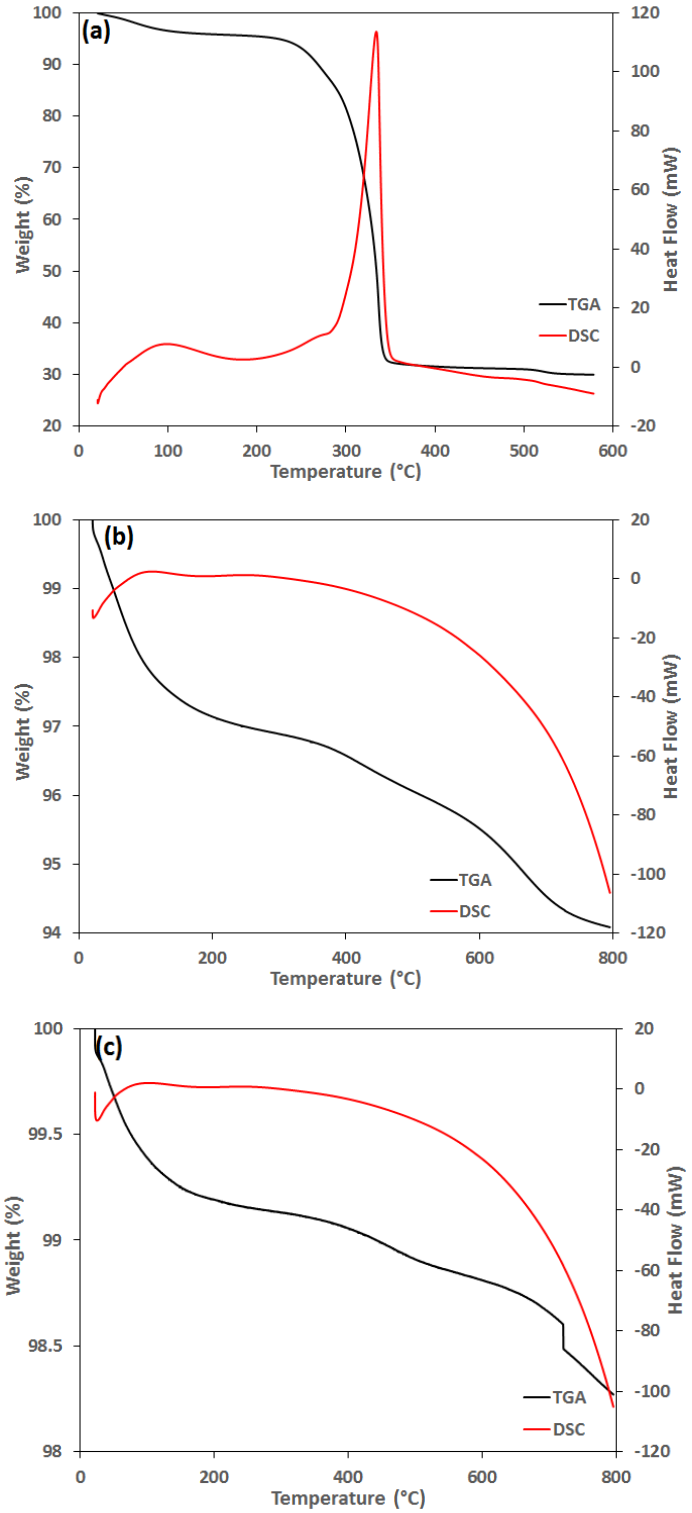

Figure S1. TGA/DSC curves of a) solid after first annealing process at 200 °C, b) **MMO-1**, c) **MMO-2**

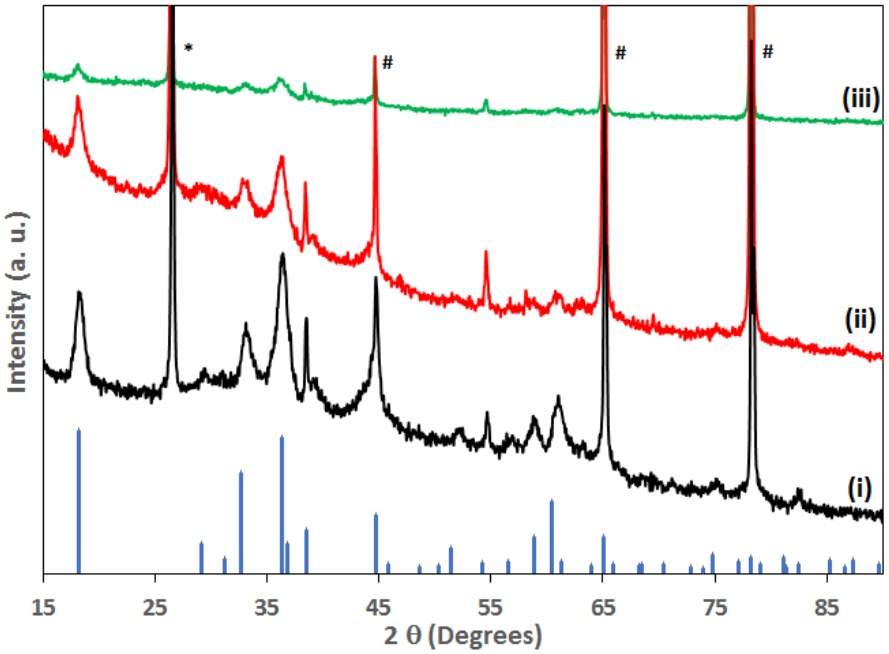

Figure S2. X-ray diffraction of **MMO-1** electrodes at different states: (i) as-prepared electrode; (ii) after 40 cycles in hydrous electrolyte; (iii) after 40 cycles in anhydrous electrolyte. * graphite, # aluminum foil in the electrode.

Table S1. Structural parameters from Rietveld refinement of **MMO-1**

				MMO-1	R_{wp} = 9.30 %			
Atom	x	y	z	Occupancy	Uiso (Å^2)	Lattice parameter (Å)		Inversion degree
Mn (oct)	0	0.5	0.5	0.999(7)	0.0099(1)	a	5.7533(5)	
Mg (tet)	0	0.25	-0.125	0.999(3)	0.0348(7)	b	5.7533(5)	
Mn (tet)	0	0.25	-0.125	0.000(3)	0.0348(7)	c	9.1323(7)	0.07%
Mg (oct)	0	0.5	0.5	0.000(7)	0.0099(1)			
O	0	0.4810(4)	0.2591(9)	1	0.005			

Table S2. Structural parameters from Rietveld refinement of **MMO-2**

				MMO-2	R_{wp} = 7.42 %			
Atom	x	y	z	Occupancy	Uiso (Å^2)	Lattice parameter (Å)		Inversion degree
Mn (oct)	0	0.5	0.5	0.996(4)	0.0057(9)	a	5.7214(1)	
Mg (tet)	0	0.25	-0.125	0.992(7)	0.0039(6)	b	5.7214(1)	
Mn (tet)	0	0.25	-0.125	0.007(3)	0.0039(6)	c	9.2982(4)	0.70%
Mg (oct)	0	0.5	0.5	0.003(6)	0.0057(9)			
O	0	0.4759(6)	0.2563(8)	1	0.0051(1)			

Table S3. Total charge and capacity corresponding to CV test in **Fig. 3**.

Sample	Electrolyte	Cycle no.	Anodic charge (C/g)	Cathodic charge (C/g)	Charge capacity (mAh/g)	Discharge capacity (mAh/g)
MMO-1	Anhydrous	1	387.0	738.5	107.5	205.1
		2	664.6	650.2	184.6	180.6
		3	652.1	652.1	181.1	181.1
		4	640.6	627.1	177.9	174.2
MMO-1	Hydrous	1	395.8	888.1	109.9	246.7
		2	610.7	772.1	169.6	214.5
		3	700.7	770.5	194.6	214.0
		4	690.2	757.5	191.7	210.4
MMO-2	Anhydrous	1	118.1	235.3	32.8	65.4
		2	185.4	215.1	51.5	59.8
		3	201.7	231.5	56.0	64.3
		4	215.1	241.1	59.8	67.0
MMO-2	Hydrous	1	201.1	283.6	55.9	78.8
		2	305.9	273.8	85.0	76.1
		3	304.9	279.7	84.7	77.7
		4	306.7	282.6	85.2	78.5

References

1. A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Hausermann, *High Pressure Res*, 1996, **14**, 235-248.

2. B. H. Toby and R. B. Von Dreele, *J Appl Crystallogr*, 2013, **46**, 544-549.

3. P. Scherrer, *Nachr. Ges. Wiss. Gottingen*, 1918, 98-100.