

Supplementary information

$M_xMn_8O_{16}$ (M = Ag or K) as Promising Cathode Materials

for Secondary Mg Based Batteries: the Role of the cation M

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Experimental Section

$Ag_xMn_8O_{16}$ was synthesized by an ambient pressure reflux and $K_xMn_8O_{16}$ was synthesized using a low temperature solvent-free method as previously reported.¹⁻³ The materials were characterized by X-ray diffraction (XRD) using a Rigaku SmartLab system (Cu K α radiation) with Bragg-Brentano focusing geometry. Elemental composition was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Thermo Scientific iCAP 6000 series spectrometer.

Thermogravimetric analysis (TGA) was conducted using a TA instruments SDT Q600 instrument. Transmission electron microscopy (TEM) data and selected area electron diffraction patterns (SAED) were collected by a transmission electron microscope (JEOL JEM 1400) equipped with a Gatan CCD camera. X-ray photoelectron

spectroscopy (XPS) experiments were carried out using a SPECS Phoibos spectrometer. Cathode samples for XPS, TEM, and SAED analysis after electrochemical cycling were isolated after charge, subsequent to 30 discharge-charge cycles at a 50 mA/g rate.

All electrochemical tests were conducted using a three-electrode assembly with silver/silver ion (Ag/Ag^+) as reference electrode and carbon counter electrode. 0.5 M magnesium bis(trifluoromethylsulfonylimide) ($\text{Mg}(\text{TFSI})_2$) in acetonitrile (CH_3CN) / dipropylene glycol dimethyl ether (0.5 M) was used as the electrolyte. 3 M water was added to form the water containing electrolyte. Cyclic voltammetry data was collected between voltage limits of -0.8 and +1.0 or +1.2 V at a scan rate of 0.1 mV/s.

Galvanostatic discharge/charge testing was conducted between voltage limits of -0.8 and +0.85 or +1.0 V versus Ag/Ag^+ (~-2.2 and 3.9 or 4.0 V, vs. Mg/Mg^{2+}) at a current density of 50 mA/g (0.07 mA/cm²). Rate capability tests were operated at current densities of 100 mA/g (0.14 mA/cm²) and 200 mA/g (0.28 mA/cm²).

References

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3. Y.-s. Ding, X.-f. Shen, S. Sithambaram, S. Gomez, R. Kumar, V. M. B. Crisostomo, S. L. Suib and M. Aindow, *Chemistry of Materials*, 2005, **17**, 5382-5389.

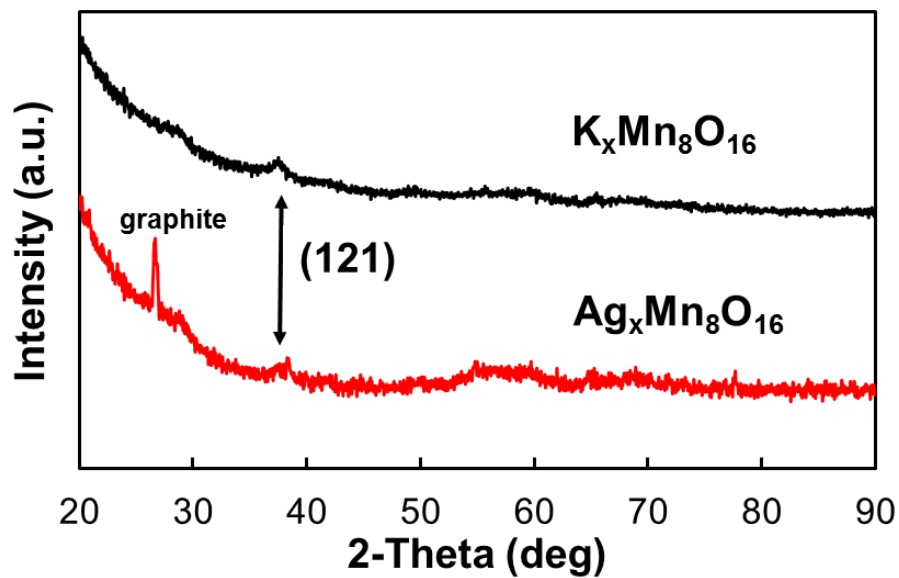


Figure S1. XRD patterns of $Ag_xMn_8O_{16}$ (red) and $K_xMn_8O_{16}$ (black) after cycling

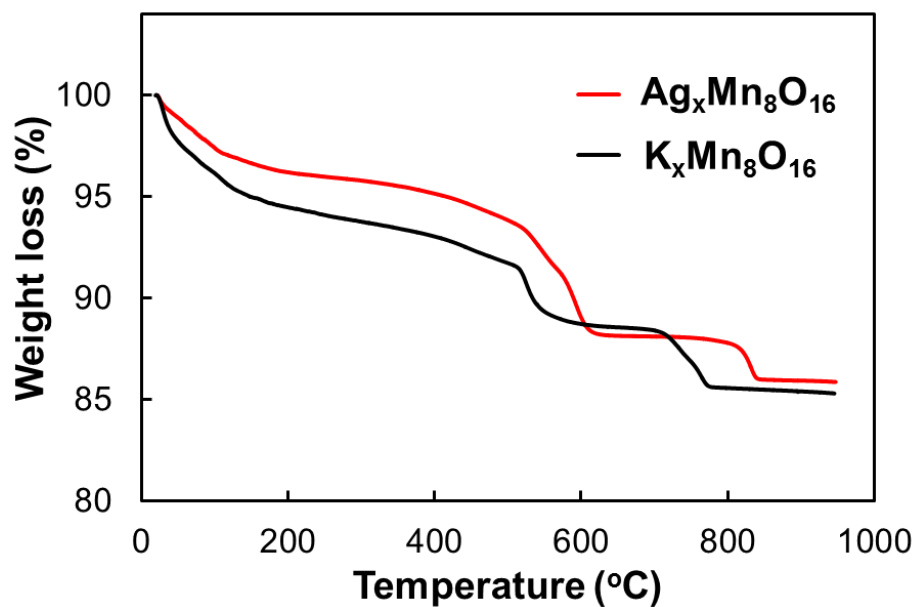


Figure S2. Thermogravimetric analysis (TGA) data of $Ag_xMn_8O_{16}$ (red) and $K_xMn_8O_{16}$ (black).

Sample	Mn 2p [eV]		O1s		
	2p _{1/2}	2p _{3/2}	State	BE [eV]	Area [%]
K _x Mn ₈ O ₁₆	654.3	642.8	O _{lattice}	528.14	56.5
			O _{surface}	528.99	37.6
			O _{adsorbed}	532.87	5.9
Cycled K _x Mn ₈ O ₁₆	653.2	641.8	O _{lattice}	528.21	9.5
			O _{surface}	530.66	55.3
			O _{adsorbed}	532.60	35.2
Ag _x Mn ₈ O ₁₆	653.8	642.3	O _{lattice}	527.99	52.8
			O _{surface}	529.46	23.0
			O _{adsorbed}	531.36	24.2
Cycled Ag _x Mn ₈ O ₁₆	652.8	641.3	O _{lattice}	528.90	8.7
			O _{surface}	NA	NA
			O _{adsorbed}	531.72	91.3

Table S1. Mn 2p binding energies, O 1s binding energies and relative areas of K_xMn₈O₁₆ and Ag_xMn₈O₁₆.