# Supporting Information

# The Influence of Hydration Energy on Alkali-earth Intercalated Layered Manganese Oxides as Electrochemical Capacitors

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#### **EXPERIMENTAL SECTION**

#### Materials

Manganese(II) nitrate tetrahydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 98%, Loba Chemie), lithium hydroxide (LiOH, 98%, Sigma-Aldrich), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%, Chem Merck), calcium nitrate tetrahydrate (Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 97%, Daejung), strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub>, 99%, Himedia), barium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>, 99%, Himedia), lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O, 99%, Alfa Aesar), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, Carlo Erba), carbon black (TIMCAL), polytetrafluoroethylene preparation (PTFE, 60 wt. % dispersion in H<sub>2</sub>O, Sigma Aldrich), and ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.5%, Sigma-Aldrich) are analytical grade and used without further purification. Nickel foam (200 g m<sup>-2</sup> with a thickness of 1 mm, Gelon) was used as a current collector. Deionized water was purified by Milli-Q system (DI water, 15 MΩ.cm, Millipore).

#### **Electrochemical evaluation**

The specific capacitance ( $C_{cv}$ ) was calculated from the CV result by the following equation  $(S1)^{1-2}$ ;

$$C_{CV} = \int \frac{I dV/\nu}{m \Delta V}$$
(S1)

where  $\int IdV/v$  (Coulomb) is a total amount of charge or integral area in the discharge process of CV curve,  $\Delta V$  is the potential window of discharge (V), and m is the total active mass of material used in each electrode.

The specific capacitance ( $C_{GCD}$ ) was also investigated from the GCD result and calculated by the following equation (S2);<sup>2-3</sup>

$$C_{GCD} = \frac{I\Delta t}{\Delta Vm}$$
 (S2)

where I is the applied current density,  $\Delta t$  is the discharge time, m is the active mass, and  $\Delta V$  is the working potential window (VS. SCE) excluding the iR drop.

Relaxation time constant ( $\tau_0$ ) or dielectric relaxation time for supercapacitor.

The  $\tau_0$  represents the discharge characteristics which corresponds to a minimum time required for fully discharging all the stored charges or the transition of electrochemical capacitor behavior from ideal resistor to ideal capacitor.<sup>2</sup> The  $\tau_0$  can be calculated from equation (S3);

$$\tau_0 = 1/(2\pi f_0)$$
 (S3)

The value of complex power can be demonstrated by following equation;

$$S(\omega) = P(\omega) + jQ(\omega)$$
 (S4)

where  $\omega = 2\pi f$  (angular frequency), *j* is imaginary number, P( $\omega$ ) is the active power and Q( $\omega$ ) is the reactive power, which are obtained from equations (S5–S6).

$$P(\omega) = \omega C''(\omega) |\Delta V_{rms}|^2 \qquad (S5)$$
$$Q(\omega) = -\omega C'(\omega) |\Delta V r_{ms}|^2 \qquad (S6)$$

where  $|\Delta V r_{ms}|^2$  represents the maximum amplitude of the ac signal which is calculated from  $|\Delta V r_{ms}| = \Delta V_{max}/\sqrt{2}(V_{max})$ . C'( $\omega$ ) and C''( $\omega$ ) are the real part and the imaginary part of the complex capacitance, respectively given from equations (S7-S8);

$$C'(\omega) = -Z''(\omega) / \{\omega | Z(\omega)|^2\}$$
(S7)  
$$C''(\omega) = Z'(\omega) / \{\omega | Z(\omega)|^2$$
(S8)

where Z' and Z" represent the real and the imaginary parts of the complex impedance Z, respectively.

The sweep-rate dependence of the response current at applied voltage can quantitively distinguish the capacitance contribution including the surface mechanism and the diffusion-controlled process. The response current can be obtained from the following equation  $(S9)^{2, 8}$ ;

$$i(V) = k_1 v + k_2 v^{0.5}$$
 (S9)

where i(V) is the current at an applied voltage, v is the scan rate.  $k_1v$  and  $k_2v^{0.5}$  represent the surface mechanism and diffusion-controlled bulk reactions, respectively.

### **Computational details**

All the calculations reported in this article were performed by Vienna ab initio simulation package (VASP)<sup>9-11</sup> based on the periodic plane-wave density functional theory (DFT). The interactions between ion cores and valence electrons were accounted by the projector-augmented wave  $(PAW)^{12}$  pseudopotentials. The exchange and correlative interactions between electrons were treated within the generalized gradient approximation (GGA)<sup>13</sup> with the Perdev-Burke-Ernzerhof (PBE)<sup>14</sup> parameterization. The additional van der Waals (vdW) contributions were obtained through the semiempirical D2 method of Grimme (DFT-D2).<sup>15</sup> The effect of 3d electron correlation can be improved by considering on-site Coulomb (U) and exchange (J) interactions<sup>16</sup>. An on-site Hubbard term of U–J is 3.9 eV <sup>17</sup> applied for Mn atoms. The cut-off energy for expanded plane-wave basis set was set to 450 eV. The convergence thresholds for full geometry optimizations were set to  $10^{-5}$  eV and 0.005 eV/Å for each electronic steps and ionic steps, respectively. The vacuum space ( $d_{vac}$ ) at least 20 Å was set among repeating slabs along the c direction to avoid periodic interactions. The 15  $\times$  15  $\times$  15 Å unit cell box was used for the calculation of isolated molecule and hydrated ions. The Brillouin zone integration is sampled grid using the Monkhorst–Pack (MP)<sup>18</sup> meshes with the  $5 \times 5 \times 1$  k-points mesh for surfaces. All calculations for isolating charged systems were corrected with the Makov<sup>19</sup> and Neugebauer<sup>20</sup> methods.

The binding energies  $(E_b)$  of water molecules to the cations in the vacuum state were determined as follow:

$$E_b = E_{\text{cation}+n\text{H2O}} - E_{\text{ion}} - nE_{\text{H2O}}$$
(S10)

The mechanisms of intercalation/deintercalation reaction processes can be represented by the following reactions;

$$[Mn_{2}^{3+}Mn^{4+}O_{z} - M^{2+}] + nH_{2}O \rightleftharpoons [Mn_{3}^{4+}O_{z} - (H)_{2}(OH)_{2}] + M(H_{2}O)_{n-2}^{2+} + 2e^{-}$$
(S11)  
$$[Mn_{3}^{4+}O_{z} - (H)_{2}(OH)_{2}] + 2Li(H_{2}O)_{n}^{+} + 2e^{-} \rightleftharpoons [Mn_{2}^{3+}Mn^{4+}O_{z} - 2Li^{+}] + (n+2)H_{2}O$$
(S12)

Sample X: Mn Ratio Li: Mn Ratio Ca-MnO<sub>x</sub> 0.15 \_ Ca-MnO<sub>x</sub> (after cycled) 0.02 0.24 Sr-MnO<sub>x</sub> 0.10 -Sr-MnO<sub>x</sub> (after cycled) 0.08 0.19 Ba-MnO<sub>x</sub> 0.15 -Ba-MnO<sub>x</sub> (after cycled) 0.12 0.13

after cycled with the CV, where X=Li, Ca, Sr, and Ba.



Figure S1. XRD patterns of the wet samples of the as-prepared manganese oxides.

**Table S1.** The structural cation-to-Mn ratio of the as-prepared manganese oxide electrodes



Figure S2. SEM images of the as-prepared layered manganese oxides: (a) Li-MnO<sub>x</sub>, (b) Ca-

MnO<sub>x</sub>, (c) Sr-MnO<sub>x</sub>, and (d) Ba-MnO<sub>x</sub>.



**Figure S3.** The TGA curves of the as-synthesized  $MnO_x$  under air atmosphere at a heating rate of 10 °C/min.



Figure S4. Mn 2p XPS spectra of the as-prepared manganese oxide samples.

The oxidation state of samples can be calculated from the deconvoluted peaks at the Mn  $2p_{3/2}$  peak including ~641.7 eV (Mn<sup>3+</sup>), and ~643.3 eV (Mn<sup>4+</sup>).<sup>21</sup> The average oxidation states of Li–MnO<sub>x</sub>, Ca–MnO<sub>x</sub>, Sr–MnO<sub>x</sub>, and Ba–MnO<sub>x</sub> are +3.42, +3.42, +3.43, and +3.43, respectively.



**Figure S5.** The specific capacitance of the as-prepared Ca-MnO<sub>x</sub> in the 0.5 M  $Li_2SO_4$  and Na<sub>2</sub>SO<sub>4</sub> as a function of the scan rate.



Figure S6. The specific capacitance of the as-prepared- $MnO_x$  as a function of the scan rate.



Figure S7. CV curves of (a) Li-MnO<sub>x</sub>, (b) Ca-MnO<sub>x</sub>, (c) Sr-MnO<sub>x</sub>, and (d) Ba-MnO<sub>x</sub> at various scan rates.



Figure S8. GCD curves of (a) Li-MnO<sub>x</sub>, (b) Ca-MnO<sub>x</sub>, (c) Sr-MnO<sub>x</sub> and (d) Ba-MnO<sub>x</sub> at various current densities.



**Figure S9.** The stability test of the as-prepared  $MnO_x$  at 3 A g<sup>-1</sup>.



**Figure S10.** (a.) The complex power analysis as well as (b) Bode plot of Li-MnO<sub>x</sub>, Ca-MnO<sub>x</sub>, Sr-MnO<sub>x</sub>, and Ba-MnO<sub>x</sub>.

The relaxation-time constant ( $\tau_0$ ) was calculated by the complex power analysis diagram in Figure S10a. The  $\tau_0$  values correspond to the crossing frequency of Li-MnO<sub>x</sub>, Ca-MnO<sub>x</sub>, Sr-MnO<sub>x</sub>, and Ba-MnO<sub>x</sub> which are equal to 4.04, 3.35, 2.55, and 3.70 s, respectively. The phase angles of all samples (See Figure S10b) are below  $-90^\circ$  as low frequency range demonstrating a pseudocapacitor.<sup>22</sup>



**Figure S11.** *Ex*-situ Raman spectra of the pristine and the charged  $\delta$ -MnO<sub>x</sub> electrodes.

Notably, the peak observed at ~640 cm<sup>-1</sup> corresponds to the birnessite- $MnO_2^{23}$  and the intermediate phase of MnOOH (birnessite-type) can be observed at 575 cm<sup>-1</sup> after charged.<sup>24</sup>

Table S2. E0 and Mn oxidation states obtained from ex situ Mn K-eage XANES spectra	a.

Sample	Applied potential	Absorption threshold	Mn oxidation
		energy (eV)	state
Li-MnO <sub>x</sub>	-	6550.65	3.68
Ca-MnO <sub>x</sub>	-	6550.60	3.67
Sr-MnO <sub>x</sub>	-	6550.80	3.73
Ba-MnO <sub>x</sub>	-	6550.87	3.75
	-0.1 V vs. SCE	6550.61	3.67
Li-MnO <sub>x</sub>	0.8 V vs. SCE	6551.70	4.00
	-0.1 V vs. SCE return	6550.70	3.70
	-0.1 V vs. SCE	6550.30	3.58
Ca-MnO <sub>x</sub>	0.8 V vs. SCE	6551.23	3.86
	-0.1 V vs. SCE return	6550.38	3.60
	-0.1 V vs. SCE	6550.70	3.70
Sr-MnO <sub>x</sub>	0.8 V vs. SCE	6551.45	3.92
	-0.1 V vs. SCE return	6550.70	3.70
	-0.1 V vs. SCE	6550.60	3.67
Ba-MnO <sub>x</sub>	0.8 V vs. SCE	6551.20	3.85
	-0.1 V vs. SCE return	6550.60	3.67

Cations	Exp. (kcal mol <sup>-1</sup> ) <sup>25</sup>	DFT (kcal mol <sup>-1</sup> )	
Li <sup>+</sup>	122	204	
Ca <sup>2+</sup>	381	500	
Sr <sup>2+</sup>	346	465	
Ba <sup>2+</sup>	315	436	

**Table S3.** The DFT binding energies for the first hydration shell ( $n_{H2O} = 6$ ) for different cations.

**Table S4.** The specific capacitances of manganese oxide electrodes compared with other reports.

Materials	Structure	Morphology	Electrolyte	Capacitance	Cycling	Ref.
					stability	
MnO <sub>2</sub>	pyrolusite	hollow	0.5 M	159.2 F g <sup>-1</sup>	81.5% after	[26]
	and	microspheres	Na <sub>2</sub> SO <sub>4</sub>	at 2 mV s <sup>-1</sup>	10,000 cycles	
	ramsdellite	-			-	
α-MnO <sub>2</sub>	hollandite	nanospheres	0.5 M	$138.4 \text{ F g}^{-1}$	90% after	[27]
		_	Na <sub>2</sub> SO <sub>4</sub>	at 1 A $g^{-1}$	15,000 cycle	
Li <sup>+</sup> -layered	birnessite	Nanosheets	0.2 M	147 F g <sup>-1</sup> at	99% after	[28]
MnO <sub>2</sub>			Li <sub>2</sub> SO <sub>4</sub>	$0.5 \text{ mA cm}^{-2}$	1,000 cycles	
					-	
Cs0.2MnO2	birnessite	hollow	0.5 M	155 F g <sup>-1</sup>	~100% after	[29]
		microflowers	K <sub>2</sub> SO <sub>4</sub>	at 1 A $g^{-1}$	1,000 cycles	
					•	
Li-MnO <sub>x</sub>	birnessite	Nanosheets	1.0 M	157 F g <sup>-1</sup>	~100% after	[2]
			Na <sub>2</sub> SO <sub>4</sub>	at 0.5 A $g^{-1}$	1,000 cycles	
					-	
Na-MnO <sub>x</sub>	birnessite	Nanosheets	1.0 M	109 F g <sup>-1</sup>	~100% after	[2]
			Na <sub>2</sub> SO <sub>4</sub>	at 0.5 A $g^{-1}$	1,000 cycles	
				C C	•	
Li-MnO <sub>x</sub>	birnessite	Nanosheets	0.5 M	148.2 F g <sup>-1</sup>	~100% after	This
			Li <sub>2</sub> SO <sub>4</sub>	at 1 A $\tilde{g^{-1}}$	1600 cycles	work
Ca-MnO <sub>x</sub>	birnessite	Nanosheets	0.5 M	172.6 F g <sup>-1</sup>	96 % after	This
			Li <sub>2</sub> SO <sub>4</sub>	at 1 A $g^{-1}$	11,000 cycles	work
				E E		

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