Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Activation of MnO_2 cathode by water-stimulated Mg^{2+} insertion for magnesium ion battery

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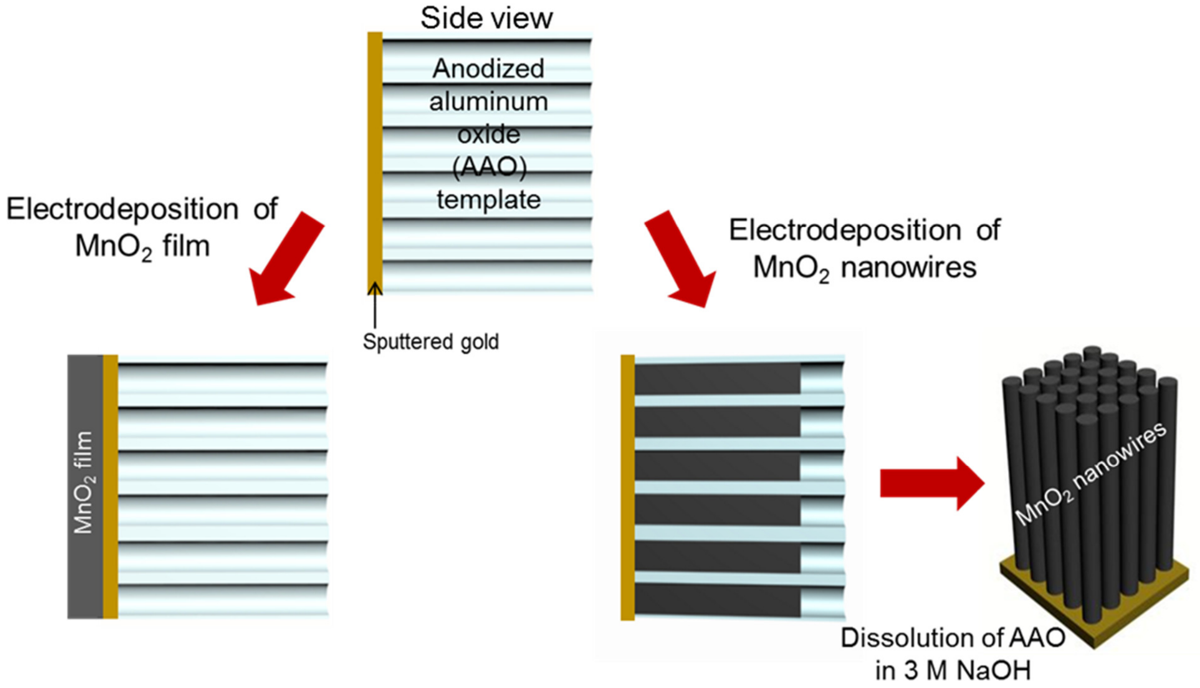


Figure S1. Schematic of electrodeposition of MnO_2 process. Anodized aluminum oxide (AAO) template was used as substrate/template for both film and nanowire structured MnO_2.

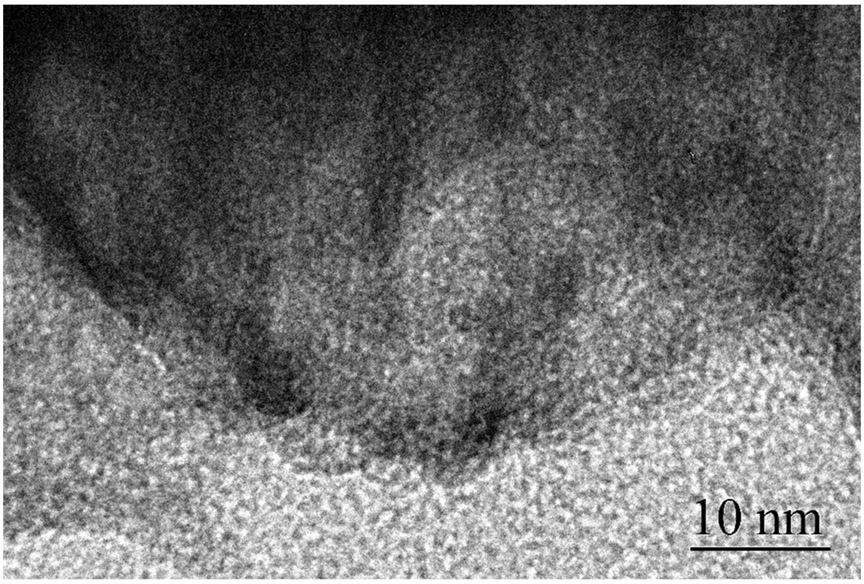


Figure S2. High resolution TEM of as-prepared MnO_2 nanowire

Table S1. List of electrolytes used in this work. Water concentration was confirmed by Karl-Fisher Coulometer.

Electrolyte	**H_2O/Mg^{2+} Ratio**
i) 0.1 M Mg^{2+} / no water (i.e. 0.1 M $Mg(ClO_4)_2$ Anhydrous)	**0** (= 0/0.1)
ii) 0.5 M Mg^{2+} / 0.6 M H_2O (i.e. 0.1 M $Mg(ClO_4)_2 \cdot 6H_2O$ + 0.4 M $Mg(ClO_4)_2$ Anhydrous)	**1.2** (= 0.6/0.5)
iii) 0.2 M Mg^{2+} / 0.6 M H_2O (i.e. 0.1 M $Mg(ClO_4)_2 \cdot 6H_2O$ + 0.1 M $Mg(ClO_4)_2$ Anhydrous)	**3** (= 0.6/0.2)
iv) 0.1 M Mg^{2+} / 0.6 M H_2O (i.e. 0.1 M $Mg(ClO_4)_2 \cdot 6H_2O$)	**6** (= 0.6/0.1)
v) 0.1 M Mg^{2+} / 1.2 M H_2O (i.e. 0.1 M $Mg(ClO_4)_2 \cdot 6H_2O$ + 0.6 M H_2O)	**12** (= 1.2/0.1)

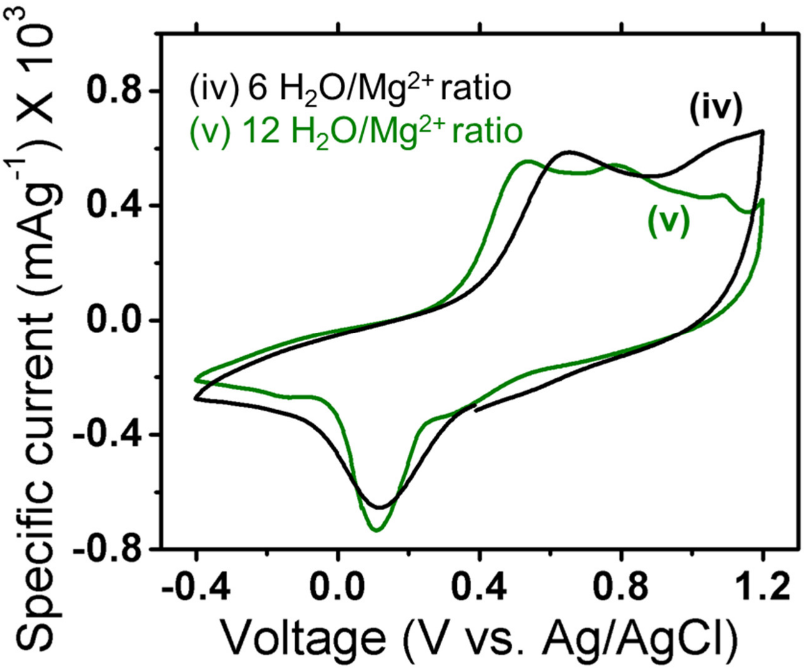


Figure S3. Cyclic voltammograms of MnO_2 nanowire electrodes in electrolytes with 6 H_2O/Mg^{2+} ratio and 12 H_2O/Mg^{2+} ratio measured at a scan rate of 0.5 mVs^{-1}.

Figure S2 compares the CV curves of MnO_2 nanowire electrode measured in the electrolyte with 12 and 6 H_2O/Mg^{2+} ratios. Although the cathodic peak intensities of the CV curves from the two electrolytes are similar, the calculated capacity is higher in the electrolyte with 6 H_2O/Mg^{2+} ratio. The observed decrease in Mg^{2+} insertion in the electrolyte with 12 H_2O/Mg^{2+} ratio is believed to be due to the size of the coordinated Mg^{2+} ion and water molecule clusters which may hinder the insertion of Mg^{2+} ions into MnO_2. Moreover, in the electrolyte with 12 H_2O/Mg^{2+} ratio, there are additional small peaks observed in anodic scan direction which can be attributed to the side reactions involving water molecules upon the increase in water concentration.

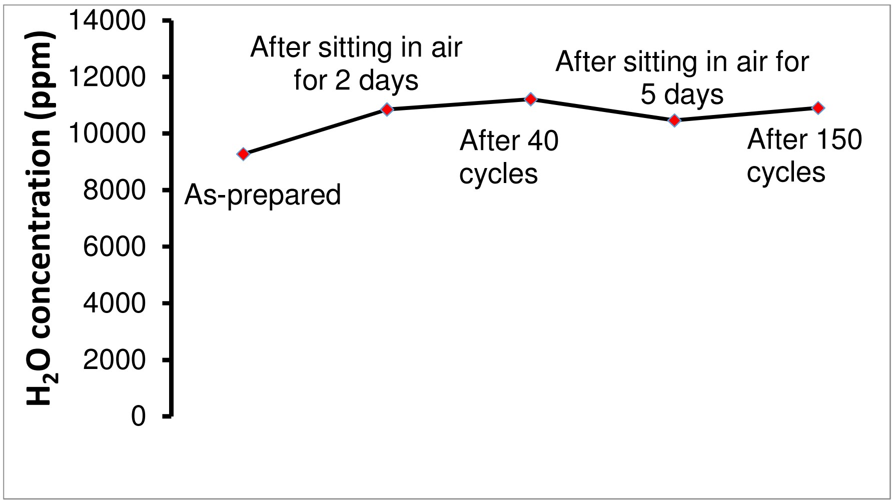


Figure S4. Concentration of water of 0.1 M $Mg(ClO_4)_2 \cdot 6H_2O$/PC at various states measured by Karl-Fisher Coulometer.

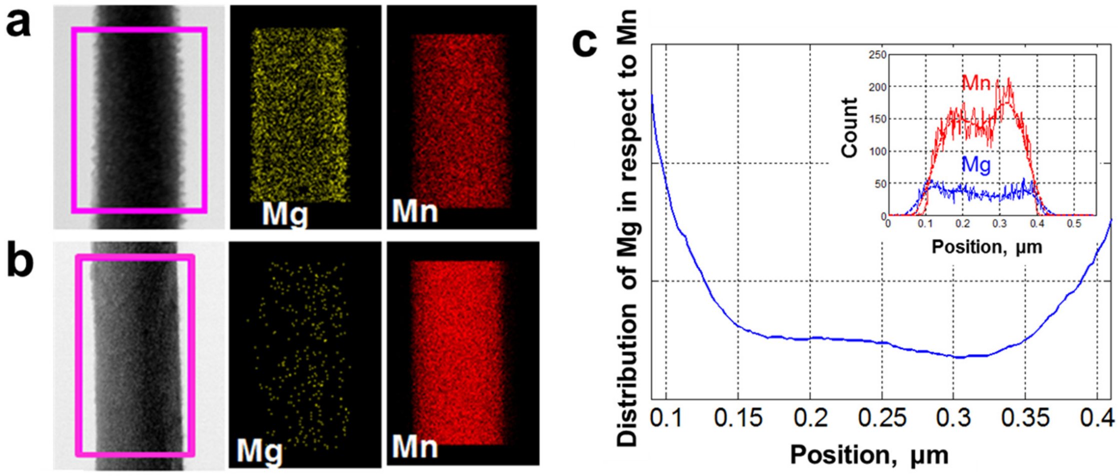


Figure S5. TEM EDS analysis of MnO_2 nanowire. Elemental mapping of Mg and Mn for MnO_2 nanowire (a) after discharged at -0.4 V (vs. Ag/AgCl) and (b) after recharged at 1.2 V (vs. Ag/AgCl) by holding potential experiment in the electrolyte with 6 H_2O/Mg^{2+} ratio. (c) TEM elemental line scan results (inset) and analysis result representing the aspect of Mg distribution within the discharged MnO_2 nanowire (a).

Figure S5a shows TEM EDS elemental mapping images of Mg and Mn of a discharged MnO_2 nanowire electrode (held at -0.4 V vs. Ag/AgCl). The presence of Mg is clearly observed in the nanowire. In addition, it can be seen that the surface of the discharged MnO_2 nanowire became very rough compared to the as-prepared MnO_2. This is probably the result of a structural change and volume expansion of MnO_2 upon the insertion Mg^{2+} ions upon the extensive holding potential experiment at a reductive potential value of -0.4 V vs. Ag/AgCl. In the MnO_2 nanowire electrode (Figure S5b) held at 1.2 V followed by discharging at -0.4 V, it is clear that almost all of the Mg^{2+} ions had been removed, indicating the great reversibility of Mg^{2+} insertion/deinsertion process of this system. Figure S5c (inset) shows an EDS line scan analysis of discharged MnO_2 nanowire electrode. In order to study the distribution of magnesium within the nanowire, we took the Mn line scan analysis trend as uniform distribution and relative distribution of Mg in respect to Mn was analyzed (Figure S5c) using the overlapping Mn and Mg line scan range. It shows that Mg is more concentrated near the surface/edge of MnO_2 nanowire rather than the center, which implies that Mg^{2+} ions are first inserted into the outer shell of the MnO_2 when chronoamperometric measurement is applied, hence it is more concentrated near the surface/edge of MnO_2 nanowire rather than the center. This also suggests that it is possible to obtain higher specific capacity and rate performance when MnO_2 electrodes with smaller particle sizes are utilized.

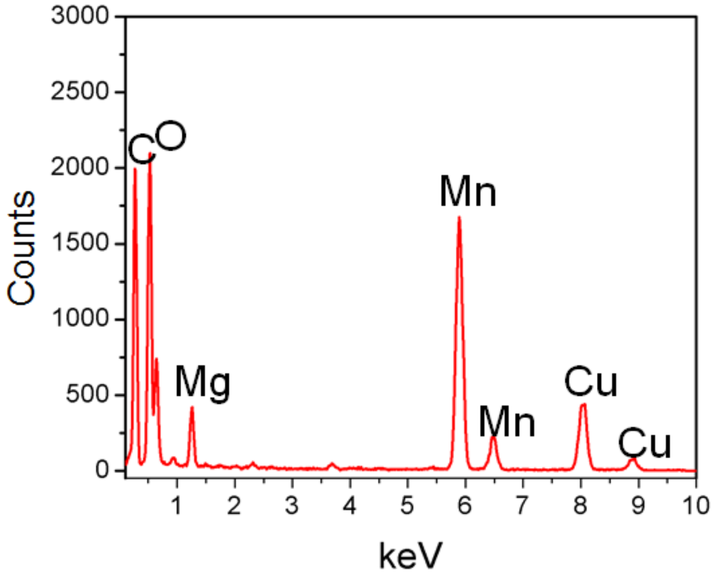


Figure S6. EDS spectrum of discharged MnO_2 nanowire after 11 CV cycles in the electrolyte with $6H_2O/Mg^{2+}$ ratio**.**

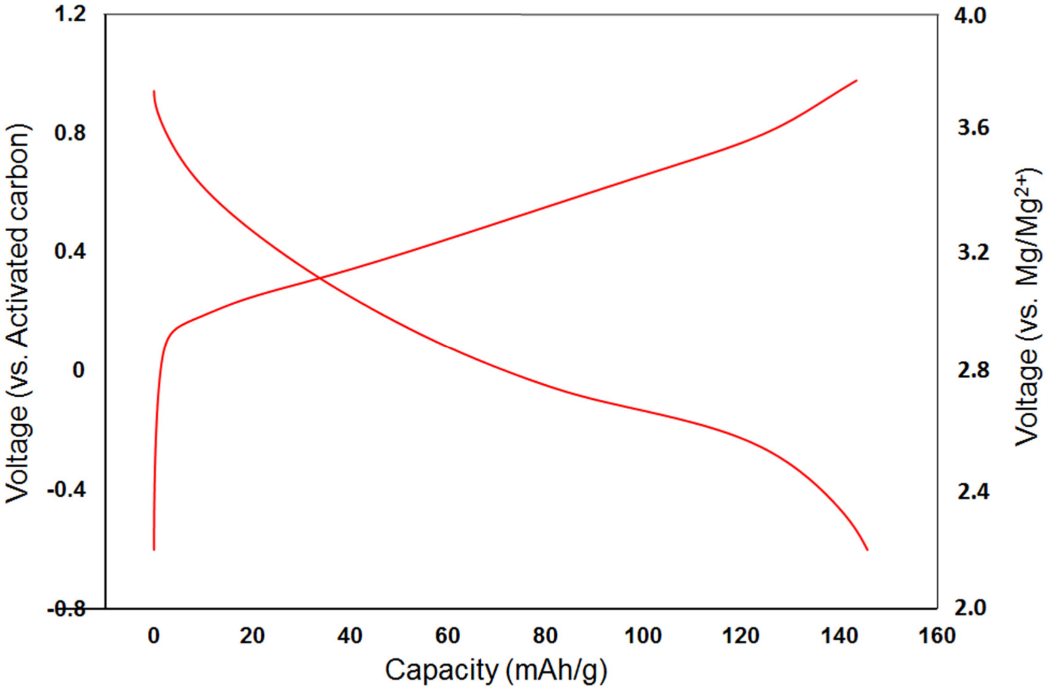


Figure S7. Galvanostatic charge and discharge curve of MnO_2 nanowire electrode in 0.1 M $Mg(ClO_4)_2 \cdot 6H_2O$/PC electrolyte at a 1.6 C rate. Activated carbon electrode was used as both reference and counter electrode.

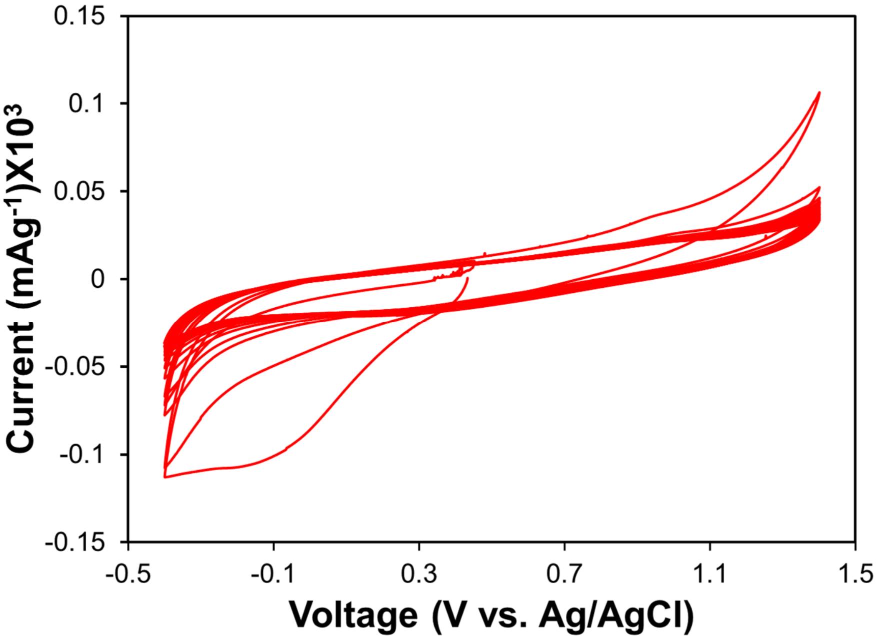


Figure S8. CV of MnO2 nanowire electrode measured in 0.1 M Mg(ClO_4)$_2$/PC for 23 cycles at a scan rate of 0.5 mVs^{-1}.

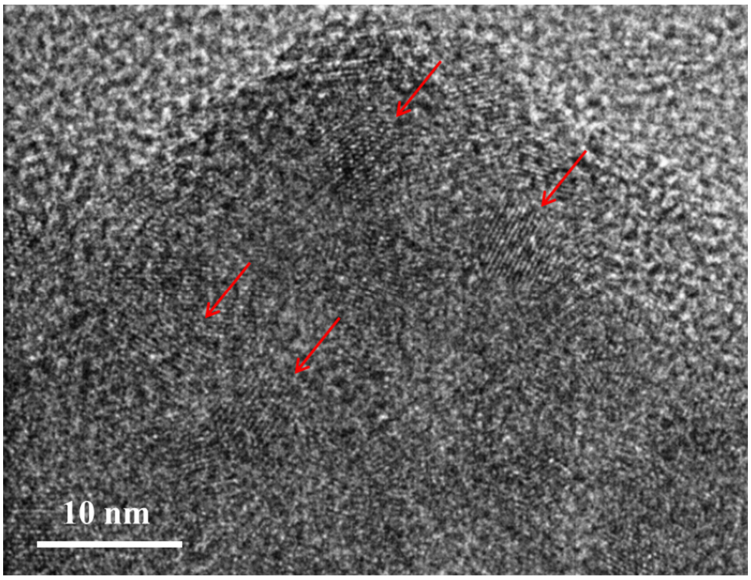
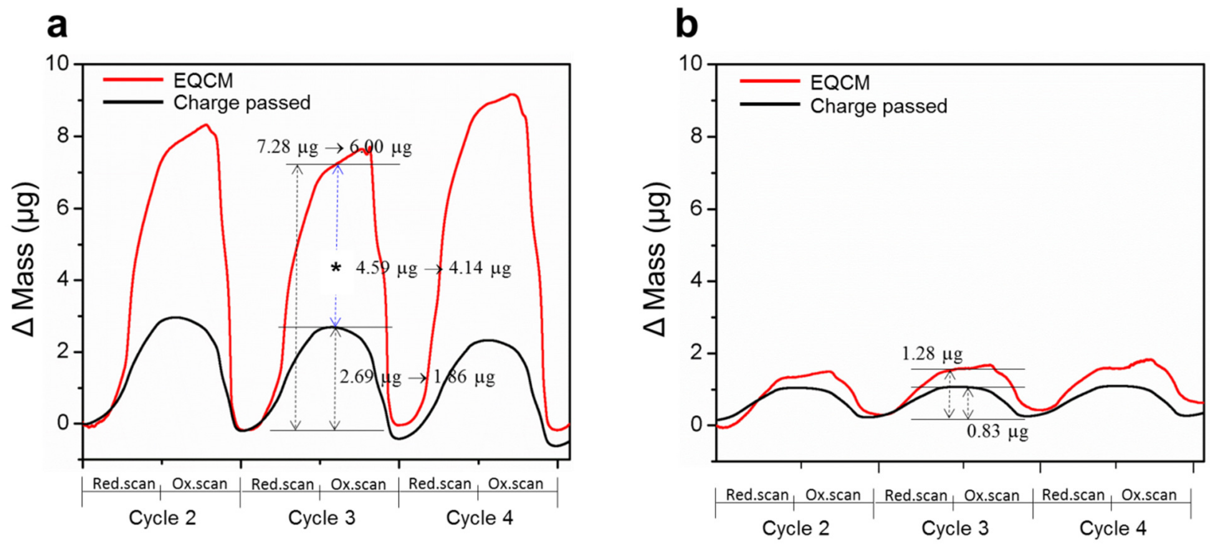


Figure S9. High resolution TEM image of MnO_2 nanowire electrode after cycling in 0.1 M $Mg(ClO_4)_2 \cdot 6H_2O$/PC for 10 cycles. Crystal domains with ~ 6 nm sizes are indicated by red arrows. Corresponding EDS analysis (Fig. S6) showed that there is no electrolyte residue remained.

EQCM Data Analysis



Sauerbrey equation was used to calculate the mass change based on the frequency change of the quartz crystal electrode:

$$\Delta \mathrm{f} = -C_f \cdot \Delta m$$

where Δf is observed frequency change in Hz, Δm is the change in mass per unit area in g/cm^2, and C_f is the sensitivity factor for the crystal in Hz µg^{-1} cm^2. Prior any measurement the EQCM was calibrated for C_f value using Cu plating/stripping technique in 10 mM of $CuSO_4$ and 1 M of H_2SO_4 solution. The mass changed based on the amount of charge passed was calculated according to Faraday’s law.

Assuming that the mass change calculated by the amount of charge passed during CV scan is solely coming from the Mg^{2+} insertion/deinsertion, the difference in mass change values between EQCM and amount of charge (marked as *) was regarded as the mass change by incorporation of the water molecules into MnO_2. However, it should be noted that the difference in mass change values (*) was also observed in dry Mg electrolyte condition (< 1000 ppm) as can be seen from Figure 8b. Thus, the mass change values observed for dry Mg electrolyte were regarded as background signals which may have resulted by the surface-adsorbed Mg^{2+} species without water incorporation and other possible non-water related ion-pairing interaction at the electrode surface. The mass change due to water incorporation (*) and mass changed due to Mg^{2+}

insertion were determined to be 4.14 μg and 1.86 μg, respectively. After converting these masses into moles of H_2O and Mg, it was determined that about 3 equivalent moles of water molecule per 1 mole of Mg^{2+} are estimated to co-exist in MnO_2 after the reductive scan in the water containing Mg electrolyte. While it is possible that these components contributing to the background may behave differently in the wet condition than in dry condition, note that the presented water incorporation amount only gives us an approximation value.