Electronic Supplementary Information
Conversions of Mn oxides to nanolayered Mn oxides in electrochemical water oxidation at near neutral pH, all to a better catalyst: catalyst evolution

Mohammad Mahdi Najafpour*<sup>a,b</sup>, Behzad Haghighi,<sup>a,b</sup> Davood Jafarian Sedigh<sup>a</sup> and Mohadeseh Zarei Ghobadi<sup>a</sup>

<sup>a</sup>Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran
<sup>b</sup>Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

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Experimental

Materials
All reagents were purchased from commercial sources (Merck, Aldrich and Daejung) and were used without further purification.

Synthesis of compounds
All oxides were synthesized by previously reported methods.\textsuperscript{1-3}

Characterization
TEM and SEM images were obtained with Philips CM120, VEGA\textregistered TESCAN-XMU and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-K\textalpha radiation).

Preparation of electrochemical cell\textsuperscript{4}
We constructed an electrochemical cell consisting of two half-cells, in which the reference half-cell included a platinum plate as an electrode and 1 M KCl solution as electrolyte (cathode). The electrode of working half-cell was the same as the reference electrode which dipped into a 0.1 M LiClO\textsubscript{4} solution (anode). The electrodes of the half-cells were connected by a wire to provide charge carrying in the external circuit. In order to maintain electrical neutrality in each half-cell, a salt bridge was applied. It was constructed using a glass U-tube filled with a mixture of 5% agar in 1M KCl. In anode half-cell, Mn oxide compounds were suspended in the electrolyte under continuous stirring such that they collide with positively charged working electrode. In this case, by applying constant potential of 2 V, Mn oxides can oxidize in the encounter with electrode.
Fig. S1 Set up for electrochemical water oxidation.
Fig. S2  Pourbaix diagrams for Mn. Layered Mn oxide is the most stable Mn oxide in high enough potential. Image is from ref.5 with modification.
Fig. S3 TEM image from Mn$_2$O$_3$ after using as water oxidizing catalysts in a water electrolysis device for two weeks. Orange and white arrows show old phase and new layered Mn oxide. As shown in the image, the layers are extended around the old Mn oxides.
Fig. S4 SEM images of CaMn$_3$O$_6$. 
Fig. S5 SEM images of CaMn$_3$O$_6$ (attached to the electrode) after electrochemical water oxidation at pH = 6.3 for 330 hours.
Fig. S6 SEM images of CaMn$_3$O$_6$ (dispersed in solution) after electrochemical water oxidation at pH = 6.3 for 330 hours.
Fig. S7 SEM images of CaMn$_4$O$_8$. 
Fig. S8 SEM images of CaMn$_4$O$_8$ (attached to the electrode) after electrochemical water oxidation at pH = 6.3 for 330 hours.
Fig. S9 SEM images of CaMn$_4$O$_8$ (dispersed in solution) after electrochemical water oxidation at pH = 6.3 for 330 hours.
Fig. S10 SEM images of Mn$_2$O$_3$. 
Fig. S11 SEM images of Mn$_2$O$_3$ (attached to the electrode) after electrochemical water oxidation at pH = 6.3 for 330 hours.
Fig. S12 SEM images of Mn$_2$O$_3$ (dispersed in solution) after electrochemical water oxidation at pH = 6.3 for 330 hours.
Fig. S13 SEM images of Mn$_3$O$_4$. 
Fig. S14 SEM images of Mn$_3$O$_4$ (attached to the electrode) after electrochemical water oxidation at pH = 6.3 for 330 hours.
Fig. S15 SEM images of Mn$_3$O$_4$ (dispersed in solution) after electrochemical water oxidation at pH = 6.3 for 330 hours.
Fig. S16 SEM images of layered Mn Oxide.
Fig. S17 SEM images of layered Mn oxide.
Water Oxidation

Oxygen evolution from aqueous solutions in the presence of (NH₄)₂Ce(NO₃)₆ (Ce(IV)) was measured using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout. The reactor was maintained at 25.0 ºC in a water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continually with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, water in the reactor was replaced with Ce(IV) solution. Without catalyst, Ce(IV) was stable in this condition and oxygen evolution was not observed. After deaeration of Ce(IV) solution with argon, manganese oxides as several small particles were added, and oxygen evolution was recorded with the oxygen meter under stirring (Fig. S4). The formation of oxygen followed, and oxygen formation rates per manganese site were obtained from linear fits of the data by the initial rate.

Fig. S18. The reactor set-up for oxygen evolution experiment from aqueous solution in the presence of Ce(IV) and manganese oxide within Faujasite zeolite.
Fig. S19 Oxygen evolution from Mn$_2$O$_3$ before (red) and after using as water oxidizing catalyst in a water electrolysis device for two weeks ([Ce(IV)] = 0.11 M, 40 mL, catalyst = 2.0 mg ).
Fig. S20 Oxygen evolution from CaMn$_3$O$_6$ (red) and after using as water oxidizing catalyst in a water electrolysis device for two weeks ([Ce(IV)] = 0.11 M, 40 mL, catalyst = 5.0 mg).
Fig. S21 Oxygen evolution from CaMn₄O₈ (red) and after using as water oxidizing catalyst in a water electrolysis device for two weeks ([Ce(IV)] = 0.11 M, 40 mL, catalyst = 2.0 mg ).
Fig. S22 Oxygen evolution from Mn₃O₄ (red) and after using as water oxidizing catalyst in a water electrolysis device for two weeks ([Ce(IV)] = 0.11 M, 40 mL, catalyst = 2.0 mg ).
References