Electronic Supplementary Information

Chemical etching manganese oxides for electrocatalytic oxygen reduction reaction

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Experimental

Synthesis of MnO and Mn_2O_3

The preparation of pristine MnO and Mn_2O_3 microspheres followed a two-step route: Synthesis of $MnCO_3$ precursors through a co-precipitation method and calcination of $MnCO_3$ under different conditions.[S1, S2] Briefly, 0.338 g of $MnSO_4 \cdot H_2O$ and 0.79 g of NH_4HCO_3 were separately dissolved in 20 mL and 40 mL of deionized water. Then, the NH_4HCO_3 solution was directly added into the $MnSO_4$ solution under sonication. The mixture was stirred for 30 minutes and aged at room temperature. The as-obtained precipitates were centrifuged and washed sequentially with deionized water and absolute alcohol several times. After being vacuum-dried at 60 °C overnight, the precursors were calcined at 400 °C for 6 h in H_2/Ar to obtain porous MnO microspheres. The Mn_2O_3 microspheres were prepared by calcining

$MnCO_3$ at 600 °C for 10 h in air.

Synthesis of mixed-valent MnO_x

The MnO or Mn_2O_3 was used as the pristine materials to synthesize MnO_x ($1 < x < 2$). In a typical procedure, 50 mg MnO or Mn_2O_3 was treated with 25 mL of CAN acidic solution with vigorous stirring under different reaction conditions (Table S1). The synthesized materials were centrifuged, washed with water and absolute alcohol, and finally dried overnight at 60 °C in air.

Table S1 The reaction conditions of processing MnO or Mn_2O_3 with CAN acidic solution.

Samples	Reaction conditions			
	Precursor	**Concentration/mol L^{-1}**	**time/h**	**Temperature/K**
MnO_x-1	MnO	0.1	1	298
MnO_x-2	MnO	0.5	1	298
MnO_x-3	MnO	1	1	298
MnO_x-4	Mn_2O_3	2	3	353
MnO_x-5	Mn_2O_3	2	3	373
MnO_x-6	Mn_2O_3	2	3	393

Synthesis of bulk MnO and Mn_2O_3

The bulk MnO and Mn_2O_3 were synthesized by conventional solid-state method. Typically, the bulk MnO was prepared by calcining the commercial manganese acetate tetrahydate at 400 °C for 10 h in H_2/Ar, while manganese acetate tetrahydate was calcinated at 600 °C for 10 h in air to obtain bulk Mn_2O_3.

Material characterization

The prepared materials were characterized by different analytical techniques, including power X-ray diffraction (XRD) on a Rigaku X-2500 diffractometer using Cu Kα radiation, scanning electron microscopy (SEM, JEOL JSM-7500F), transmission electron microscopy (TEM, Philips Tecnai F20), X-ray photoelectron spectroscopy (XPS, Perkin Elmer PHI 1600 ESCA system), and N_2 adsorption/desorption measurement (BEL Sorp mini). The oxidation state of Mn was measured by chemical titration: 10 mg obtained MnO_x samples were dissolved in 15 mL 0.5 M H_2SO_4 and 5 mL 83 wt.% H_3PO_4 with an excess of $Fe(NH_4)_2(SO_4)_2$ solution. The mixed solution was titrated with calibrated $KMnO_4$ solution. The relevant equations of chemical titration include:

$$MnO_x + (2x-2)Fe^{2+} + 2xH^+ = Mn^{2+} + (2x-2)Fe^{3+} + xH_2O \tag{1}$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ = Mn^{2+} + 5Fe^{3+} + 4H_2O \tag{2}$$

Table S2 The Mn oxidation states of MnO_x obtained by chemical titration.

Samples	**Mn valence state**	**Composition**
MnO	2	MnO
MnO_x-1	2.24	$MnO_{1.12}$
MnO_x-2	2.30	$MnO_{1.15}$
MnO_x-3	2.34	$MnO_{1.17}$
Mn_2O_3	2.98	$MnO_{1.49}$
MnO_x-4	3.20	$MnO_{1.60}$
MnO_x-5	3.48	$MnO_{1.74}$
MnO_x-6	3.64	$MnO_{1.82}$

Electrochemical tests

Electrochemical measurements were carried out with a standard three-electrode cell under room temperature. Platinum foil and saturated calomel electrode (SCE) were served as the counter electrode and reference electrode, respectively. A glassy carbon electrode (GCE) loaded with a thin catalyst film was used as the working electrode. The thin catalyst film was prepared as follows: 3 mg of as-synthesized samples and 7 mg of carbon powders (Carbon Vulcan XC-72) were dispersed in 1 mL of isopropanol solvent with 50 μL of Nafion (5 wt.%, Sigma-Aldrich) through 30 minutes sonication in order to make a homogenous ink. The carbon powders were used to improve the conductivity. Then, 10 μL of the prepared suspension was loaded on a rotation ring-disk electrode (RRDE, diameter 5.61 mm) and dried overnight under isopropanol atmosphere at room temperature. All tests were conducted in 0.1 M aqueous KOH electrolyte saturated with high-purity O_2 by bubbling O_2 for at least 30 minutes and maintained under O_2 atmosphere during the test. The RRDE measurement was performed within a potential range of 0.1 to -0.8 V (ORR) versus SCE at a scanning rate of 5 mV s^{-1}. Unless stated, all potentials of SCE were calibrated as +0.99 V with respect to the reversible hydrogen electrode (RHE). Calculation of kinetic current density (I_k) follows equation (3):

$$I_k = \frac{i i_d}{i_d - i} \tag{3}$$

where i is measured current density and i_d is the limiting current density.

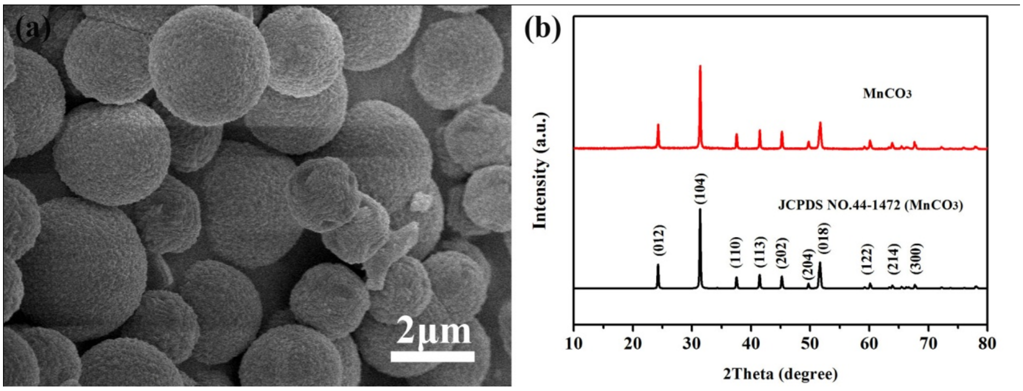

Fig. S1 SEM image and XRD pattern of precursor $MnCO_3$.

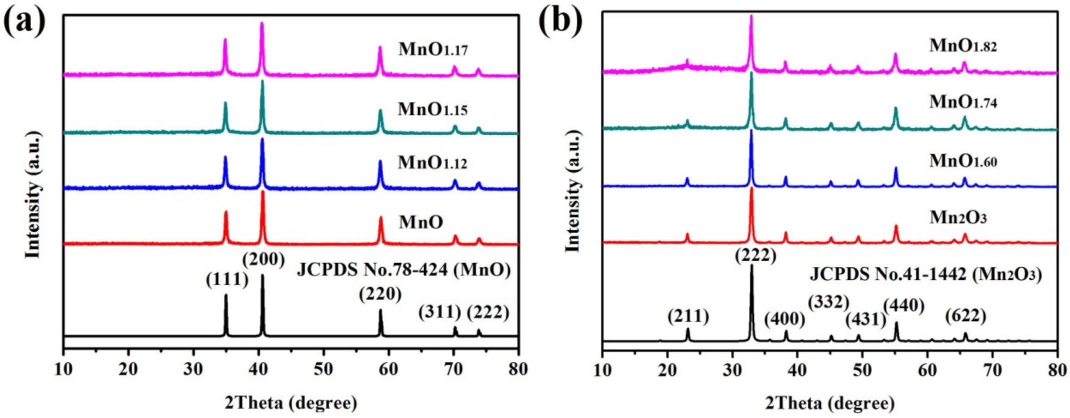

Fig. S2 XRD patterns of the synthesized manganese oxides.

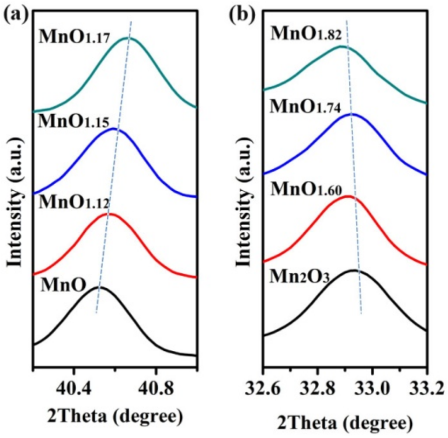

Fig. S3 Enlargement of the strongest diffraction peaks of synthesized manganese oxides shown in Fig. S2.

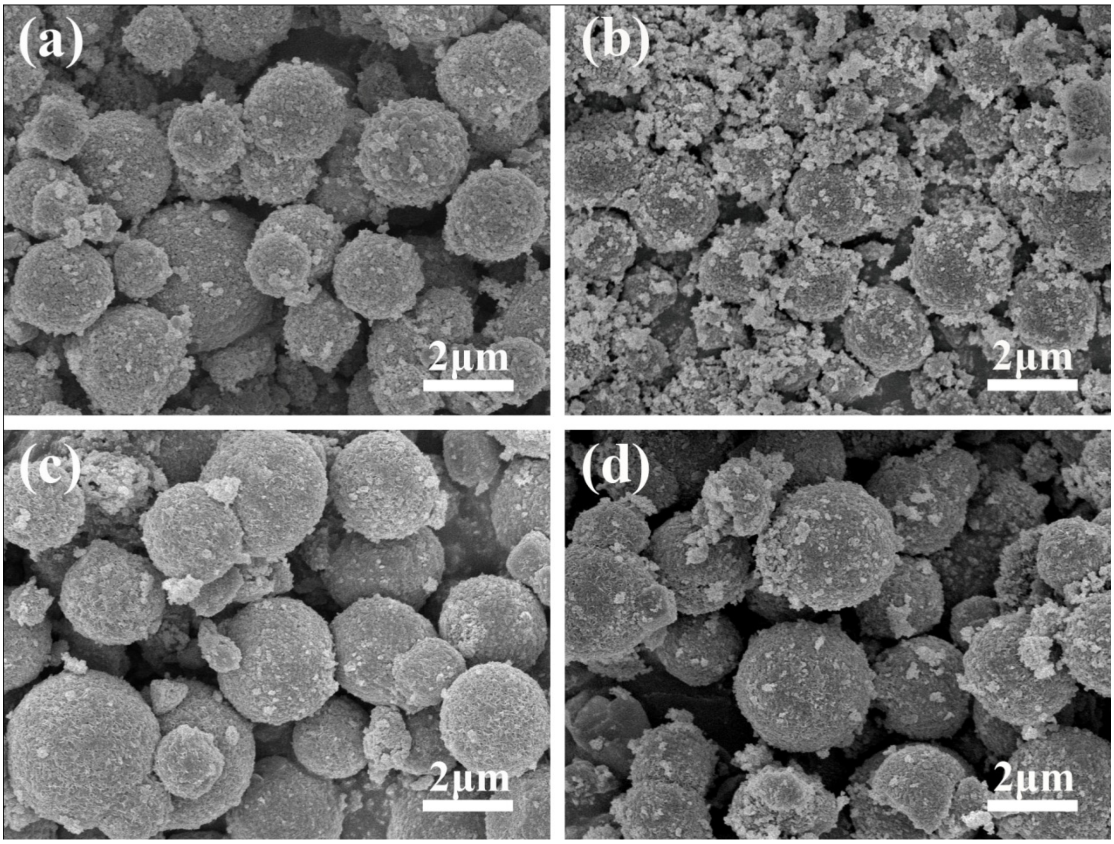

Fig. S4 SEM images of (a) $MnO_{1.12}$, (b) $MnO_{1.17}$, (c) $MnO_{1.60}$, and (d) $MnO_{1.82}$.

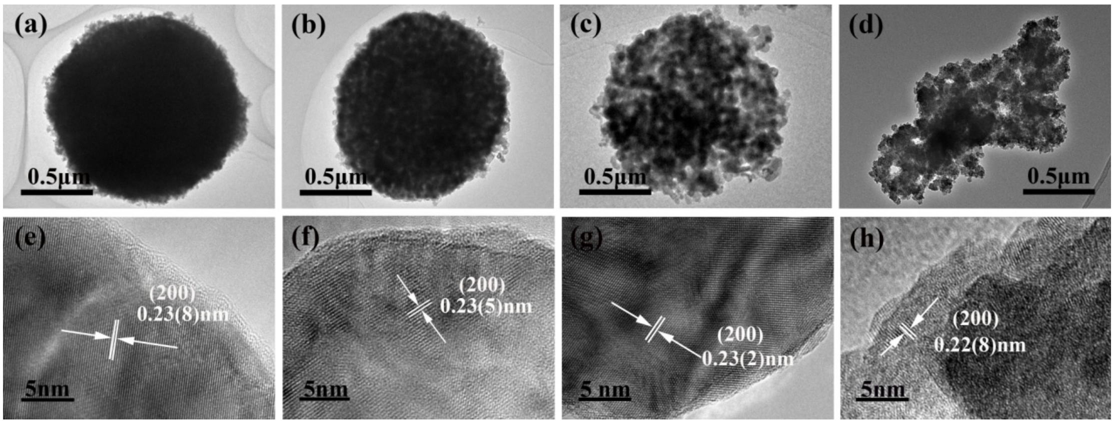

Fig. S5 TEM images of (a,e) MnO, (b,f) $MnO_{1.12}$, (c,g) $MnO_{1.15}$, and (d,h) $MnO_{1.17}$.

The parenthesis value indicates uncertainty.

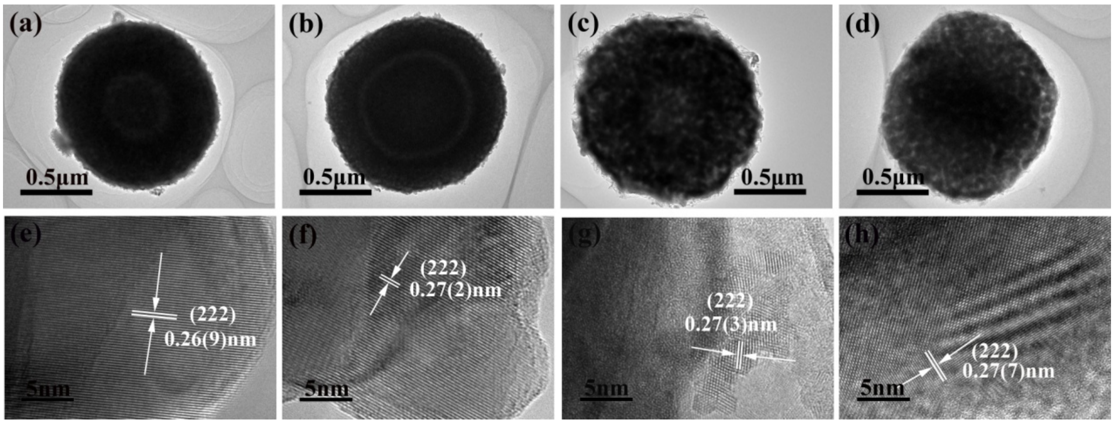

Fig. S6 TEM images of (a,e) Mn_2O_3, (b,f) $MnO_{1.60}$, (c,g) $MnO_{1.74}$, and (d,h) $MnO_{1.82}$.

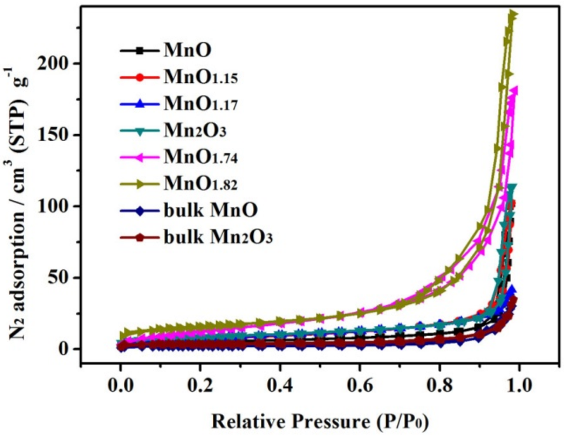

Fig. S7 N_2 sorption isotherms (measured at 77K) of MnO_x ($1<x<2$)

Table S3 Pore volume and BET specific surface area of MnO_x.

Samples	**Pore volume ($cm^3\ g^{-1}$)**	**Surface area ($m^2\ g^{-1}$)**
MnO	0.158	14.98
$MnO_{1.15}$	0.158	24.24
$MnO_{1.17}$	0.156	25.54
Mn_2O_3	0.176	29.39
$MnO_{1.74}$	0.178	44.57
$MnO_{1.82}$	0.192	54.74

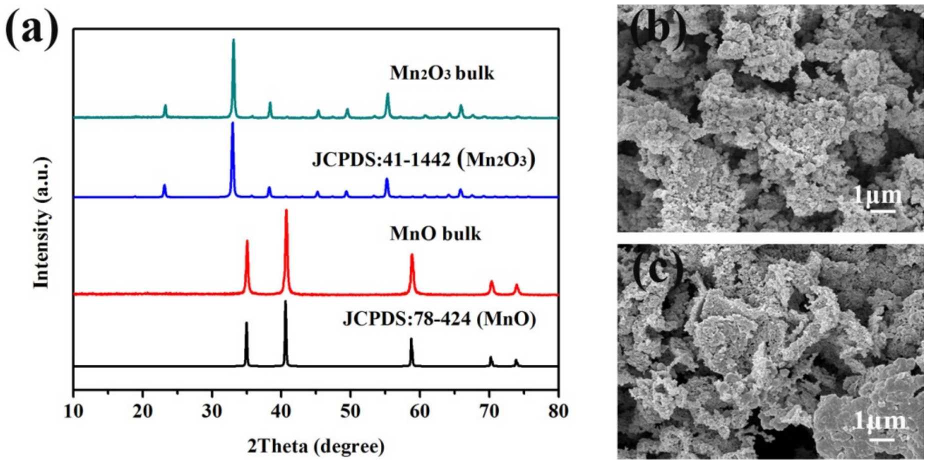

Fig. S8 (a) XRD patterns and (b,c) SEM images of (b) bulk MnO and (c) bulk Mn_2O_3.

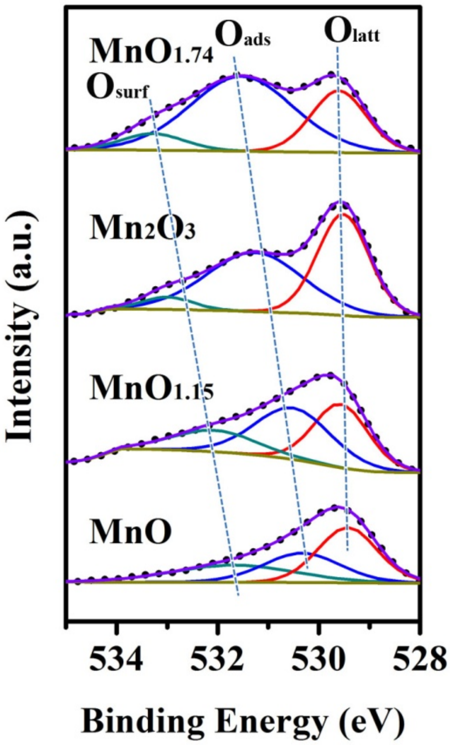

Fig. S9 O1s spectra of the synthesized MnO, $MnO_{1.15}$, Mn_2O_3, and $MnO_{1.174}$. O_{sur}, O_{ads}, and O_{latt} represent molecular H_2O fixed on surface, adsorbed oxygen species such as O_2^{2-} or OH^-, and lattice oxygen, respectively.

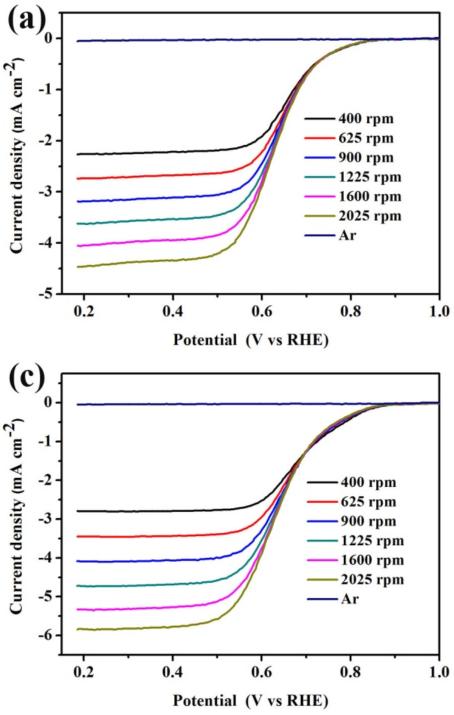

Fig. S10 LSVs of (a) MnO, (b) $MnO_{1.12}$, (c) $MnO_{1.15}$, and (d) $MnO_{1.17}$ recorded in Ar- and O_2-saturated 0.1 M KOH solution.

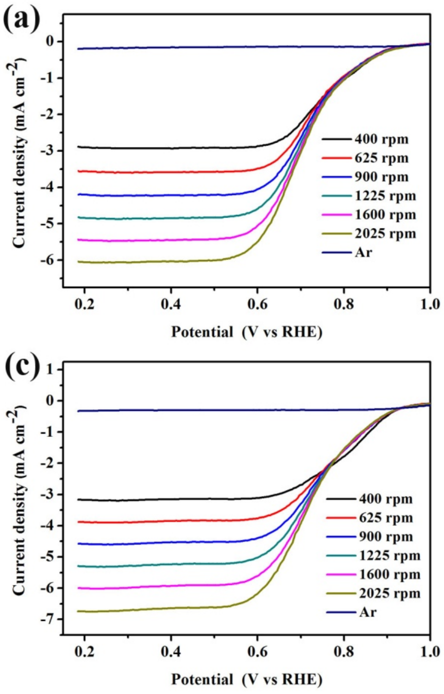

Fig. S11 LSVs of (a) Mn_2O_3, (b) $MnO_{1.60}$, (c) $MnO_{1.74}$, and (d) $MnO_{1.82}$ recorded in Ar- and O_2-saturated 0.1 M KOH solution.

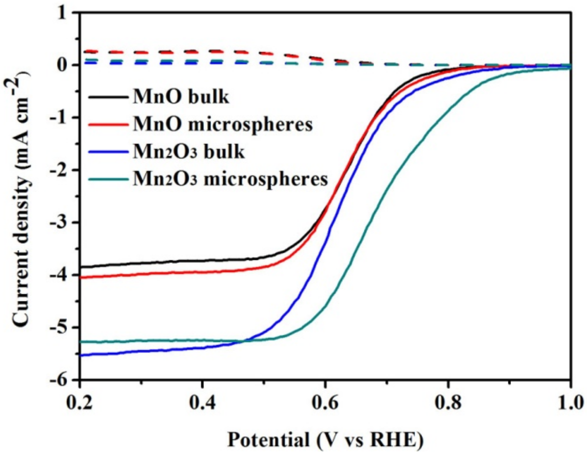

Fig. S12 The polarization curves of MnO (bulk and microspheres) and Mn_2O_3 (bulk and microspheres) recorded at 1600 rpm in O_2-saturated 0.1 M KOH solution.

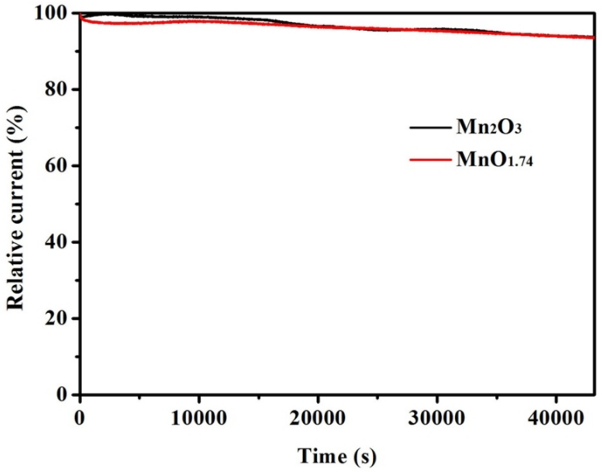

Fig. S13 Chronoamperometric curves (percentage of retained current as a function of operation time) of Mn_2O_3 and $MnO_{1.74}$.

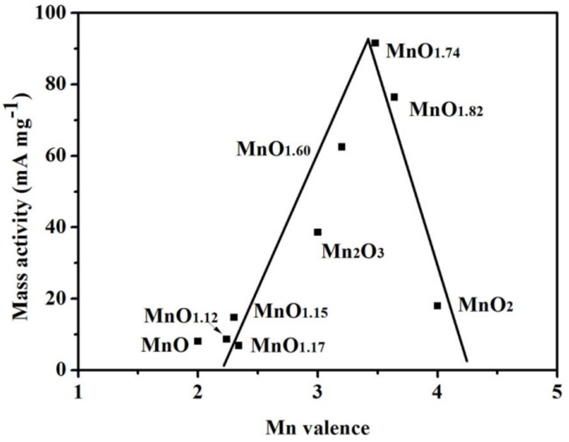

Fig. S14 Relationship between the Mn valence and the mass kinetic activity determined at 0.7 V. Result of commercial microsized MnO_2 powders is also listed.

Reference:

s1. X. Liu, J. Du, C. Li, X. Han, X. Hu, F. Cheng and J. Chen, *J. Mater. Chem. A,* 2015, **3**, 3425.

s2. Y. Z. Wang, X. Shao, H. Y. Xu, M. Xie, S. X. Deng, H. Wang, J. B. Liu, H. Yan, *J. Power Sources,* 2013, **226**, 140.