Supplementary Information

Development of improved MnO_x nanoparticles for Oxygen Reduction Reaction

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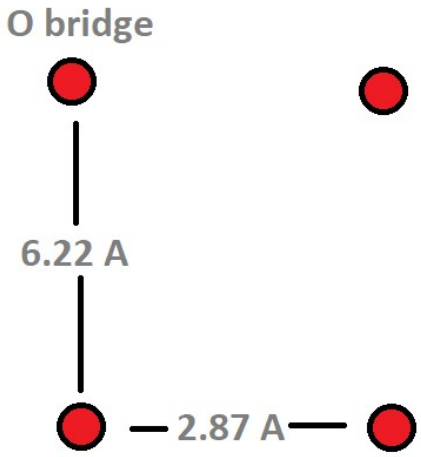

Figure S1 – β -MnO_2 (110) unit cell model used in the kMC simulation.

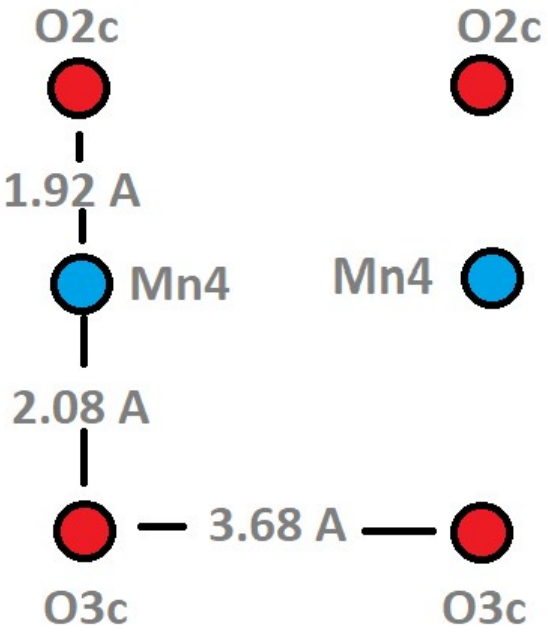

Figure S2 - Mn_3O_4 (110) unit cell model used in the kMC simulation.

Kinetic Model

The pre-exponential factor for a surface reaction is:[1]

$$k_0 = \frac{k_b T}{h}$$

where k_b is the Boltzmann constant and h is the Planck constant. The pre-exponential factor for the adsorption process was taken as:

$$k_0 = \frac{pA}{\sqrt{2\pi k_b m T}} \tag{3.3}$$

where p is the gas partial pressure, A is the site area, and m is the gas molecular weight.

For the desorption process, there is an approximation[2] for a non-activated process given by:

$$k_0 = \left(\frac{k_b T}{h}\right) \exp\left\{\frac{0.3 S^0_{gas}}{R} + 3.3 - \left(\frac{1}{3}\right)\left\{18.6 + \ln\left[\left(\frac{m}{m_{Ar}}\right)^{\frac{3}{2}}\left(\frac{T}{298}\right)^{\frac{5}{2}}\right]\right\}\right\} \tag{3.4}$$

where S is the gas entropy and m_{Ar} is the Ar molecular weight. The gas entropy was extracted from NIST database.[3]

The chemical equations used for the β-MnO_2 (110) are described below.[2]

1) $OH^* + OH^* \rightleftarrows H_2O^*_2 + O^*$
2) $H_2O^* \rightleftarrows H_2O(g) + *$
3) $O_2(g) + * \rightleftarrows O2^*$
4) $HO^* + O_2^* \rightleftarrows O^* + OOH^*$
5) $OOH^* + OH^* \rightleftarrows O^* + O^* + H_2O(g)$

Unlike the previous case, there are three possible sites – a Mn4 site and two distinct O sites– with different chemical environments and, consequently, distinct reactivities. A total number of 24300 sites (8100 of each type) were considered in the simulation. The ORR reaction pathway for the Mn_3O_4 (110) surface is shown below, where *2, *3 and # stand for O2c, O3c and Mn4, respectively.[4]

1) $OH^*_2 + OH^*_2 \leftrightarrows H_2O^*_2 + O^*_2$
2) $OH^*_3 + OH^*_3 \leftrightarrows H_2O^*_3 + O^*_3$
3) $H_2O^*_2 \leftrightarrows H_2O(g) + *_2$
4) $H_2O^*_3 \leftrightarrows H_2O(g) + *_3$
5) $O_2(g) + *_2 \leftrightarrows O_2^*_2$

6) $O_2(g) + *_3 \leftrightarrows O_2*_3$

7) $O_2*_2 + \# \leftrightarrows O*_2 + O\#$

8) $HO*_2 + O\# \leftrightarrows O*_2 + OH\#$

9) $O_2*_3 + OH*_3 + \# \leftrightarrows O*_3 + O*_3 + OH\#$

10) $OH*_2 + OH\# \leftrightarrows O*_2 + H_2O\#$

11) $OH*_3 + OH\# \leftrightarrows O*_3 + H_2O\#$

12) $H_2O\# \leftrightarrows H_2O(g) + \#$

The dissociative adsorption of H_2 on the O sites leads to two adsorbed OH species on each O site, as occurring for the MnO_2 (001) surface. The following steps (eq. 1-6) occurring in both O sites are similar to those discussed for MnO_2 (001) surface. However, the presence of the Mn4 site allows the diffusion of O and H between the Mn4 and O3c or O2c site (eq 7-12). As a result, H_2O molecules are formed on (and desorbed from) all three sites. The activation energy values were extracted from literature,[4,5] and the pre-exponential factors were calculated as discussed in the previous section.

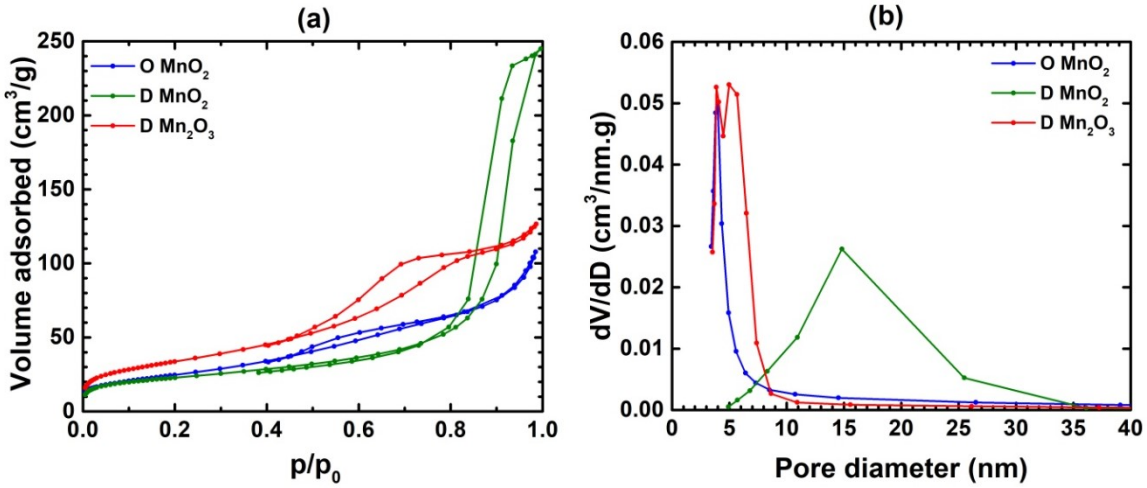

Figure S3 - Textural analysis of the samples with (a) N_2 adsorption-desorption isotherms and (b) BJH pore size distributions.

Table S1 - Specific surface area, pore volume, and pore size values of the samples synthesized.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
O-MnO_2	91	0.16	7.0
D-MnO_2	80	0.37	18.4
D-Mn_2O_3	122	0.19	6.3

Table S2 – Parameters obtained from the Rietveld refinement results of the O-MnO_2 and D-Mn_2O_3 samples.

		O-MnO_2	**D-Mn_2O_3**
γ-MnO_2	amount (%)	4.5	-
	a (Å)	7.39	-
	b (Å)	4.28	-
	c (Å)	3.08	-
	size (nm)	16	-
β-MnO_2	amount (%)	81.9	-
	a (Å)	4.35	-
	b (Å)	4.35	-
	c (Å)	2.85	-
	size (nm)	22	-
ε-MnO_2	amount (%)	13.6	-
	a (Å)	2.75	-
	b (Å)	2.75	-
	c (Å)	4.39	-
	size (nm)	28	-
Mn_2O_3	amount (%)	-	100
	a (Å)	-	9.4
	b (Å)	-	9.4
	c (Å)	-	9.4
	size (nm)	-	21

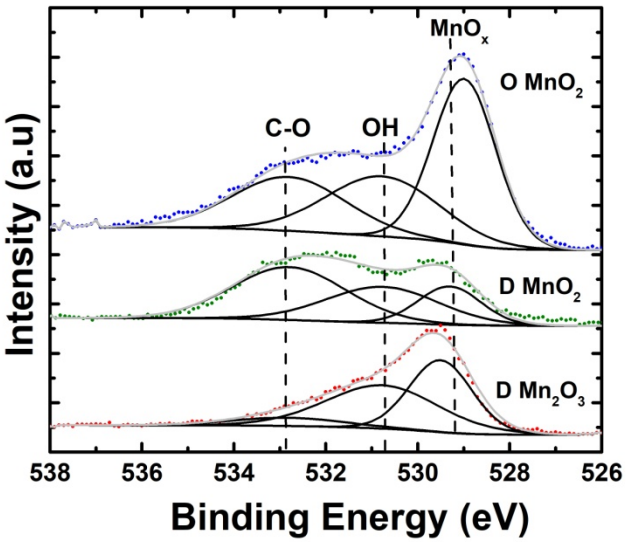

Figure S4 – O 1s XPS spectra of the samples synthesized.

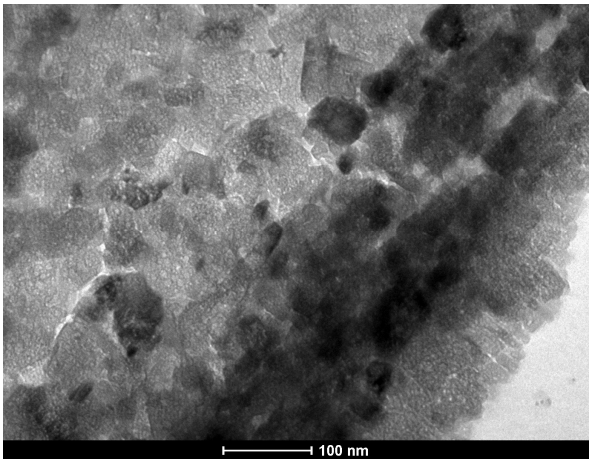

Figure S5 – TEM image of the D-Mn_2O_3 sample after reduction + ORR treatments at 500 ^oC.

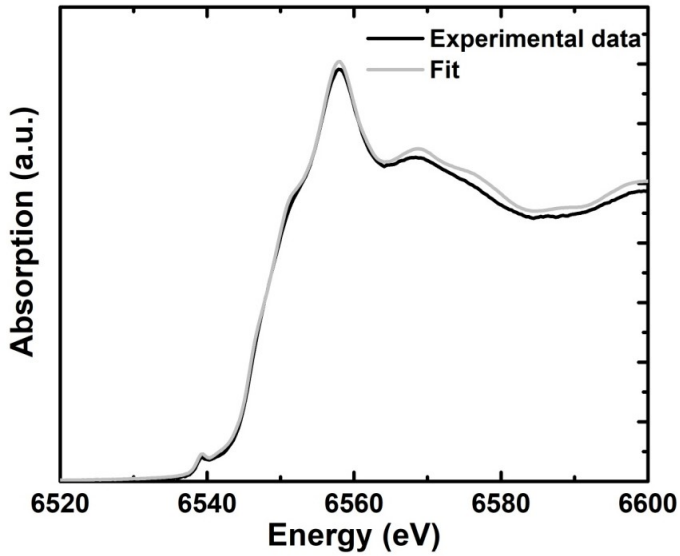

Figure S6 – Typical fit result of XANES measurement at Mn K edge of O-MnO_2 sample at 500 ^{o}C under H_2 atmosphere after 7.8 min from the beginning of the reduction treatment.

References

1 D. Kopac, M. Hus, M.Ogrizek, B. Likozar, *J. Chem. Phys. C,* 2017, **121,** 17941-19949.

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