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# Investigation of High Oxygen Reduction Reaction Catalytic Performance on Mn-Based Mullite $\mathrm{SmMn}_{2} \mathrm{O}_{5}$-Supplement 

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## Citation:

Liu, Jieyu, Meng Yu, Xuewei Wang, Jie Wu, et al. 2017. "Investigation of high oxygen reduction reaction catalytic performance on Mn-based mullite SmMn2O5." Journal of Materials Chemistry A 5(39): 20922-20931.

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## Supporting Information

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## 1

2 Following the computational hydrogen electrode (CHE) method proposed by 3 Norskov, ${ }^{1-3}$ zero voltage is defined based on the reversible hydrogen electrode (RHE), 4 in which the reaction
$5 \quad \mathrm{H}^{+}+\mathrm{e}^{-} \rightarrow 1 / 2^{1} \mathrm{H}_{2}$
is defined to be in equilibrium at zero voltage, at all values of pH , at all temperatures, and with $\mathrm{H}_{2}$ gas pressure at 101325 Pa .

8 Thus, the total chemical potential of the proton-electron pair as a function of 9 applied potential $U$ can be calculated as:

$$
\begin{equation*}
\mu_{H^{+}}+\mu_{e^{-}}(U)=1 / 2^{\mu_{H 2}-e U} \tag{2}
\end{equation*}
$$

The oxygen chemical potential then can be interpreted as:

$$
\begin{equation*}
\mu_{o}(U, p H)=\mu_{H_{2} O}-2\left(\mu_{H^{+}}+\mu_{e^{-}}(U)\right)=\mu_{H_{2} O^{-}}-\mu_{H 2}+2 e U \tag{3}
\end{equation*}
$$

0.1 M KOH was used as the electrolyte for oxygen reduction reaction (ORR)

15 this work is referred to the experimental condition, i.e. $\mathrm{pH}=13$

16 The chemical potential of each element in $\mathrm{SmMn}_{2} \mathrm{O}_{5}$ crystal is related by the

17 Gibbs free energy of the bulk oxide: ${ }^{4}$
$18 \quad \mu \stackrel{S m M n_{2} O_{5}}{S}+2 \mu{ }_{S m}^{S m M n_{2} O_{5}}+5 \mu_{o}(U, p H=13)=E_{S m M n_{2} O_{5}}^{\text {bulk }}$
$19 \stackrel{S_{S M M}}{\mu m n_{2} O_{5}}, \mu_{M n}^{S m M n_{2} O_{5}}$ and $\mu_{0}(U, p H=13)$ are the chemical potentials of samarium,
20 manganese and oxygen, respectively. ${ }^{E_{S M M n_{2} O_{5}}^{b u l k}}{ }^{\text {bu }}$ is the total energy of bulk per formula
21 unit $\mathrm{SmMn}_{2} \mathrm{O}_{5}$.

1 Take ${ }^{\mu}{ }^{\mathrm{SmMn}_{2} O_{5}} \mathrm{Mn}_{5}$ as the independent chemical potential.
2 Rearranging equation (4):
$3 \quad \mu{ }_{M n}^{S m M n_{2} O_{5}}=1 / 2\left[E_{S m M n_{2}} 0_{5}-\mu{ }_{S m}^{\text {bulk }}{ }_{S m M n_{2} O_{5}}-5 \mu_{0}(U, p H=13)\right]$
4 For binary metal oxides, the chemical potential of metals can be written as:

$$
\begin{equation*}
\mu_{M}^{M O_{n}}=E_{D F T}^{M O_{n}}-n \mu_{0}(U, p H=13) \tag{6}
\end{equation*}
$$

6 where M denotes the metal element ( Sm or Mn ), and $E_{D F T}^{M O_{n}}$ is the calculated total 7 energy of the corresponding oxides. To prevent bulk $\mathrm{SmMn}_{2} \mathrm{O}_{5}$ from decomposing 8 into lower order binary metal oxides, the chemical potential of a metal constituent in

9 the mullite should be smaller than that in the lower order binary metal oxides:
$10 \quad \mu{ }_{M}^{S m M n_{2} O_{5}}<\mu_{M}^{M O_{n}}$
crystal to construct the phase diagram.
$13 \Delta \mu_{S m}=\mu_{S m}-E_{S m}^{\text {bulk }}$

1 S2. Passivation of 8-layer (001) $\mathrm{MnO}_{3}-2$ slab

2


3 Figure S1. The local density of states (LDOS) of layer-1 to layer-4 of the 8-layer (001)
$4 \mathrm{MnO}_{3}-2$ slab. The black line represents the total DOS of the bottom four layers (layer-

51 to layer-4).

## 6 S3. Stability of mullite $\mathrm{SmMn}_{2} \mathrm{O}_{5}$ (001) surfaces

7 The relative stability of $\mathrm{SmMn}_{2} \mathrm{O}_{5}$ (001) surfaces under the given applied potential (U
$8=0.8 \mathrm{~V})$ and $\mathrm{pH}(\mathrm{pH}=13)$ were calculated based on the following equation: ${ }^{4}$

10 where $\Gamma_{i}$ is the surface energy, i donates the type of slab, $A_{s}$ is the surface area of the
 12 numbers of $\mathrm{O}, \mathrm{Mn}$ and Sm atoms in the slab, respectively. $\mu_{o}(U=0.8 \mathrm{~V}, p H=13)$ is

13 defined as equation (3). $\mu^{\mathrm{SmMn}_{2} \mathrm{O}_{5}}$ is the chosen independent chemical potential, which
14 is connected with ${ }^{\mu}{ }_{S m}^{S_{S M M} O_{2}}$ by equation (5).

15

## 1

2 The calculated binding energies of $\mathrm{O}^{*}\left({ }^{\Delta E_{O^{*}}}\right), \mathrm{OH}^{*}\left({ }^{\Delta E}{ }_{O H^{*}}\right), \mathrm{OO}^{*}\left({ }^{\Delta E}{ }_{o O^{*}}\right)$ and
$3 \mathrm{OOH}^{*}\left({ }^{\Delta E}{ }_{\text {оон }}{ }^{*}\right)$ are defined as the reaction energies of the following reactions:
$4 \quad \mathrm{H}_{2} \mathrm{O}^{(g)}+{ }^{*} \rightarrow \mathrm{O}^{*}+\mathrm{H}_{2}^{(g)}$
$5 \quad \mathrm{H}_{2} \mathrm{O}^{(g)}+* \rightarrow \mathrm{OH}{ }^{*}+1 / 2 \mathrm{H}_{2}^{(g)}$
$6 \quad 2 \mathrm{H}_{2} \mathrm{O}^{(g)}+* \rightarrow \mathrm{OO}+2 \mathrm{H}_{2}^{(g)}$
$7 \quad 2 \mathrm{H}_{2} \mathrm{O}^{(g)}+* \rightarrow \mathrm{OOH}^{*}+3 / 2 \mathrm{H}_{2}^{(g)}$
8 where * donates an adsorption site on the surface. $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{H}_{2}$ are in the gas phase.

9 Thus:
$10 \Delta E_{o^{*}}=E_{D F T}^{O^{*}}+E_{H_{2}(g)}-E_{H_{2} O^{(g)}}-E_{*}$
$11 \Delta E_{O H}^{*}=E_{D F T}^{O H^{*}}+1 / 2_{H_{2}} E^{(g)}-E_{H_{2} O^{(g)}}-E_{*}$
$\Delta E_{o O^{*}}=E_{D F T}^{O O^{*}}+2 E_{H_{2}(g)}-2 E_{H_{2} 0^{(g)}}-E_{*}$
$\Delta E_{O O H}{ }^{*}=E_{D F T}^{O O H^{*}}+{ }^{3} / 2_{H_{2}}{ }^{(g)}-2 E_{H_{2} O^{(g)}}-E_{*}$

## 1

## S5. Theoretical activity

2 The free energy change for each step in the main test can be calculated as: ${ }^{1-3}$

3

$$
\begin{equation*}
\Delta G_{i}=\Delta E_{i}+\Delta(Z P E)_{i}-T \Delta S_{i}+e U+\kappa T \operatorname{In} 10 \times \Delta p H \tag{18}
\end{equation*}
$$

4 where $\mathrm{i}=1,2,3,4$ corresponds to steps from Equation (1) to (4) in the main test, $\Delta E$ 5 is the reaction energy, $\triangle Z P E$ is the change of zero-point energy, T is temperature, $\Delta S$ is 6 the difference in entropy, U is the electrode potential vs. standard hydrogen electrode 7 (SHE) and $\kappa$ is boltzmann constant. All these parameters can be obtained from DFT

$$
\begin{equation*}
G_{O O^{*}}=E_{D F T}^{O O^{*}}+Z P E_{O O^{*}}-T S_{O O^{*}}^{0} \tag{23}
\end{equation*}
$$

1

## 1 S6. Two-electron pathway

2 We considerd a similar associative mechanism for the less efficient two-electron 3 pathway for hydrogen peroxide production.
$4 \quad \mathrm{OH}^{*}+\mathrm{O}_{2}+\mathrm{e}^{-} \rightarrow \mathrm{OO}^{*}+\mathrm{OH}^{-}$
$5 \quad \mathrm{OO}^{*}+\mathrm{H}_{2} \mathrm{O}+\mathrm{e}^{-} \rightarrow \mathrm{OOH}^{*}+\mathrm{OH}^{-}$
$6 \quad \mathrm{OOH}^{*}+\mathrm{H}_{2} \mathrm{O}+e^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{OH}^{-}$

7 In this case, the equilibrium potential is $0.68 \mathrm{~V} .{ }^{7}$ We ploted the free energy

8 evolution diagram in Figure S2. It is shown that the potential is limited by the 9 protonation from $\mathrm{OO}^{*}$ to $\mathrm{OOH}^{*}$ on the surface of $\mathrm{MnO}_{3}-1$ slab. The ORR steps in the

10 two-electron pathway are thermodynamically favorable only under low electrode

11 potential.


12
13 Figure S2. The free energy diagram of two-electron pathway to produce $\mathrm{H}_{2} \mathrm{O}_{2}$ on the surface of $\mathrm{MnO}_{3}-1$ slab.

1 S7. Synthesis of $\mathrm{SmMn}_{2} \mathrm{O}_{5}$, and $\mathrm{MnO}_{x}$

2 All metal salt precursors were analytical grade and used as received. 0.2777 g
$3 \mathrm{Sm}\left(\mathrm{NO}_{3}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ (Aladdin) was dissolved in 50 ml deionized water ( $18.25 \mathrm{M} \Omega$ )

4 followed by adequate stirring. Then $0.0593 \mathrm{~g} \mathrm{KMnO}_{4}$ and 0.2143 g
$5 \mathrm{Mn}\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2} \bullet 6 \mathrm{H}_{2} \mathrm{O}$ (Aladdin) were added to the solution simultaneously and

6 constantly stirred for at least 30 min . The corresponding mole ratio of $\mathrm{Sm}-\mathrm{to}-\mathrm{Mn}$ is

7 approximately 1:2. $5.5 \mathrm{~mL} \mathrm{NaOH}(1 \mathrm{M})$ was dropwise added to the mixture and

8 continued to stir for several minutes. After that, the precursor was transferred into a

9100 ml stainless steel Teflon-lined autoclave, followed by a standard hydrothermal

10 treatment at $200{ }^{\circ} \mathrm{C}$ for 24 h . The final precipitate was washed with nitric acid (5\%)

11 and distilled water for several times, and dried at $100{ }^{\circ} \mathrm{C}$ for $12 \mathrm{~h} . \mathrm{MnO}_{\mathrm{x}}$ was prepared
12 via the similar procedure without adding $\mathrm{Sm}\left(\mathrm{NO}_{3}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$. If we change the ratio of

13 Sm -to-Mn, final products would become a mixture of $\mathrm{SmMn}_{2} \mathrm{O}_{5}, \mathrm{MnO}_{x}$ and even
$14 \mathrm{Sm}(\mathrm{OH})_{3}$ (Figure S 3 ). Specifically, extra Sm might introduce $\mathrm{Sm}(\mathrm{OH})_{3}$, while excessive Mn could lead to complicated $\mathrm{MnO}_{\mathrm{x}}$.


1 Figure S3. XRD spectra of the as-prepared $\mathrm{SmMn}_{2} \mathrm{O}_{5}$ and the reference samples by 2 changing the stoichiometric ratio of metal precursors.

3

## 4 S8. Electrode preparation

5 The catalyst inks were prepared by physically mixing 5 mg of catalyst powder and/or
63 mg of Vulcan X-72 (Carbot Corp.) with $30 \mu \mathrm{~L}$ of Nafion (5 wt. \%, Aldrich) and 970
$7 \mu \mathrm{~L}$ of ethanol, followed by at least 40 min ultrasonication to form homogeneous

8 mixtures. ${ }^{8} 10 \mu \mathrm{~L}$ of these mixtures were carefully dropped onto glassy-carbon (GC)

9 electrodes ( $5-\mathrm{mm}$ diameter) and dried in a sealed glass beaker which had been pre-

10 saturated with ethanol vapor in order to slow down drying rate, which was proven to

11 be important for obtaining uniform coatings. ${ }^{9,10}$ Finally, all of the electrodes had a

12 composition of $250 \mu \mathrm{~g}_{\text {oxide }} \mathrm{cm}^{-2}$ disk and/or $150 \mu \mathrm{~g}_{\text {carbon }} \mathrm{cm}^{-2}$ disk , except for $\mathrm{Pt} / \mathrm{C}$ used as

13 a reference. The Pt/C catalyst ink was made by dispersing Pt/C (Johnson Matthey

1

6 fitted lines of Koutecky-Levich plot ( $\mathrm{J}^{-1}$ vs. $\omega^{-0.5}$ ) at different potentials. The

7 Koutecky-Levich equation is given as below:
$8 \quad \frac{1}{J}=\frac{1}{J_{L}}+\frac{1}{J_{K}}=\frac{1}{B \omega^{0.5}}+\frac{1}{J_{K}}$
$9 \quad B=0.62 n F C_{O_{2}} D_{O_{2}}^{2 / 3} v^{-1 / 6}$

$$
\begin{equation*}
J_{K}=n F k C_{O_{2}} \tag{37}
\end{equation*}
$$

where J is the measured current density, $\mathrm{J}_{\mathrm{L}}$ and $\mathrm{J}_{\mathrm{K}}$ are known as the diffusion-limited and kinetic-limited current density of ORR, respectively. ${ }^{12} \mathrm{~F}\left(96485 \mathrm{C} \mathrm{mol}^{-1}\right)$ is the

13 Faraday constant, ${ }^{C_{O_{2}}}\left(1.2 \times 10^{-6} \mathrm{~mol} \mathrm{~cm}{ }^{-3}\right)$ is the bulk concentration of oxygen, ${ }^{D_{O_{2}}}$
$14\left(1.9 \times 10^{-5} \mathrm{~cm}^{2} \mathrm{~s}^{-1}\right)$ is the diffusion constant for oxygen in 0.1 M KOH and $\mathrm{v}(0.01$ $\mathrm{cm}^{2} \mathrm{~s}^{-1}$ ) is the kinetic viscosity. ${ }^{13}$ The constant 0.62 in B is adopted when the rotating speed $\omega$ is expressed in rad/s. The Tafel slope was obtained from Tafel's equation:

$$
\begin{equation*}
\eta=a+b \lg J_{K} \tag{38}
\end{equation*}
$$

18 where $\eta$ represents the overpotential, and $\mathrm{J}_{\mathrm{K}}$ is the kinetic current density with masstransport correction by

$$
\begin{equation*}
1 \quad J_{K}=\frac{J_{L} \times J}{J_{L}-J} \tag{39}
\end{equation*}
$$



3 Figure S4. LSV curves of (a) $\mathrm{Pt} / \mathrm{C}$ and (b) $\mathrm{SmMn}_{2} \mathrm{O}_{5}-\mathrm{NRs} / \mathrm{C}$ at various rotating speed,

4 and the corresponding K-L plots of (c) $\mathrm{Pt} / \mathrm{C}$ and (d) $\mathrm{SmMn}_{2} \mathrm{O}_{5}$-NRs/C at different 5 potentials.

6 For RRDE analysis, the electron transfer number and proportion of peroxide were

7 calculated by
$8 \quad n=\frac{4 I_{D}}{I_{D}+\left(I_{R} / N_{C}\right)}$
$9 \quad \% \mathrm{HO}_{2}^{-}=100 \frac{2\left(I_{R} / N_{C}\right)}{I_{D}+\left(I_{R} / N_{C}\right)}$

4 Briefly, the collection efficiency $\left(\mathrm{N}_{\mathrm{C}}\right)$ was calibrated in Ar-saturated electrolyte with
50.1 M KOH and $4 \mathrm{mM} \mathrm{K}_{3} \mathrm{Fe}(\mathrm{CN})_{6}$, using the same electrodes as those used in ORR

6

7

8

9
$10 \quad N_{C}=\frac{I_{R}-I_{R_{0}}}{I_{D}}$

11 where $I_{D}$ and $I_{R}$ are the disk and ring current averaged over the last 10 s during 60 s
12 measurements. ${ }^{I_{0}}$ is the averaged ring current with the disk disconnected.


13
The calibration process follows the one reported by previous researchers. ${ }^{14}$ measurements. The electrodes were rotated at a certain angular velocity and then chronoamperometric measurement was performed. The disk and ring potential were fix to be 0.1 V and 1.5 V vs. RHE, respectively. The $\mathrm{N}_{\mathrm{C}}$ is calculated according to the following equation

$$
\begin{equation*}
N_{C}=\frac{I_{R}-I_{R_{0}}}{I_{D}} \tag{42}
\end{equation*}
$$

14 Figure S5. (a) $\mathrm{N}_{\mathrm{C}}$ of RRDE loaded with catalysts. (b) Oxygen reduction currents at

15 ring and disk $\mathrm{SmMn}_{2} \mathrm{O}_{5}-\mathrm{NRs} / \mathrm{C}$ and $\mathrm{Pt} / \mathrm{C}$ catalysts.

2 EIS measurement of $\mathrm{SmMn}_{2} \mathrm{O}_{5}$ catalyst $\left(250 \mu \mathrm{~g} \mathrm{~cm}^{-2}\right.$ disk $)$ was performed at 0.84 V vs.

3 RHE in 0.1 M KOH from 10 kHz to 0.1 Hz . A sinusoidal voltage with an amplitude 4 of 10 mV was applied to the initial voltage. The ohmic resistance of electrolyte

5 between working and reference electrode $\left(\mathrm{R}_{\mathrm{s}}\right)$ was observed to be $\sim 42 \Omega$ from Figure

6 S6. The corrected potential was calculated by the following equation:
$7 \quad E_{i R-\text { corrected }}=E_{\text {applied }}-i R_{s}$


Figure S6. EIS plot of $\mathrm{SmMn}_{2} \mathrm{O}_{5}$ NRs .

## 1 S11. ORR acitvity comparation

2 Table S1. The ORR activities of selected manganese-based oxides.

| Catalyst | $\mathrm{E}_{\text {onset }}$ <br> $(\mathrm{V}$ vs. RHE) | $\mathrm{E}_{1 / 2}$ <br> $(\mathrm{~V}$ vs. RHE) | $\mathrm{J}_{\mathrm{L}}$ <br> $\left(\mathrm{mA} / \mathrm{cm}^{2}\right)$ | n | Structure | Ref. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{SmMn}_{2} \mathrm{O}_{5} / \mathrm{C}$ | 0.817 | 0.746 | 5.45 | 3.78 | Nanorod | This <br> work |
| $\alpha-\mathrm{MnO}_{2} / \mathrm{GC}$ | $0.89^{\perp}$ | $0.8^{\perp}$ | $3.4^{*}$ | 3.89 | Nanorod | 15 |
| $\beta-\mathrm{MnO}_{2} / \mathrm{C}$ | 0.85 | 0.7 | 2.77 | 2.4 | Nanorod | 16 |
| $\sigma-\mathrm{MnO}_{2} / \mathrm{C}$ | 0.7 | 0.66 | 2.67 | 2.4 | Microsphere | 16 |
| $\mathrm{MnO}_{\mathrm{x}}$ | $0.83^{\perp}$ | 0.73 | 5.7 | NA | Thin film | 17 |
| $\mathrm{Mn}_{3} \mathrm{O}_{4} @ \mathrm{NGO}$ | 0.83 | $0.66^{\perp}$ | 3.7 | 3.81 | Ellipsoid | 18 |
| $\mathrm{MnO@GC}$ | $0.77^{\perp}$ | $0.64^{\perp}$ | $4.5^{\perp}$ | NA | Nanoparticle | 19 |

3 * The diameter of GC electrode is 4 mm .
$4 \perp$ Estimated form LSV.
5
6

7

8

9

10
11
12


Figure $\mathbf{S 7}$. XRD spectra of $\mathrm{Sm}_{2} \mathrm{O}_{3}$.


3
Figure S8. Representative TEM images of $\mathrm{SmMn}_{2} \mathrm{O}_{5}$-NRs

## 4 Reference

5 1. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, J. Phys. Chem. B, 2004, 108, 17886-17892.
7 2. J. Rossmeisl, J. K. Nørskov, C. D. Taylor, M. J. Janik and M. Neurock, J. 8 Phys. Chem. B, 2006, 110, 21833-21839.
3. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Norskov, Energy Environ. Sci., 2010, 3, 1311-1315.
4. Y.-L. Lee, M. J. Gadre, Y. Shao-Horn and D. Morgan, Phys. Chem. Chem. Phys., 2015, 17, 21643-21663.
5. P. W. Atkins, in Physical Chemistry, 6th ed., Oxford University Press: Oxford, U. K., 1998, 485, 925-927.
6. L. D. Chen, J. K. Nørskov and A. C. Luntz, J. Phys. Chem. Lett., 2015, 6, 175179.
7. V. Viswanathan, H. A. Hansen, J. Rossmeisl and J. K. Nørskov, J. Phys. Chem. Lett., 2012, 3, 2948-2951.
8. J. Suntivich, H. A. Gasteiger, N. Yabuuchi and Y. Shao-Horn, J. Electrochem. Soc., 2010, 157, B1263.
9. R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, Nature, 1997, 389, 827-829.
10. R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, Phys. Rev. E, 2000, 62, 756-765.
11. Y. Garsany, O. A. Baturina, K. E. Swider-Lyons and S. S. Kocha, Anal. Chem., 2010, 82, 6321-6328.
12. Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, Nat. Mater., 2011, 10, 780-786.
13. S. Wang, D. Yu, L. Dai, D. W. Chang and J.-B. Baek, ACS Nano, 2011, 5, 6202-6209.
14. R. Zhou, Y. Zheng, M. Jaroniec and S.-Z. Qiao, ACS Catal., 2016, 6, 47204728.
15. W. Xiao, D. Wang and X. W. Lou, J. Phys. Chem. C., 2010, 114, 1694-1700.
16. Y. Meng, W. Song, H. Huang, Z. Ren, S.-Y. Chen and S. L. Suib, J. Am. Chem. Soc., 2014, 136, 11452-11464.
17. Y. Gorlin and T. F. Jaramillo, J. Am. Chem. Soc., 2010, 132, 13612-13614.
18. J. Duan, S. Chen, S. Dai and S. Z. Qiao, Adv. Funct. Mater., 2014, 24, 20722078.
19. Y. Gorlin, C.-J. Chung, D. Nordlund, B. M. Clemens and T. F. Jaramillo, ACS Catalysis, 2012, 2, 2687-2694.

