Facet-dependent catalytic activity of MnO electrocatalysts for oxygen reduction and oxygen evolution reactions

Chung-Hao Kuo,^a Islam M. Mosa,^a Srinivas Thanneeru,^a Vinit Sharma,^b Lichun Zhang,^b Sourav Biswas,^a Mark Aindow,^b S. Pamir Alpay,^b James F. Rusling,^a Steven L. Suib,^{a,b,*} Jie He^{a,*}

^a Department of Chemistry, ^b Department of Materials Science and Engineering and Institute of Materials Science, University of Connecticut, Storrs, CT 06269 USA. Emails: <u>steven.suib@uconn.edu</u> (SS); jie.he@uconn.edu (JH)

1. Materials

The ultra-pure water was obtained and purified using High-Q, Inc. system with model 103S. Manganese(II) chloride tetrahydrate (>98%), cobalt(II) chloride hexahydrate (>99%), sodium hydroxide (95%), oleic acid (90%), 1-octadecene (90%) were purchased from Sigma-Aldrich and sodium oleate (>97%) were purchased from Fisher Scientific Inc. All chemicals were used without further purification unless otherwise noted.

2. Synthesis of Mn(oleate)₂ precursors and nanocrystals

2.1 Synthesis of Mn(oleate)₂

Mn(oleate)₂ was synthesized using a reported method with slight modification.¹ Briefly, in a 250 mL round-bottom flask, manganese(II) chloride tetrahydrate (50 mmol, 9.9 g), sodium oleate (105 mmol, 32.0 g) was added to 180 mL of a mixed water/EtOH/hexane (5:4:9, vol) solvent. The mixture was refluxed overnight under strong stirring. After cooling down to room temperature, the reaction mixture was then washed with water and extracted with hexane. The orange waxy solid of Mn(oleate)₂ was obtained after dried under vacuum.

2.2 Synthesis of Co(oleate)₂

In a typical synthesis of $Co(oleate)_2$, cobalt(II) chloride hexahydrate (10 mmol, 2.4 g), oleic acid (20 mmol, 5.6 g) and NaOH (20 mmol, 0.8 g) were added to 63 mL of a mix water/EtOH/hexane (20:8:35) solvent in a 250 mL flask. The mixed solution was heated for 4 h at 80 °C and then cooled to room temperature. The reaction mixture was then washed with water and extracted with hexane. The deep purple waxy solid of $Co(oleate)_2$ was obtained after removal of solvent under vacuum.

2.3 Synthesis of MnO nanolowers and different morphologies

In a typical synthesis, $Mn(oleate)_2 (2 \text{ mmol}, 1.24 \text{ g})$ and 10 g of 1-ocdacene were placed in a 25 mL of three-necked flask equipped with a condenser. The reaction was heated by heating mantle with a temperature regulator. The reaction mixture was first heated at 80°C and vacuum treated for 30 min to remove residual moisture. After refilled with argon, the reaction was further heated to 320°C at a rate of 10°C/min. The clear orange solution gradually turned to greenish suspension when reached 320°C and the mixture was stirred at 320°C for another 30 min. After cooling down to room temperature, the crude product was precipitated with an excess of acetone and collected by centrifugation. After washed for three time with hexane and acetone, the collected product was redispersed in hexane and stored. To synthesize MnO nanocrystals of polypods and octahedrons, oleic acid (OA) was introduced as a free ligand. With various $Mn(oleate)_2/OA = 1:0.27$), and MnO octahedra $(Mn(oleate)_2/OA = 1:0.9)$ can be obtained.

2.4 Synthesis of MnO nanocrystals with Co dopants

To synthesize cation doped MnO nanocrystals, a similar procedure was used. A mixture of $Mn(oleate)_2(2 \text{ mmol}, 1.24 \text{ g})$, $Co(oleate)_2$ with molar percentage of 5% and 10%, and 10 g of 1-ocdacene were placed in the flask. The reactions were heated at 80°C under vacuum for 30 minutes and heated to 320°C at a rate of 10°C/min with 30 minutes duration time at 320°C under Argon. After cooling down to room temperature, the crude product was precipitated with addition of acetone and collected by centrifugation.

3. Electrochemical studies

Linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and chronoamperometry experiments were obtained with a CHI 660A electrochemical workstation. For electrochemical oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) studies, pyrolytic graphite carbon working electrodes were used (surface area ~ 0.13 cm²) equipped with a rotating disc working electrode (RDE) configuration. A carbon rod was used as a counter electrode and saturated calomel electrode (SCE) as the reference electrode. The potentials reported in this work are referenced to the reversible hydrogen electrode (RHE) and denoted as RHE potential. To prepare the working electrode, 4 mg of catalysts and 1 mg of carbon (VulcanXC-72) were dispersed in 1 mL of water/EtOH by sonication. 85 µL of Nafion solution was added to the above mixture and sonicated for another 20 min. 10 µL of solution was then dropped on the working electrode surface and dried overnight before use. CV curves were iR-compensated and performed from 0.41 to 1.81 V (vs. RHE) with a sweep rate of 5 mV s⁻¹ in oxygen saturated 0.1 M of KOH solution. The working electrode was rotated at 1600 rpm. The electrochemical impedance spectra were collected by applying an AC voltage with 5 mV amplitude in a frequency ranged from 0.1 to 10⁵ Hz. To check fitting results, selected experimental data were also fitted using the ZSimDemo software package (version 3.2). In this procedure, RC initial estimates were obtained using a circle fitting function. Similar fitting parameters were obtained using both software packages.

The calculation methods of mass activity and TOF of electrochemical studies in this work is presented as following. Mass activity (A g⁻¹) values were obtained from deposited the catalytic materials on the working electrode (~0.03 mg) with measured current density (*j*, A cm⁻²) at $\eta = 0.35$ V. Turnover frequency (TOF) values were obtained using the following equation and assuming all materials on the working electrode are involved in the reaction, using TOF=*j*S/4Fn, where *j* (A cm⁻²) is the measured current density at $\eta = 0.35$ V, S (cm²) represent the surface area of the working electrode, F (C mol⁻¹) is Faraday's constant, and n (mol) is the moles of the metal atom on the working electrode. The standard rate constant (K⁰) can be obtained using the measured charge transfer resistance (*R_{cl}*) and calculated using the following formulas:

$$i_0 = \frac{R T}{n F R_{ct}}$$

$$k^o = \frac{i_0}{n F C}$$

Where i_0 is the exchange current in A, R is the gas constant, T is the absolute temperature, n is the number of electrons transferred (assumed to be 4 in OER for all catalyst for comparison), F is Faraday's constant, C is the saturated concentration of oxygen in 0.1 M KOH.

Koutecky-Levich (K-L) plots were used to interpret the ORR results measured at different rotating speed. The number of electron transferred per one oxygen molecule (n) can be obtained from K-L plots by applying the following equations:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

 $B = 0.2nFC_0(D_0)^{2/3}v^{-1/6}$

Where, J is the measured current density, J_K is the kinetic current, J_L is the diffusion limiting current, ω is the rotation speed of the electrode in rpm, B is the reciprocal of the slope of the K-L plots, F is Faraday constant (96485 C mol⁻¹), C₀ is the saturated concentration of oxygen in 0.1 M KOH (1.2×10^{-6} mol cm⁻³), D₀ is the diffusion coefficient of O₂ (1.9×10^{-5} cm² s⁻¹), and v is kinematic viscosity of the electrolyte (0.01cm² s⁻¹).

4. Characterization

The crystallinity of as-synthesized materials was characterized using a Rigaku UltimaIV powder X-ray diffractometer (PXRD) with Cu K_a radiation and a tube voltage of 40 kV and current of 44 mA. The PXRD patterns were collected over a 2θ range of 5~75° with a continuous scan rate of 2.0° min⁻¹. Morphologies of catalysts were studied using high resolution transmission electron microscopy (HR-TEM). HRTEM studies were carried out using the JEOL 2010 transmission electron microscope with an accelerating voltage of 200 kV and the 2006 Tecnai T12 TEM/STEM equipped with EDAX EDS system. TEM samples were prepared by casting the suspension of material on a carbon coated copper grid (300 mesh). In addition, the elemental maps of the specimen were collected using a Gatan imaging filter detector. The image filtering was carried out using the O K-, Mn K- and Co L-edges at 532, 540 and 456 eV, respectively. The structural model of interfacial features observed in the HRTEM images was established and analyzed using Crystalmaker software.

For the surface analysis, the X-ray photoelectron spectroscopy (XPS) was performed on a PHI model 590 spectrometer with multi-probes (Physical Electronics Industries Inc.), using Al K_a (λ = 1486.6 eV) as the radiation source. The powder samples were pressed on carbon tape mounted on adhesive copper tape stuck to a sample stage placed in the analysis chamber. The XPS spectra were analyzed and fitted using CasaXPS software (version 2.3.12). The C 1s photoelectron line at 284.6 eV was used as a reference for correction of the surface charging. A mixture of Gaussian (70%) and Lorentzian (30%) functions was used for the least-squares curve fitting procedure. The XAFS data were collected at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory utilizing beam line X18A. A Silicon (111) double crystal monochromator was used to monochromatize the synchrotron radiation. The incident and transmitted beam intensities were monitored using ionization chambers filled with N₂. The samples were diluted by h-BN with a ratio of (1:8) then pressed into pellets and mounted in front of transmission detector. Before the measurements were taken, a thin Mn foil reference was used for energy calibration. The XANES data were analyzed using Athena software where background and post and pre-edge corrections were made.

5. Computational details

The first-principles computation is performed within the framework of density functional theory (DFT), using the projector augmented wave method as implemented in the Vienna *ab initio* simulation package.² In present spin polarized calculations, the exchange correlation interaction is treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhoff (PBE) functional.³ The electronic wave functions were expanded in a plane wave basis with a cut off energy of 400 eV. It is worth mentioning here that due to the errors associated with the on-site Coulomb and exchange interactions,⁴ DFT based methods are known to fail to reproduce an accurate description of the electronic structure for strongly correlated systems such as transition metal oxides⁵ and rare-earth compounds.⁶ In such cases, the accuracy of DFT can be improved by incorporating a Hubbard-model-type correction (U), which accounts for localized *d* and *f* orbitals. Hence, in the present work to describe the localized nature of the manganese *d* states, all the calculations are performed using U = 4 eV, which is well-optimized value particularly for MnO.^{5b,c,7}

In case of bulk MnO, the relaxation of atomic positions and optimization of lattice parameters are performed by the conjugate gradient method. The atomic positions are relaxed until the maximum component of the force on each atom is smaller than 0.02 eV/Å. The Brillouin zone sampling was done using a Monkhorst-Pack mesh of 4 x 4 x 4, to achieve the convergence within 0.1 meV per formula unit. The optimized lattice parameter of the bulk MnO (4.51 Å) is slightly overestimated with respect to available experimental results (4.445Å).⁸ The overestimation of lattice parameters is also observed in earlier DFT based studies.^{5a,8-9} The relative stability of

MnO(100), MnO(110), and MnO(111) surfaces is calculated using 9, 9, and11-layer slabs respectively separated by a vacuum spacing of 12 Å (top view of the low index planes is shown in figure **X**). During geometry relaxation a Γ -centered 5 x 5 x 1 k-point mesh was considered.

The surface energy (γ) for a symmetric slab is given by:

Surface energy (γ) = (E_{slab} - n × E_{MnO Bulk}) / 2A

where, γ is the surface energy, E_{slab} and $E_{MnO Bulk}$ are the total energy of the surface and bulk MnO respectively, n is the number of MnO formula units and A is the area of the two-dimensional unit cell. The factor 2 takes into account symmetric nature of the slab used in the present work.

To fully exploit the nature of above mention surfaces, we also study the interaction between the surfaces and the spices from the surrounding environment such as gas-phase oxygen (both neutral atomic and molecular oxygen) and OH on different facet of MnO surfaces. Here, for each surface facet we determine exact orientation and preferential adsorption site for O, O_2 and OH using our DFT energetics. The adsorption energy E_{ad} is the energy of the fully relaxed surface with the adsorbate minus the sum of energies of the isolated relaxed surface and isolated adsorbate.



Figure S1. Low-magnification TEM images of MnO nanoflowers.



Figure S2. Size distribution of MnO nanoflowers measured from TEM images by averaging more than 100 particles.



Figure S3. Low-magnification TEM images of MnO polypods.



Figure S4. Low-magnification TEM images of MnO polyhedra.



Figure S5. Low-magnification TEM images of MnO octahedral nanocrystals.



Figure S6. The powder X-Ray diffraction pattern of MnO octahedral nanocrystals.



Figure S7. X-ray absorption near-edge spectra (XANES) of the manganese oxide references (a) and MnO nanocrystals (b) depicted with normalized y-axis.



Figure S8. The average oxidation state of Mn for MnO nanocrystals derived from Mn K-edge absorption threshold.



Figure S9. (a,b) TEM images of 5 mol% (a) and 10 mol% (b) Co doped MnO nanoflowers. (c) Size distribution of Co doped MnO nanoflowers, 5 mol% Co (red) and 10 mol% Co (black). (d-g) TEM energy-dispersive X-ray (EDX) elemental mapping of 10 mol% Co doped MnO nanoflowers and the corresponded TEM image (g). The molar ratio of Co/Mn from EDX mapping is 1:12. Yellow, red and cyan colors indicate the Mn-rich, O-rich and Co-rich domains, respectively.



Figure S10. Low-magnification TEM images of of 10%-Co MnO material.



Figure S11. Low-magnification TEM images of of 5%-Co MnO material.



Figure S12. The powder X-Ray diffraction patterns of 10% Co-MnO material.

Catalysts		Oxygen E	Oxygen Reduction Reaction				
	η at $J = 10$ mA cm ⁻² (V) ^a	Mass activity at $\eta = 0.35 \text{ V} (\text{A g}^{-1})^b$	Resistance $R_{ct}(\Omega)^{c}$	TOF at $\eta = 0.35 \text{ V} (\text{s}^{-1})^d$	$k^{o} (cm s^{-1})^{e}$	E_i at $J = -3 \text{ mA cm}^{-2} (\text{V})^{\text{f}}$	$\frac{E_{1/2}/E_{onset}}{(\mathrm{V})^g}$
Nanoflowers	-	5.60	275	1.32×10 ⁻⁴	0.0016	0.73	0.77/0.91
Polypods	0.58	17.75	256	4.19×10 ⁻⁴	0.0017	0.78	0.81/0.87
Octahedra	-	4.34	1406	1.02×10^{-4}	0.0003	0.57	0.61/0.88
C-MnO	-	0.52	3595	1.22×10 ⁻⁵	0.0001	-	0.59/0.65
10% Co-MnO	0.64	22.16	196	5.23×10 ⁻⁴	0.0022	0.73	0.79/0.88
5% Co-MnO	0.64	17.65	266	4.16×10 ⁻⁴	0.0016	0.71	0.78/0.88

Table S1. Summarized OER and ORR activities of MnO catalysts.

All data in the tables are extracted from the LSV and EIS experiments in 0.1 M KOH at a rotation speed of 1600 rpm vs RHE. ^a Overpotential measured from LSV at a current density of 10 mA/cm². ^b Mass activity calculated from LSV at overpotential at 0.35 V. ^C The charge transfer resistance (R_{ct}) obtained from EIS analysis at 1.76 V vs RHE. ^d The turnover number calculated from LSV at overpotential at 0.35 V. ^e The potential obtained at a current density of -3 mA/cm². ^g The half-way potential and onset potential obtained from LSV.



Figure S13. The LSV spectra of cobalt doped MnO and MnO nanoflowers catalysts for (a) OERs and (b) ORRs. The curves were *i*R-compensated and performed with a sweep rate of 5 mV s⁻¹ in oxygen saturated 0.1 M KOH solution at a rotation speed of 1600 rpm.



Figure S14. CV curves at 5 mV/s for MnO polypods in both oxygen-saturated and argon-saturated 0.1 M KOH solution at a rotation speed of 1600 rpm.



Figure S15. (A) LSV curves of the MnO NPs at different rotation speeds. (B) The corresponding Koutecky–Levich plots at different potentials from 0.71 to 0.51 V vs. RHE ($-0.3 \sim -0.5$ V vs. SCE).

	MnO (100)		MnO (110)		MnO (111)	
Surface energy (meV/ Å ²)	60		110		170	
Adsorbate	E _{ad} (eV)	BD (Å)	E _{ad} (eV)	BD (Å)	$E_{ad} (eV)$	BD (Å)
0*	-2.950	1.60	-0.446	1.79	-0.018	1.97
O_2	-2.619	1.65	-0.725	1.84	-0.298	2.12
OH*	-2.998	1.71	-3.428	1.96	-1.868	2.16

Table S2. DFT (GGA+U) based calculated surface energy (γ) and adsorption (Ead) and binding distances (BD)for (100), (110) and (111) surface of MnO.



Figure S16. The representative of OH* adsorbate species on different MnO lattice surfaces. H is in white, O is in red, and Mn is in yellow.



Figure S17. *i-t* Chronoamperometric response of MnO polypods at 0.66 V vs. RHE.

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