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Supporting Information

Nitrogen-Rich Manganese Oxynitrides with Enhanced Catalytic Activity in the Oxygen Reduction Reaction

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Rietveld Analysis

Initial structural models were constructed using the reported structures of $\text{Mn}_6\text{N}_{5.26}$ (ICSD #290804) for MnON(1) and MnON(2), and Mn_3N_2 (ICSD #290803) for MnON(3); cation sites were filled by manganese, while anion sites were filled by nitrogen. Since the scattering factor of nitrogen using X-ray radiation is close to that of oxygen, we cannot distinguish nitrogen and oxygen. Thus, the refinements of anion sites indicate the total occupancies of both oxygen and nitrogen though the refinements of the structural models include only nitrogen. For the refinement of MnON(1) and MnON(2), we fixed the occupancy of the cation site as unity. As a result, MnON(1) was found to have nearly stoichiometric cation/anion ratio while MnON(2) was anion-deficient ratio. For the refinement of MnON(3), the refinements of the occupancies in Mn2, N1 and N2 sites with fully occupied Mn1 site were performed. The refined occupancies of Mn2 and N1 sites were unit within the error, thus these we fixed these occupancies as unit and the occupancy of only N2 site was refined. As described in the manuscript, the quantitative values of anion occupancy calculated from chemical analysis deviate approximately 0.1 from those derived from XRD. This deviation can be attributed to impurity phases ($\text{Na}_{0.364}\text{MnO}_2(\text{H}_2\text{O})_{0.544}$, $\text{Mn}(\text{OH})_2$) and absorption O/OH layer suggested by XPS analysis, and possible cation vacancies. Refined structural parameters of these oxynitrides are summarized in Table 1 and Table S1-S3.

Table S1 Structural parameters of MnON(1)

Site	<i>g</i>	<i>X</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
Mn	1	0	0	0	0.455(17)
N	0.998(8)	0	0	1/2	0.998(6)

Table S2 Structural parameters of MnON(2)

Site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
Mn	1	0	0	0	0.586(2)
N	0.889(9)	0	0	1/2	1.35(6)

Table S3 Structural parameters of MnON(3)

Site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
Mn1	1	0	0	0	0.20(10)
Mn2	1	0	0	0.3323(3)	0.41(5)
N1	1	0	0	0.1532(8)	1.05(12)
N2	0.338(17)	0	0	1/2	= <i>B</i> (N1)

Electron diffraction

Weak spots assigned as 002 were found in MnON(3) with three-fold superlattice along the c-axis.

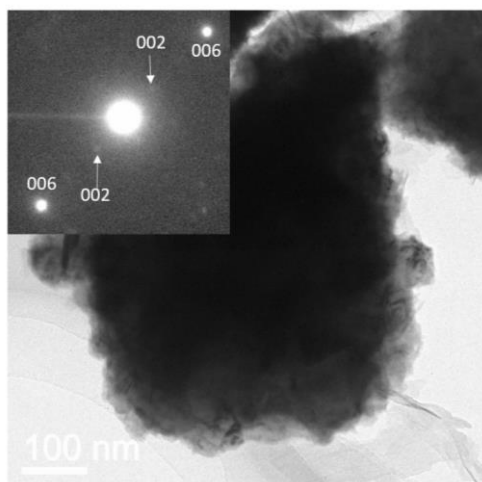


Figure S1 TEM and electron diffraction images of MnON(3).

XPS analysis

In three manganese oxynitrides, the energies of Mn2p doublet peaks were almost the same energies before (~641.9 and ~653.5 eV). O and N peaks were found at 529.5 and 395.8 eV, respectively, suggesting M-O and M-N bonding. The oxygen peaks have tails toward higher energy, implying OH species on the surface. After the Ar etching, the energies of Mn2p doublet peaks shifted toward lower energy (~640.1 and ~651.9 eV). This shift indicates the reduction of Mn but the reduction by Ar etching is possible. The positions of O and N peaks were not significantly different from those before the etching, but the shapes of the tails were changed by the etching.

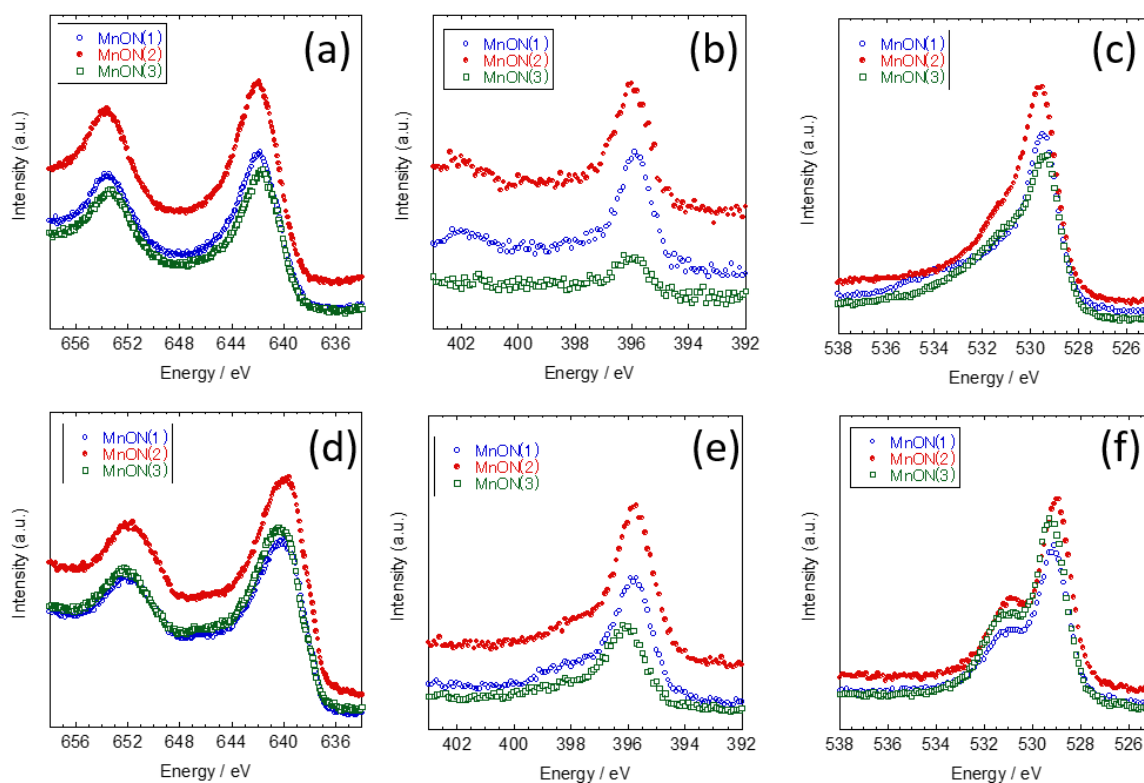


Figure S2 XPS spectra of (a) Mn2p, (b) N1s, and (c) O1s of manganese oxynitride powder before Ar etching and those of (d) Mn2p, (e) N1s, and (f) O1s after three-minutes Ar etching.

DFT calculation

Non-polarized Density of States (DOS) and Crystal Orbital Hamilton Populations (COHP) were calculated by the Vienna ab initio Simulation Package and Lobster codes. The optimized lattice parameter of cubic MnO was $a = 0.4081$ nm. MnN was optimized as tetragonal structure with the lattice parameters of $a = 0.4010$ nm and $c = 0.4003$ nm. Chemical bonding was analyzed by COHP as projected from plane-wave bases set.

Figure S3 shows the pDOS and pCOHP of stoichiometric MnO and MnN with rocksalt structures. As expected, the states composed of the interaction between Mn $d_z^2/d_{x^2-y^2}$ and O/N p orbitals are predicted just below the Fermi level (Figure S3 (a, b)). The Fermi level of MnN located at higher energy than that of MnO, but less electron occupy at its antibonding states (Figure S3 (c)). Hence, this calculation supports our expectation of electronic structures in manganese oxynitrides although the simple octahedral motif of manganese oxynitrides does not consider a possible cation vacancy, and the distribution of nitrogen/oxygen/vacancy in the anion site and the distortion of octahedron.

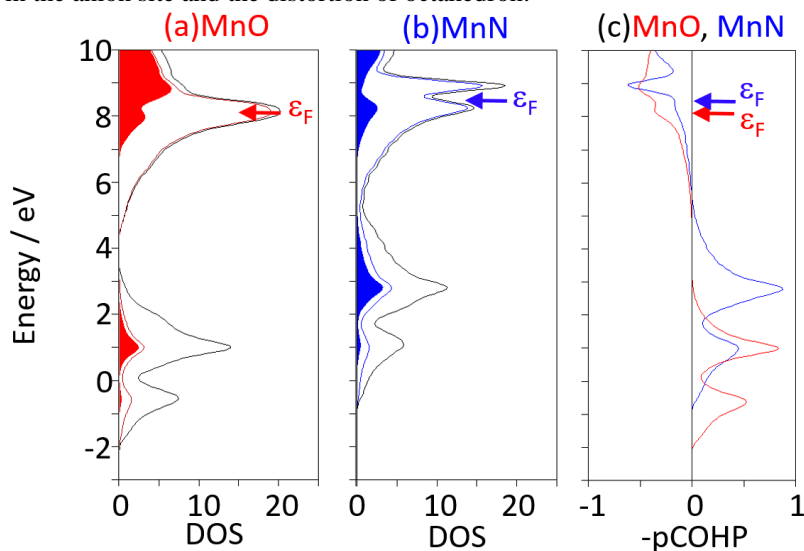


Figure S3 pDOS of (a) MnO and (b) MnN with rocksalt structures derived by non-spin polarized calculation. Black and red/blue lines represent total DOS and pDOS for Mn, respectively. Shaded areas show the projection of Mn $d_{x^2-y^2}$ and d_z^2 orbitals. (c) pCOHP of average Mn-O and Mn-N interactions are shown. Arrows donate the Fermi levels.

Comparison with perovskite oxides

The comparison between manganese oxynitrides and perovskite oxides suggests that the highest onset potential of the ORR currents can be explained by ~ 1 electron in the antibonding e_g state.

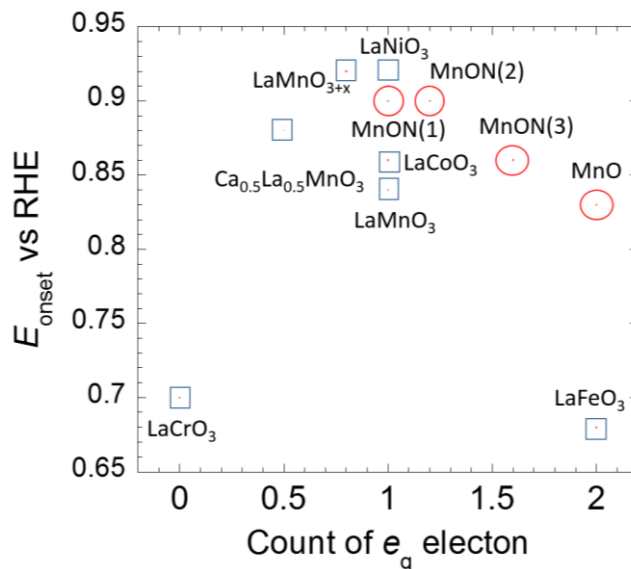


Figure S4 Relationship between count of e_g electron using octahedral motif and onset potential of the ORR. Circles represent the onset potential of oxide and oxynitrides having rocksalt structure in O₂-saturated 1M KOH solution converted from Hg/HgO electrode: $E_{\text{vs RHE}} = E_{\text{vs MMO}} + 0.098 \text{ V} + 0.059 \times \text{pH}$. Squares show the potential at 25 mAc^{m-2} of perovskite oxides in O₂-saturated 0.1 M KOH solution [J. Suntivich et al., *Nat Chem* **2011**, 3, 546].