Electrochemical oxidation of oxygen reduction (ORR) in alkaline media has recently attracted much attention in connection with the development of liquid and solid alkaline fuel cells and metal-air batteries. Manganese oxides are among the most attractive ORR catalysts, combining activity, stability, environmental friendliness, and reasonably low cost. Recently some of us investigated the influence of crystal structure and composition of manganese oxides on their specific (real surface-weighted) electrocatalytic activity in the ORR, and in the reactions of hydrogen peroxide oxidation and the ensuing lower peroxide yield during the ORR are corroborated by the lower barrier for the dissociation of hydrogen peroxide adsorbed on the surface of Mn₃O₄ arising from adsorbate-adsorbate interactions. We provide the arguments in favor of the outersphere nature of initial O₂ reduction steps and demonstrate that this hypothesis does not contradict the experimental trends observed for ORR and hydrogen peroxide reduction reactions on Mn₂O₃ and MnOOH.

The manuscript is arranged as follows. After presenting essential experimental and computational details (Experimental and computational details section), we briefly summarize our previous experimental data regarding the ORR and HPRR on various Mn oxides, and introduce the ORR mechanism proposed in previous publications (Short summary of the previously published data sub-section). Experimental RRDE data for various Mn oxides measured at different catalyst loadings are presented in Experimental RRDE data sub-section. In Periodical DFT calculations sub-section we present results of periodic DFT calculations and discuss tentative potential-determining steps for MnOOH and Mn₃O₄ in the framework of the thermodynamic approach. It appears however that the latter is not sufficient for explaining the experimental observations. Thus, Quantum chemical modeling of activation barriers for the elementary steps sub-section is devoted to discussing ORR mechanisms comprising various inner- and outer-sphere elementary steps and estimating their activation barriers. In order to bridge computational results with the experimental data, in Microkinetic modeling: confronting computational data to experimental results sub-section we present the results of kinetic modeling and analyze RRDE curves simulated for various sets of reaction rate constants. Concluding remarks section concludes the manuscript. Here we analyze the assets and the limitations of our approach and propose an outlook for the future developments.

We dedicate this work to Professor Radoslav R. Adzic, whose seminal works on the ORR are the cornerstone of all ongoing studies of the ORR on metal and oxide electrodes. He discovered numerous subtle features, including the role of oxygen-containing adsorbates in the ORR in alkaline media, the role of oxides as the supports for the ORR catalysts, and proposed realistic kinetic schemes accounting for adsorbed intermediates.
with the BET surface area of 25 m²·g⁻¹ was obtained by the heat-treatment of MnOOH in air at 240°C. The sample with the BET surface area of 27 m²·g⁻¹ was obtained by calcination of an amorphous product of comproportionation of Mn(CH₃COO)₂ and KMnO₄ in air at 550°C for 12 h,¹¹ its electrochemical and electrocatalytic properties were discussed in Ref. 4. The sample with the BET surface area of 8 m²·g⁻¹ (see RRDE data in the SI) was obtained by milling of the commercially available Mn₂O₃ ("Reachim", Russia). ᵅMnO₂ (pyrolusite, 48 m²/g) was fabricated by the heat-treatment of MnOOH at 600°C. Mn₃O₄ (hausmanite, 13 m²·g⁻¹) was obtained by the heat-treatment of MnOOH in argon atmosphere at 600°C. According to the XRD data, all samples were pure phases and did not contain crystalline impurities. Carbon of the Sibunit family with the BET and BJH (Barrett-Joyner-Halenda method) surface areas equal to 65 and 52 m²·g⁻¹, respectively, was kindly provided by Dr. P.A. Simonov. It was obtained by hydrocarbon pyrolysis followed by activation as described in Ref. 12.

Electrochemical measurements were performed in 1 M NaOH electrolyte prepared from Acros Organics 50 wt% aqueous solution in a three-electrode cell at 25°C using Autolab potentiostat (PG-STAT302N) equipped with an analog scan generator. All parts of the electrochemical cell in contact with the alkaline electrolyte were from Teflon. The RRDE tip comprised a glassy carbon (GC) disc and a Pt ring. Sibunit carbon-oxide compositions with the 1:1 (wt) ratio were deposited on the GC disc as described in Ref. 4 to achieve oxide loadings of 23, 30, and 91 μg per cm² of the GC disc. Potentials were measured versus HgO/Hg (IJ Cambria Scientific) in the same layer in order to simulate the RRDE current-potential curves. Only one surface layer together with the adsorbed inter-sorbates to keep the initial surface structure. A part of the O atoms was frozen during the optimization of adsorption centers. The geometry of the active center and the positions of Mn atoms correspond to the anti-ferromagnetic state of the Mn oxides with various crystal structures and compositions making sure that the electrode potential was comprised in the interval of their stability. Poux et al. and Ryabova et al.¹–⁵ optimized the preparation of oxide/carbon composites (carbon addition is required for the improvement of the conductivity of the catalytic layers, its role being discussed in Refs. 5, 23) and investigated electrochemical and electrocatalytic properties of Mn oxides with various crystal structures and compositions making sure that the oxygen evolution reaction current density DFT calculations were performed using the VASP program package¹³ with PAW¹⁴ pseudopotentials and the RPBE-GGA functional.¹⁵ The asymmetric four Mn-layer supercells which mimic the MnOOH (110) (8 surface Mn atoms) and Mn₂O₃ (111) (16 surface Mn atoms) surfaces were constructed from the corresponding bulk structures. An energy cutoff of 600 eV and 2 × 2 × 1 (Mn₂O₃) and 3 × 2 × 1 (MnOOH) k-point meshes were used in all the calculations. The dipole corrections were applied in the direction perpendicular to the surfaces. Only one surface layer together with the adsorbed intermediates was relaxed until the change in total energy of the system was less than 10⁻⁹ eV. The obtained lattice parameters for Mn₂O₃ are: a = b = c = 9.59205 Å, α = β = γ = 90.0°. For α-MnOOH:

\[ a = b = c = 9.59205 \, \text{Å}, \quad \alpha = \beta = \gamma = 90.0°. \]

Active surfaces of Mn₂O₃ (111) and MnOOH (110) oxides were constructed implying 0.5 monolayer (ML) Oad and 0.5 ML HOad coverages. Under experimental conditions, these coverages correspond to somewhat different overpotentials (see Results and discussion section). However, this potential shift is not sufficient to cancel out the pronounced difference in the oxides’ electrochemical activities toward oxygen reduction. The possible partial coverage of the surfaces with water molecules was addressed neither in the periodical DFT calculation, nor in the microkinetic modeling, as the primary effect is believed to be related largely to the differences in Mn oxides reactive centers configuration and not to the differences in the oxide-water interactions specifics (which is the inevitable assumption on the current stage). In all the calculations a 20 Å vacuum region was introduced to avoid the interaction between the slabs.

The thermodynamics of electrochemical reactions was addressed by means of computational standard hydrogen electrode approach. Zero-point energy and entropy corrections were introduced to compute Gibbs free energies for the reactions involving ORR adsorbates.

Cluster calculations were performed at the DFT level using the B3LYP functional as implemented in the Gaussian 09 program suite. The O and H atoms of the adsorbates and oxide clusters were described by the standard 6-311+G(d,p) basis set. The effect of inner electrons of the Mn atoms was included in a relativistic Effective Core Potential Llan2, while a basis DZ quality was employed to describe Mn valence electrons. The spin-polarized Kohn-Sham formalism was used to treat the open shell systems.

The clusters were constructed using the geometry of Mn₂O₃ (111) and MnOOH (110) surfaces optimized at the periodical DFT calculations. Each cluster contained 8 Mn atoms, with the two central Mn atoms mimicking the reaction center. The closest Mn atoms on the oxide surfaces were chosen as potential candidates for the reaction centers.

The geometry of the active center and the positions of Mn and O atoms in the clusters were frozen during the optimization of adsorbates to keep the initial surface structure. A part of the O atoms was saturated by auxiliary hydrogen atoms to achieve electroneutrality at the model clusters. The ground state multiplicities for the Mn oxide clusters were determined to be 16 and 14 for Mn₂O₃ and MnOOH clusters and 17 and 15 for the “cluster + OO_ad systems. The spin densities of the Mn atoms correspond to the anti-ferromagnetic state of the model clusters.

The resulting structures were visualized using VESTA program.²¹

Results and Discussion

Short summary of the previously published data.—The ORR on Mn oxides has been extensively studied in the past (see Ref. 22 and refs. therein). It appears however that some studies neglected cathodic instability of oxide materials, subjecting them to cycling within wide potential limits exceeding the interval of their stability. Poux et al. and Ryabova et al.¹–⁵ optimized the preparation of oxide/carbon compositions (carbon addition is required for the improvement of the conductivity of the catalytic layers, its role being discussed in Refs. 5, 23) and investigated electrochemical and electrocatalytic properties of Mn oxides with various crystal structures and compositions making sure that the electrode potential was comprised in the interval of the oxide stability. Figure 1 summarizes the key experimental data published in Refs. 1–5. Panel (a) shows kinetic ORR currents of Mn oxides at 0.9 V vs. RHE normalized to their respective BET surface areas against the formal potential (Ε formal) of the surface Mn(III)/Mn(IV) redox couple determined from cyclic voltammograms (CVs). One should notice an exponential increase of the electrocatalytic activity with the E formal and ca. factor of 50 difference between the kinetic current of the most (MnO₂) and the least (MnOOH) active Mn oxide.

To better understand the ORR mechanism, Poux et al.¹² and Ryabova et al.²² studied catalytic and electrocatalytic hydrogen peroxide
(the likely ORR intermediate) reactions on various oxide materials as a function of the electrode rotation rate and the H2O2 concentration. Panel (b) represents Levich-Koutecky plots for the hydrogen peroxide reduction (HPRR) limiting currents measured at 0.65 V vs. RHE, while panels (c) and (d) compare ORR and H2O2 current-potential curves for Mn oxides. For α-Mn2O3, the HPRR current at 0.65 V vs. RHE is equal to the one measured on a Pt/C electrode and attains a diffusion-limited value suggesting fast H2O2 reduction. Meanwhile, for MnOOH and Mn3O4 the HPRR current is much inferior of the diffusion-limited value and independent of the rotation rate (Figures 1b–1d), evidencing a surface chemical step limiting the HPRR and the ORR at potentials below ca. 0.8 V vs. RHE.

The experimental data for the ORR and hydrogen peroxide reactions on Mn oxides briefly presented above and described in more detail in Refs. 1–5 could be rationalized using microkinetic modeling within a “series” innersphere ORR mechanism assuming that the O2 detail in Refs. 1–5 could be rationalized using microkinetic modeling.

Figure 1. (a) Kinetic ORR currents at 0.9 V vs. RHE against the formal potential, E1, of the surface MnIV/MnIII redox couple. (b): Levich-Koutecky (LK) plots of the HPRR currents at 0.65 V vs. RHE. (c,d): RDE voltammograms in N2-purged 1 M NaOH + 0.84 mM H2O2 (solid lines) and O2-saturated 1 M NaOH (triangles) at 900 rpm and 10 mV s−1. Catalyst loadings on the GC electrode are 91 μg cm−2 manganese oxide + 91 μg cm−2 Shibunit carbon. Color codes: blue (MnOOH), orange (Mn2O3), red (MnO2). Currents are normalized to the BET surface area of corresponding oxides (a) and to the electrode geometric area (b-d). Error bars represent standard deviations from at least two independent repeated measurements. Data for Pt/C (black) are presented for comparison. Data are reproduced from Refs. 2–4.

Then, adsorbed O2− is reduced into adsorbed HO2− denoted HO2ad:

\[ O_{2ad} + H_2O + e^- \rightleftharpoons HO_2ad + OH^- \]  \[ \text{(3)} \]

The different peroxide yields observed using the RRDE and further discussed in Experimental RRDE data section (Figure 2) as well as the HPRR limiting currents (Figure 1) are explained by the large difference in the rate constant for step (5) for the studied Mn oxides. The ORR current at 0.9 V vs. RHE is strongly affected by the rate constants of steps 2–3, but also by the formal potential and by the difference in the rate constant for step (5) for the studied Mn oxides. This observation highlights the fact that the peroxide yield depends on the rate of the HPRR.

Kinetic modeling performed within the ORR mechanism comprising steps 1–5, allowed us to reproduce the experimental data for the oxygen and hydrogen peroxide reactions on various Mn oxides taking into account the experimentally determined E1 values for step 1 and assuming material-dependent kinetics for steps 2 and/or 3, and 5.3,4 The different peroxide yields observed using the RRDE and further discussed in Experimental RRDE data section (Figure 2) as well as the HPRR limiting currents (Figure 1) are explained by the large difference in the rate constant for step (5) for the studied Mn oxides. The ORR current at 0.9 V vs. RHE is strongly affected by the rate constants of steps 2–3, but also by the formal potential and by the kinetics of step 5, fast reduction of HO2− preventing its possible oxidation at 0.9 V. Note that the ratio of rate constants for the step 5 (k5) for Mn2O3 and for MnOOH was estimated from the kinetics of electrochemical reduction and chemical decomposition of HO2− as ca. 103.3 It is worth noting however that steps (1–5) are tentative and correspond to the combinations of at least two elementary steps. This scheme should be treated as possible but not unique, and in this work we apply molecular modeling in order to either support it or propose an alternative.

Experimental RRDE data.—Figure 2 demonstrates RRDE data for four Mn oxides. At all potentials and loadings, peroxide yields increase in the series Mn2O3 < MnOOH < Mn3O4 < MnOOH, which agrees well with the decrease of the HPRR limiting currents (see Figures 1b–1d). This observation highlights the fact that the peroxide yield depends on the rate of the HPRR.

For all studied oxides except of the Mn2O3 the peroxide yields depend on the oxide loading, increasing when the loading decreases
(Figures 2 and S2). Such a behavior is expectable and has been extensively discussed in previous publications, the reason is the total number of active cites at the working electrode. As the number of active sites capable of adsorbing hydrogen peroxide intermediate increases, the probability of its re-adsorption increases as well, thus reducing the amount of H₂O₂ escaping from the catalytic layer and reacting at the ring. It is interesting to note that for Mn₂O₃ the peroxide yield at the ring does not change as the oxide loading decreases from 91 down to 30 μg·cm⁻², but then slightly increases for the loading of 23 μg·cm⁻² (magenta curve in Figure S2). Such a non-linear dependence of the hydrogen peroxide yield on the loading suggests possible contribution of the H₂O₂ generated at the GC support when the loading is low.

Since the key quantity is the number of active surface sites, the peroxide yield should not only depend on the catalyst loading but also on the specific surface area of the catalyst. Figure S3 shows RRDE data for three Mn₂O₃ samples with S BET surface areas of 8, 25 and 27 m²·g⁻¹. One may notice that even for the low surface area sample the yield of the peroxide detected at the ring at low electrode potentials does not exceed 2.5%.

The low peroxide yields observed for Mn₂O₃ could be rationalized either by assuming a “direct” ORR pathway (proceeding via the O-O bond breaking in a O₂ molecule), or a “series” ORR pathway occurring via intermediate formation of H₂O₂ provided that its catalytic decomposition (e.g. in step 5) is faster than its desorption in step 4. These different scenarios will be explored below with the help of quantum chemical calculations.

**Periodical DFT calculations.**—Periodical DFT calculations were used for estimating adsorption energies of the reaction intermediates: OOd, HOOad, HOad, and Oad assumed within a “series” mechanism. As it was previously mentioned, four-layer slabs were constructed to mimic MnOOH (110) and Mn₂O₃ (111) surfaces. These calculations allowed us to assess surface restructuring of the two oxides, at least at a qualitative level. Given the large size of the Mn₂O₃ (111) cell (190 atoms in the asymmetric cell) and the difficulties associated with accurate ab initio calculations for large systems, in our calculations only one surface layer was optimized, which induces some degree of inaccuracy in the obtained geometries of the surfaces. The results should thus be treated as an initial guess of the surface reconstruction trends. Figure 3 shows the geometries of the optimized first layers of Mn oxide surfaces. The active centers, which are assigned to the closest Mn atoms, are marked in the Figure. Both surfaces show significant changes in the positions of Mn octahedra after the relaxation procedure. For MnOOH (110), the distance between Mn(1) and Mn(2) atoms (“active center”) is decreased from 3.76 to 3.49 Å, while other distances between the surface Mn atoms are increased by 0.2–0.3 Å. In case of the Mn₂O₃ (111) surface, the distance between the closest Mn(1) and Mn(2) atoms decreases from 3.16 Å to 2.98 Å, while other distances on the surface increase by 0.2–0.3 Å.

The intermediates of the ORR reaction (OOOd, HOOad, HOad, Oad) were placed on the Mn(2) atoms of the active centers. The subsequent geometry relaxation provided the structures of the O-containing adsorbates at the MnOOH and Mn₂O₃ surfaces. Table S2 shows the geometries of the adsorbates and lists the corresponding bond lengths and angles in the structure. It can be seen that molecular oxygen is relatively weakly adsorbed at the model surfaces, with the Mn-Oo distance being 1.96–2.05 Å. The HOOad intermediate adopts

![Figure 3. Surface layers of Mn₂O₃ (a) and MnOOH (b) oxides (0.5 ML HOOad coverage), as obtained from periodical DFT calculations.](image)
different configurations upon adsorption at Mn$_2$O$_3$ and MnOOH surfaces. In the case of Mn$_2$O$_3$, a stabilizing interaction between the OH group of the peroxide moiety and the O$_{ad}$ adsorbate of the neighboring Mn atom can be noticed, which is absent for the MnOOH surface due to larger Mn-Mn distances. The bond lengths between Mn atoms and O$_{ad}$ (1.60 Å) and HO$_{ad}$ (1.76–1.79 Å) adsorbates are similar for the two surfaces.

In the framework of thermodynamic approaches, the free energy difference for the surfaces with various adsorbed intermediates is used to assess the kinetics of multistep processes without computing reaction activation energies. This simplification assumes a straightforward relationship between the activation energy and the reaction free energy, which is not obvious, especially for the inner-sphere steps. For the ORR, free energy diagrams are usually constructed for the reaction pathway involving successive interconversion of the adsorbed OO$_{ad}$, HO$_{ad}$, OH$_{ad}$ and O$_{ad}$ intermediates. Despite the thermodynamic approach remains a convenient and valid method for comparing adsorption energies of the intermediates and for the initial screening of potential catalysts, sometimes it fails to describe the experimental trends and to give correct predictions on the nature of the reaction limiting step.

In this work, we followed a simplified procedure to evaluate the interaction energies of the ORR intermediates with the Mn oxide surfaces, which did not involve an extensive search for the minimum energy surface at a given potential with the account for the fractional occupation of the surface by water molecules. Instead, we used MnOOH (110) and Mn$_2$O$_3$ (111) surfaces at 0.5 ML OH$_{ad}$ and 0.5 ML O$_{ad}$ coverage and computed the free energy diagrams for the potentials, which correspond to these coverages based on the available experimental information (formal potentials of the two oxides). Under these conditions, the 0.5 ML coverage corresponds to the potential of ca. 0.98 V for Mn$_2$O$_3$ and 0.9 V for MnOOH. The free energy diagrams for the two oxides, calculated for these potentials, are shown in Figure 4.

The free energy diagram suggests that for MnOOH the potential determining step (PDS) involves HOO$_{ad}$ formation from OO$_{ad}$, while for Mn$_2$O$_3$ the PDS could be attributed to the OH$_{ad}$ desorption step. While supporting the higher activity of Mn$_2$O$_3$, the thermodynamic approach fails to explain the most notable difference between the O$_{ad}$ (1.60 Å) and HO$_{ad}$ (1.76–1.79 Å) adsorbates are similar for the Mn atom can be noticed, which is absent for the MnOOH surface due to larger Mn-Mn distances. The bond lengths between Mn atoms and O$_{ad}$ (1.60 Å) and HO$_{ad}$ (1.76–1.79 Å) adsorbates are similar for the two surfaces.

Figure 4. Free energy diagrams for MnOOH (110) and Mn$_2$O$_3$ (111) at 0.9 and 1.0 V vs. RHE, respectively.

In the next section we address the successive steps in the ORR mechanism, discuss possible elementary steps and estimate their activation barriers.

Quantum chemical modeling of activation barriers for the elementary steps.—In a number of publications the ORR on Pt and Au electrodes in alkaline media was discussed in the framework of an outer-sphere mechanism. Given the low adsorption energies of O$_2$ at MnOOH and Mn$_2$O$_3$ oxide surfaces (−0.03 and +0.07 eV, respectively), the outer-sphere scenario cannot be excluded. Within an outer-sphere mechanism, the first steps of the ORR can be expressed as follows:

\[
O_2 + e^- \rightarrow O_2^-(2')
\]

\[
O_2^- + e^- + H_2O \rightarrow HO_2^- + OH^- \quad (3')
\]

HO$_2^-$ species can then adsorb at the oxide surface:

\[
HO_2^- + OH_{ad} + e^- \rightarrow HO_2O_{ad} + OH^- \quad (4')
\]

Then, the bond breaking in HO$_2^-$ should occur, which according to the experimental evidence does not involve charge transfer. In what follows we will show that it is likely to occur through an adsorbate-mediated mechanism:

\[
HO_2O_{ad} + OH_{ad} \rightarrow O_{ad} + OH^+_ad + OH^- \quad (5')
\]

The O$_{ad}$ species is then converted into OH$_{ad}$ in step (1).

Alternatively, the low H$_2$O$_2$ yield observed for Mn$_2$O$_3$ could be explained by the existence of a “direct” 4e$^-$ pathway, where the O-O bond is broken before the formation of HO$_2^-$. The O-O bond rapture can be introduced by considering an irreversible dissociation of an adsorbed O$_2^-$ involving an electron transfer step:

\[
O_2^-_{ad} + OH_{ad} + e^- \rightarrow 2 O_{ad} + OH^- \quad (3'')
\]

In what follows we consider feasibility of different ORR pathways based on relevant calculations.

Feasibility of the “direct” ORR pathway (O$_2^-_{ad} + OH_{ad} + e^- \rightarrow 2 O_{ad} + OH^- - step 3'').—As discussed in Experimental RRDE data section, the low hydrogen peroxide yield and the remarkably high activity of the Mn$_2$O$_3$ oxide might be related to the “direct” ORR pathway involving bond breaking in the O$_2$ molecule. This scenario implies the possibility of the O$_2$ adsorption on two neighboring Mn atoms of the oxide. We addressed such a scenario for both O$_2$ and O$_2^-$ species, as the lifetime of O$_2$ in alkaline media is sufficient for its adsorption after the first electron transfer (ET) step (which in this case should proceed in an outer-sphere regime). Adsorption of O$_2$ and O$_2^-$ species was considered within cluster approach, which involves some uncertainties related to the finite cluster size and boundary effects, but allows modeling charged species.

The model clusters were constructed from the “periodical” oxide surfaces optimized as described above. Each cluster contained an active center (Mn(1)-Mn(2) atoms), which was supported by six additional Mn octahedra (Figure 5). The Mn-O$_2$ bond length values for the adsorbed OH computed within the cluster and periodical DFT

Figure 5. Model clusters constructed from the optimized geometries of Mn$_2$O$_3$ (111) (a) and MnOOH (110) (b) surfaces.
approaches were similar (1.79–1.80 Å), supporting the validity of the former.

We found that both for the O₂ molecule and for the O₂⁻ anion, it was not possible to stabilize adsorption on two neighboring Mn active centers even when the surface H₂O₂ adsorbates were removed. In a series of calculations performed for a model cluster representing Mn₂O₃(111) surface, the O-O bond was constrained at a set of fixed distances (1.21–2.2 Å). The Mn(1)-O₃ and Mn(2)-O₃ distances were allowed to relax in the course of optimization (Figure 6).

The resultant structures (which correspond to points on the potential energy surface for the O-O bond-breaking path) show gradual decrease in Mn(2)-O₃ bond length when the O-O bond is elongated. The interaction of the neighboring Mn atom with the oxygen molecule (Mn(1)) can be noticed only when the O-O bond length reaches 1.5 Å (Figure 6). At the O-O distance of 1.80 Å the bond is effectively broken, with the Mn(2)-O₃ bond length being close to 1.80 Å, which is already a typical value for the Oad adsorbate at the oxide surface. However, the energy barrier along this path appears to be too high for the predominance of this “direct” pathway: ca. 2.5 eV, which is calculated as the difference in the energy values for the equilibrium bond length in the adsorbed O₂ (1.27 Å) and the transition state (energy of the cluster with the O-O bond length 1.7 Å). Similar tendencies in the adsorption geometries were also observed for the O₃⁻ ion.

Based on these considerations we conclude that the “direct” path, way which should involve dissociative adsorption of O₂ at two neighboring Mn atoms at the Mn₂O₃ surface, is not feasible due to a very high activation barrier. The origin of the enhanced activity of Mn₂O₃ and the low H₂O₂ yield are thus likely to be related to other steps in the ORR mechanism, such as fast bond breaking in H₂O₂. This computational result provides a basis for considering the ‘series’ pathway as more probable. Furthermore, rather long Mn-O₃ bond lengths (ca. 2.0 Å) and the associated low adsorption energy values imply feasibility of the outer-sphere scenario for the first ET to the O₂ molecule, which is considered in the next sub-section. For outersphere reactions, the key factors which should be addressed are electrode/reactant electronic overlap, solvent reorganization responsible for the barrier height (in addition to molecular reorganization), and works of approach.

\[ \text{Calculation of barriers for the outer-sphere scenario (O}_2^+ + e^- \rightarrow O_2 \rightarrow \text{step } 2^-) \].—The spinless Anderson-Newns model (narrow band formalism) (see Refs. 35,36 for details) combined with the DFT calculations of the model Mn oxide clusters was employed to map the ET free energy surface along the solvent coordinate. The O₂⁻ – oxide surface distances used in the model calculations correspond to the energy minimum of the adsorption interaction. A value of 1.2 eV was taken for the solvent reorganization energy λ. 35 Computational investigation of Mn₂O₃ and MnOOH structures at the DFT+U level of theory suggests that for both oxides the Fermi level lies very close to the edge of the valence band, 37,38 hence we can consider the oxides as conductors when calculating the ET free energy surface. For the case of a different position of the Fermi level within the energy gap, another version of the Anderson model (suitable for semiconductors) should be employed. 39

Three orientations were considered for the O₂ approach to the active center of the model clusters: planar orientation with the O-O bond parallel to the active center plane, and two vertical orientations (1) and (2) with the O-O bond being normal to the active center plane (Figure 7). The potential energy scans along the normal to the cluster “surface” (Figure 8) allowed to specify the distances, which correspond to the minimum energy values for the cluster + O₂ systems. In Figure 8, the differences between the system energies and the energy of the cluster + O₂ at a significantly high separation (7 Å) are shown. For both oxides, Figure 8 shows very shallow minima as a function of the separation distance. For the Mn₂O₃ cluster, the minima (z_{min}) correspond to the O₂-cluster separations of 5.4, 4.6 and 5.0 Å for planar, vertical (1) and vertical (2) orientations. For MnOOH, the corresponding z_{min} values amount to 5.4, 4.4 and 5.5 Å for the same set of orientations.

Surprisingly, the O₂ approach terms do not demonstrate more repulsive trends, when the Mn atoms in the active center are O-terminated (Figure S4a), z_{min} values amounting to 5.0, 4.4 and 4.8 Å for the planar, vertical (1) and (2) orientations. The effect of Mn-O – O₂ repulsion is observed only when the O-O and Mn-O bonds are aligned, while for two other orientations the distance of the closest approach decreases as the Mn-O bonds are shorter than the Mn-OH bonds.

Possible presence of “OH vacancies” was modeled by eliminating surface OH groups from Mn(1) and Mn(2) atoms of the active center (“dehydroxylated” cluster, Figure S4b). In this case, the adsorption minima in the approach terms were shifted to shorter distances: 4.1, 3.0 and 2.9 Å for planar and two vertical orientations (1) and (2), respectively (Figure S4b). The presence of OH vacancies and the associated decrease in the closest approach distance might contribute to the lowering of the effective outer-sphere ET barrier.

The ET barriers were estimated for the three selected orientations of the O₂ molecule at O₂-cluster separations corresponding to the energy minimum values. For the “hydroxylated” surfaces of both oxides the ET barriers, ΔEₜ, were estimated as ca. 0.30 eV (in accordance with the Marcus theory, ΔEₜ = ½ΔE if zero overvoltage is assumed). In our calculations we do not consider the case of “vacancy” formation on the active center, as in alkaline media the Mn atoms are likely to be occupied either by water molecules or by adsorbed OH species, which should form a rather stable hydrogen-bonded layer. The transfer of the O₂ molecule through this layer toward the adsorption site on the Mn atom needs surmounting an additional barrier (work terms), which should be considered as well. 11,32 Hydroxylated surfaces correspond, on the other hand, to a more realistic environment for the first ET...
adsorption of O$_2$ molecule from solution is likely to be accompanied by surmounting an additional energy barrier upon approaching the surface, occupied by OH$_{ad}$ and H$_2$O molecules (which is illustrated on a qualitative level by the repulsive approach terms for the hydroxylated surface). Data on the O$_2$ approach toward Mn oxide surfaces is currently unavailable in the literature. To make a qualitative estimate one may use the reported potential of the mean force (PMF) profiles, calculated for the approach of O$_2$ toward the Ag(100) surface.$^{30,31}$ For Ag(100) the PMF is ca. 0.8 eV for O$_2$ and ca. 0.5 eV for O$_2^-$ at 2–3 Å distances, which corresponds to the adsorbed state of the molecule/anion. As the expression for the ET rate constant should include the exponential term exp(-$W/k_BT$), where $W_i$ has the order of 0.5–0.8 eV, the rate constant should decrease at least by 10 orders of magnitude both for O$_2$ and for O$_2^-$.

Thus, the additional barrier of 0.5–0.8 eV cannot be compensated by a ca. $10^{3}$–increase in the electronic transmission coefficient, which should take place when switching from an outer-sphere to an inner-sphere mechanism. In our calculations a very weak O$_2$ adsorption energy was computed without the account for the solvating media, but these results point to the absence of strong oxide/adsorbate interactions. Thus, we have no experimental or theoretical implications to consider oxygen species adsorption to be much stronger on Mn oxides than on gold or silver facets. To conclude, we predict the difference in O$_2$ outersphere reduction rates on Mn$_2$O$_3$ and MnOOH up to one order of magnitude due to the difference in the orbital overlap. We also demonstrate that the rate of this outersphere transfer of the first electron can be higher than that for the alternative innersphere step.

**Second electron transfer – the fate of the O$_2^-$ ion.**—The second electron transfer, given the feasibility of the outer-sphere scenario with the formation of O$_2^-$ species can involve either the adsorption of O$_2^-$ at the electrode surface with the following proton-coupled ET or another outer-sphere step (O$_2^-$ + H$_2$O + e$^-$ = HO$_2^-$ + OH$^-$, step 3), which can then be followed by the adsorption of HO$_2^-$. It is difficult to distinguish between these two scenarios given the current level of understanding of the reaction mechanism. It is however worth noting that the superoxide ion (O$_2^-$) is stronger adsorbed on oxide surfaces than the O$_2$ molecule.$^{30,31}$ The barrier for the outer-sphere proton coupled ET to O$_2$ is very low – ca. 0.05 eV,$^{32}$ making it an unlikely candidate for the reaction limiting step, whose rate could account for the observed difference in the activities of the MnOOH and Mn$_2$O$_3$ oxides.

Since the adsorption energy (from periodical DFT calculations) of HO$_2^-$ species at MnOOH is by ca. 0.15 eV lower as compared to that of Mn$_2$O$_3$, the higher yields of the HO$_2^-$ at the ring may be partially due to the easier desorption of HO$_2^-$ from the MnOOH surface.

**Bond breaking in the hydrogen peroxide intermediate.**—The elementary step of bond breaking in the adsorbed hydrogen peroxide intermediate was addressed in the framework of cluster calculations. The chemical bond-breaking step can be represented by step 5, which involves participation of two neighbor Mn atoms. This process was modeled as a stepwise elongation of the O-O bond of HO$_{ad}$ adsorbed at the active center, which allowed constructing of a potential energy surface. For the potential energy scan the O-O bond in HO$_{ad}$ was constrained to remain perpendicular to the active center plane, following the approach described in Refs. 31,32.

Figures 9a, 9b show the corresponding barriers for the bond breaking in HO$_2^-$ adsorbed at Mn$_2$O$_3$ and MnOOH oxide surfaces, which were estimated as ca. 0.5 eV and 0.8 eV correspondingly. The geometries of transition states (TS, lower panels of Figure 9) suggest that smaller distances between neighboring Mn atoms in Mn$_2$O$_3$ allow for the existence of stabilizing interactions between O$_{ad}$ and OH$_{ad}$, which facilitate the OH$^-$ detachment and decrease the activation barrier. For MnOOH such kind of interactions is unlikely, as the distance between the adjacent Mn centers is too large.

Thus we conclude that adsorbate-adsorbate interactions may allow for a significant reduction of the bond breaking barrier height, which

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**Figure 8.** O$_2$ - cluster interaction energy curves for a set of three orientations of O$_2$ molecule in the vicinity of hydroxylated Mn$_2$O$_3$ (a) and MnOOH (b) surfaces.
would determine higher activity of Mn$_2$O$_3$ with respect to the reduction of hydrogen peroxide species explaining the experimentally observed kinetically limited HPRR for MnOOH but not for Mn$_2$O$_3$. Note however, that the exact barrier heights should be taken with caution given the vast number of approximations and simplifications in our cluster calculations.

**Microkinetic modeling: confronting computational data to experimental results.**—To check whether the experimental data are compatible with the ORR mechanism comprising outer-sphere ET step(s) emerging from quantum chemical modeling, microkinetic modeling was performed. The model considers outersphere ET steps 2$^*$ and 3$^*$ followed by HO$_2^-$ adsorption on the oxide surface (step 4), inner-sphere reduction of HO$_2^-$ into water (step 5) and conversion of the generated O$_{ad}$ into OH$_{ad}$ (step 1). Microkinetic modeling is used to simulate the ORR RRDE and HPRR/HPOR (hydrogen peroxide oxidation) current-potential curves, which are then compared to the experimental ones. The kinetic equations and the values of the rate constants used in the simulations of the ORR RRDE current potential curves are given in the SI (Calculation of barriers for the outer-sphere scenario (O$_2$+e$^-$ $\rightarrow$ O$_{ad}$−step 2$^*$ section). The density of Mn active sites was chosen to reproduce the experimental data obtained with a 91μg cm$^{-2}$ loading of Mn oxide.

The outer-sphere reduction of O$_2$ into HO$_2^-$ (step 2$^*$) was simulated by setting the O$_2$/O$_{ad}^-$ standard potential at E$_{2^*} = 0.689$ V vs. RHE [28], while a value of E$_{3^*} = 0.933$ V was assumed for the O$_2^−$/HO$_2^−$ standard potential (step 3$^*$) in order to keep the O$_2$/HO$_2^−$ standard potential at 0.77 V vs. RHE at pH 14.22 Since E$_{2^*}$ is lower than E$_{3^*}$ the onset and the half-wave potentials of the ORR current potential curves depend on the rate constant of step (2$^*$), $k_{2^*}$, while the hydrogen peroxide oxidation reaction kinetics is strongly influenced by the rate constant of step (3$^*$), $k_{3^*}$. As discussed in Short summary of the previously published data section, the HO$_2^-$ reduction kinetics is much faster on the Mn$_2$O$_3$ oxide than on the MnOOH counterpart (cf. Figure 1). On Mn$_2$O$_3$, the reduction current below 0.85 V vs. RHE is limited by the HO$_2^-$ diffusion while on MnOOH, the HO$_2^-$ reduction limiting current is much inferior of the diffusion limit. As a consequence, a larger HO$_2^-$ escape is observed during the ORR on MnOOH compared to that of Mn$_2$O$_3$. Differences in the HO$_2^-$ reduction kinetics can be attributed to the faster HO-O bond breaking (step 5 or 5$^*$) on Mn$_2$O$_3$ compared to MnOOH predicted by quantum chemical calculations. Experimentally, a constant limiting current is observed on MnOOH over a wide range of potentials (Figures 1b, 1d) evidencing that the HO-O$_{ad}$ bond breaking (step 5 or 5$^*$) is a chemical step, i.e. not activated by the electrode potential (cf. Short summary of the previously published data and Bond breaking in the hydrogen peroxide intermediate sections).

The simulation results are collected in Figures 10a, 10b, 10c. Panel 10c shows simulated ORR RRDE (full curves) and HPRR/HPOR (dashed curves) current-potential curves. It should be mentioned that in the outer-sphere model, not only the HO$_2^-$, but also the O$_2^-$ species generated at the disc electrode may escape from the diffusion layer and be oxidized at the ring. Thus, the current due to the O$_2^-$ oxidation is added up to the oxidation of HO$_2^-$ at the ring. This is shown in Figure 10b, where the full lines correspond to the simulated HO$_2^-$ escape currents, while dashed curves are used to plot the O$_2^-$ escape currents. Note that the yields plotted in panel 10a account for the sum of the HO$_2^-$ and the O$_2^-$ escape currents.

Three simulated current-potential curves are compared in Figure 10 for different combinations of the rate constant values. In the first case (purple curves), rather fast kinetics is considered for steps (2$'$) ($k_{2^*} = 10^6$ cm$^3$ mol$^{-1}$ s$^{-1}$) and (3$'$) ($k_{3^*} = 10^8$ cm$^3$ mol$^{-1}$ s$^{-1}$) as well as for the inner-sphere HO$_2^-$ reduction kinetics. The experimentally observed diffusion-limited HPRR currents on Mn$_2$O$_3$ below 0.85 V, and the amount of HO$_2^-$ escaping the catalyst layer (cf. Figures 1 and 2) can be semi-quantitatively reproduced assuming $k_5 = 40$ s$^{-1}$. However, above 0.85 V, the HO$_2^-$ reduction current depends on the kinetics of step 1, which is linked to the formal potential of the Mn(IV)/Mn(III) redox transition. In agreement with the experiment, the Mn(IV)/Mn(III) redox potential of 0.98 V is assumed for Mn$_2$O$_3$. This set of parameters allows one to reproduce the main experimental observations for the Mn$_2$O$_3$ oxide including the half-wave potential of the ORR current-potential curve as well as the HPRR/HPOR mixed potential.

In order to reproduce the behavior of MnOOH the rate constant of step (5) was assumed to be small ($k_5 = 0.2$ s$^{-1}$) and the Mn(IV)/Mn(III) redox potential was set at 0.90 V. In the first approximation, the rate constants $k_4$ and $k_4$ (HO$_2^-$ adsorption and
of barriers for the outer-sphere scenario ($O_2 + e^- \rightarrow O_2^-$ - step 2') section).

Concluding Remarks

In this manuscript we presented experimental RDE data for the ORR on various Mn oxides supplemented with the previously published results of RDE measurements for the HPRR/HPOR. Then, we applied a number of complementary quantum chemical approaches in order to rationalize the experimentally observed differences between the most ($\text{Mn}_2\text{O}_3$) and the least active (MnOOH) oxides. We aimed to refrain from defining the activity descriptors, but rather focused on molecular-level factors, which determine the reaction mechanisms. We found that periodical DFT calculations within conventional thermodynamic approach cannot account for the differences between $\text{Mn}_2\text{O}_3$ and MnOOH, in particular with regard to the slow bond breaking in the hydrogen peroxide intermediate corroborated by the experimentally observed kinetically limited HPRR and high hydrogen peroxide yield during the ORR on MnOOH. Activation barriers of likely elementary steps were considered using cluster calculations. The latter helped us in rationalizing much faster bond breaking of the hydrogen peroxide intermediate adsorbed on the surface of $\text{Mn}_2\text{O}_3$ compared to that on MnOOH. Faster dissociation of the hydrogen peroxide adsorbed on the surface of $\text{Mn}_2\text{O}_3$ oxide is explained by adsorbate-adsorbate interactions, which decrease the activation barrier for bond-breaking in the HO$_2$-ad intermediate.

The cluster calculations also suggest that a “direct” ORR mechanism occurring through bond breaking in the O$_2$ molecule is unlikely, and that the ORR in alkaline media may involve outer-sphere ET steps for the transfer of the first and the second electrons.

According to microkinetic modeling, the experimental differences between Mn$_2$O$_3$ and MnOOH cannot be reproduced considering material-independent kinetics for the transfer of the first and the second electrons. While fast outer-sphere ET steps are compatible with the ORR on Mn$_2$O$_3$, they cannot account for the ORR on MnOOH, where at least one of the ET steps must be ca. 10 times slower than on Mn$_2$O$_3$ to reproduce the experimental data. As follows from the quantum chemical calculations, the difference of the oxides’ activity in the first ET steps might originate from the nonadiabatic regime of ET, with the stronger orbital overlap determining higher activity.

In the periodical DFT calculations we did not follow the DFT approach does not allow to reproduce the difference in the oxides’ activity in the first ET steps. Another possibility is a competing scenario involving inner-sphere steps with somewhat higher (compared to the outer-sphere ET steps) activation barriers but occurring in adiabatic limit ($k \approx 1$).

The computational results reported in this study undoubtedly involve a large number of approximations, which should be taken into account critically when comparing the calculated and experimental trends. First, the solvent-solute and the solvent-electrode interactions are taken into account neither in periodical DFT, nor in cluster calculations, as these would increase the system size to a hardly treatable one. Although examples of both implicit and explicit solvent modeling, compatible with periodical DFT methods, are starting to appear$^{35,44}$ The focus of the computational study is thus placed exclusively at the electrode/reactant interactions. Second major approximation is related to the application of the cluster approach to describe the orbital overlap effect on the ET rate for the two oxides, as this approach does not allow to reproduce the difference in the oxides’ electronic structures quantitatively. In this case, as well as in the case of the bond-breaking step, we can outline mainly geometrical factors, which affect the differences in the MnOOH and Mn$_2$O$_3$ activities.

In the periodical DFT calculations we did not follow the DFT+U approach, which in some cases allows for a more accurate account of the oxides’ electronic structure and its effect on the geometry of adsorbates and the energetics of adsorption. However, the DFT+U approach is not universal, and has some shortcomings that may cause inaccuracy in computed energies and geometrical parameters (see...
discuss discussion in Refs. 45,46. Indeed, for MnO2 oxide PBE+U tends to overestimate the equilibrium volumes and also it favors a metal-to-metallic state, rather than an insulting character as derived from the hybrid functional approaches.47

Another approximation consists in the simplification of the bond-breaking mechanism, which could involve much more complex re-arrangements in the reaction layer with the participation of H2O and OH− species. However, within the framework of the adopted approach for the potential energy surface construction, introducing a large number of degrees of freedom from solution species would make the problem unsolvable. Last, the reaction steps in the formal kinetic modeling do not directly correspond to the elementary steps, which are addressed in the computational study. This does not allow us to directly compare the values of the rate constants resulting from formal kinetic modeling and from quantum chemical calculations, but rather relay on the outlined general trends in the differences of oxides’ activity.

Common electrocatalytic reaction schemes are primarily associated with adsorbed reactants and intermediates. In this work, we follow a different strategy and show that important mechanistic aspects of the electrocatalytic reaction kinetics can be determined by factors, which do not necessarily imply the ET to the reagent in the adsorbed state. In such cases, kinetic modeling is unlikely to distinguish between outer- and inner-spheres scenarios due to the large number of experimentally inaccessible parameters involved in simulations. However, our analysis points to the higher probability of the outer-sphere scenario in the first ORR step(s) on Mn oxides based on the currently available information on the reaction layer structure.

The computational approaches used in this work were previously applied to model simpler ET reactions on metals. Here we extended this treatment to describe the kinetics of a complex multistep reaction on oxides and estimate the key parameters of the quantum mechanical ET theory (of course, within the accuracy imposed by the approximations used). Further development in the predictive analysis of electrocatalytic reaction rates on oxides should involve a more detailed specification of the reaction layer structure (classical or ab initio MD simulations) as well as more accurate estimates of ET “microscopic” parameters (reorganization energy, orbital overlap, frequency factors). Further experimental studies should include pH effects and kinetics of probe outer-sphere electrochemical reactions and their dependence on the type of oxide.

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References

1. T. Poux, A. Bonnefont, G. Keranguéven, G.A. Tsirlina, and E.R. Savinova, Chemphyschem, 15(10), 2108 (2014).
2. T. Poux, A. Bonnefont, A. Ryabova, G. Keranguéven, G.A. Tsirlina, and E.R. Savinova, Phys. Chem. Chem. Phys., 16(27), 13595 (2014).
3. A. S. Ryabova, A. Bonnefont, P. Zagrebin, T. Poux, R. Paria Sena, J. Hadermann, A. M. Abakumov, G. Keranguéven, S. Y. Istomin, E. V. Antipov, G. A. Tsirlina, and E.R. Savinova, Electrochim. Acta, 187, 161 (2016).
4. A. S. Ryabova, F.S. Napoli, T. Poux, S.Y. Istomin, A. Bonnefont, D.M. Antipin, A.Y. Baranchikov, E.E. Levin, A. M. Abakumov, G. Keranguéven, E.V. Antipov, G. A. Tsirlina, and E.R. Savinova, Electrochim. Acta, 246, 643 (2017).
5. A.S. Ryabova, A. Bonnefont, P.A. Simonov, T. Dintzer, C. Ulahq-Bouillet, Y.G. Bogdanova, G. A. Tsirlina, and E.R. Savinova, Electrochim. Acta, 246, 643 (2017).
6. S. Shenkman and R. R. Adzic, J. Electroanal. Chem., 403(1–2), 169 (1996).
7. M. H. Shao and R. R. Adzic, J. Phys. Chem. B, 109(35), 16563 (2005).
8. K. Sasaki, L. Zhang, and R. R. Adzic, Phys. Chem. Chem. Phys., 10(1), 159 (2008).
9. J.X. Wang, J. Zhang, and R. R. Adzic, J. Phys. Chem. A, 111(49), 12702 (2007).
10. V.M.B. Cristiano, J.K. Ngila, S.A. Alia, D. Beley, C. Morein, C.-H. Chen, X. Shen, and S.L. Suib, Chem. Mater., 19(7), 1832 (2007).
11. X. Cao, N. Wang, L. Wang, C. Mo, Y. Xu, X. Cai, and L. Guo, Sens. Actuators, B, 147(2), 730 (2010).
12. S. Sturovkin, G.V. Plaksin, V.A. Semikolenov, V.A. Likhodobov, and I.J. Tiuano, U.S. patent 4,978,649, 1990.
13. G. Kresse and J. Furthmüller, Phys. Rev. B, 54(16), 11169 (1996).
14. E.P. Boeioch, Phys. Rev. B, 50(24), 17953 (1994).
15. B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B, 59(11), 7419 (1999).
16. S. Gietler, Acta Crystallogr. B. Struct. Sci., 27(4), 821(1971).
17. T. Kohler, T. Armbruster, and E. Libowitzky, J. Solid State Chem., 133(2), 486 (1997).
18. J. K. Rossmeis, J. Rossmes, A. Logadotdis, L. Lindquist, J. R. Kitchin, T. Bligard, H. Jonsson, J. Phys. Chem. B, 108(46), 17868 (2004).
19. J. Rossmeis, Z. W. Hu, Z. G. K. Joros, and J. K. Nørskov, J. Electroanal. Chem., 607(1–2), 83 (2007).
20. T. Poux, F.S. Napoli, Revision D01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, L. H. P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J.J. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, C. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Chtlers, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G.A. Voth, P. Salvador, J. D. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and J. D. Fox, Gaussian Inc., Wallingford CT, 2013.
21. T. Poux, D. Tomin are gratefully acknowledged for valuable discussions, and for her help with the BET measurements. E.V. Antipov and S. Y. Istomin are gratefully acknowledged for valuable discussions and for synthesis and characterization of the samples of Mn oxides.

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