**Anti-Ferromagnetic RuO$_2$: A Stable and Robust OER Catalyst over a Large Range of Surface Terminations**

Qiuhua Liang, Anja Bieberle-Hütter,* and Geert Brocks*

**ABSTRACT:** Rutile RuO$_2$ is a prime catalyst for the oxygen evolution reaction (OER) in water splitting. Whereas RuO$_2$ is typically considered to be non-magnetic (NM), it has recently been established as being anti-ferromagnetic (AFM) at room temperature. The presence of magnetic moments on the Ru atoms signals an electronic configuration that is markedly different from what is commonly assumed, the effect of which on the OER is unknown. We use density functional theory (DFT) calculations within the DFT+$U$ approach to model the OER process on NM and AFM RuO$_2$(110) surfaces. In addition, we model the thermodynamic stability of possible O versus OH terminations of the RuO$_2$(110) surface and their effect on the free energies of the OER steps. We find that the AFM RuO$_2$(110) surface gives a consistently low overpotential in the range 0.4–0.5 V, irrespective of the O versus OH coverage, with the exception of a 100% OH-covered surface, which is, however, unlikely to be present under typical OER conditions. In contrast, the NM RuO$_2$(110) surface gives a significantly higher overpotential of $\sim$0.7 V for mixed O/OH terminations. We conclude that the magnetic moment of RuO$_2$ supplies an important contribution to obtaining a low overpotential and to its insensitivity to the exact O versus OH coverage of the (110) surface.

Efficient catalysis of the oxygen evolution reaction (OER) is important in the electrochemical production of fuels for storage of renewable energy. The OER, which constitutes a critical step in such electrochemical processes, has been the subject of many theoretical and experimental studies aimed at developing electrocatalysts with improved activity. Rhenium pentoxide (Re$_2$O$_7$) has been widely reported to be one of the best anode materials for catalyzing the OER in water splitting, having an excellent electrocatalytic activity in both acidic and basic media. Despite the relatively high cost of ruthenium obstructing large-scale commercial applications, RuO$_2$ continues to be an important material, against which future (cheaper) OER catalysts need to be benchmarked. RuO$_2$ has long been considered to be a paramagnetic metal, and most theoretical investigations assume a non-magnetic (NM) ground state for RuO$_2$ when investigating its OER performance on the atomic scale. A recent experimental neutron diffraction study on RuO$_2$ single crystals, combined with density functional theory (DFT) calculations, has established that RuO$_2$ is an anti-ferromagnet (AFM) at room temperature. Magnetism and magnetic ordering are not likely to influence the energetics of the OER directly, but the presence of substantial magnetic moments signals a preference for a local high-spin electronic configuration on the Ru atoms. This difference in electron configurations on the Ru atoms can affect the OER energetics. Indeed, a DFT study on the final step in the OER, the formation of an O$_2$ molecule from an adsorbed OOH species, has concluded that the formation energy on a ferromagnetic (FM) RuO$_2$(110) surface is $\sim$1 eV lower than that on its NM counterpart. This strongly suggests that it is important to include the true magnetic electronic ground state to elucidate the success of RuO$_2$ as a catalyst for the OER.

RuO$_2$ has a rutile structure, and its most prominent surface for the OER is the (110) surface. The unit cell of the stoichiometric (110) surface contains two differently coordinated Ru atoms, one that is 6-fold coordinated by O atoms and one with a 5-fold coordination. The latter, coordinatively unsaturated (CUS), surface Ru atom is exposed and thought to be a reaction center for the OER. This clean surface, with exposed Ru atoms, does not persist under electrochemical conditions, as it will be covered by O or OH species, or a mixture of the two. Early DFT calculations of the OER on NM RuO$_2$ showed a difference of only $\sim$0.1 V in the...
overpotential between a fully O-terminated surface and a fully OH-terminated surface. Later, more refined calculations on NM RuO₂ identified a more advantageous reaction path, where an adsorbed OOH species transfers its H atom to a neighboring O site on the surface. Obviously, such an event can only take place if a neighboring O site is available, as OH sites block this transfer. This makes it necessary to revisit the phase diagram of O vs OH termination of the RuO₂(110) surface, and its effect on the OER process.

In the present paper, we study the OER on the AFM RuO₂(110) surface by means of DFT calculations. We establish the electronic structure and the magnetic moments of the surface Ru atoms as a function of O/OH coverage and calculate the O/OH coverage as a function of the applied potential and the pH (Pourbaix diagram). We investigate the entire OER, calculate the free energies of all reaction steps involved, and determine the overpotential, which is the prime parameter to judge the electrochemical activity toward the OER. In addition, we explore the dependence of the free energies and overpotential on the OH surface coverage and surface phases of the RuO₂(110) surface. We show that the AFM RuO₂(110) surface is more active for the OER than a NM RuO₂(110) surface. Except for the fully OH-terminated surface, the surface configuration has in fact little effect in determining the electrocatalytic activity of AFM RuO₂ toward the OER, explaining the versatility of this material under different pH conditions.

**COMPUTATIONAL DETAILS**

The DFT calculations are carried out with the Vienna Ab Initio Simulation Package (VASP), which uses the projector-augmented plane wave (PAW) technique, and a plane wave basis set. DFT exchange and correlation are treated at the level of the generalized gradient approximation (GGA), using the Perdew–Burke–Ernzerhof (PBE) functional. Following ref 14, to better model on-site electron–electron repulsion, which is instrumental in correctly describing the magnetism in RuO₂, we use the DFT+U approach in the form proposed by Dudarev et al., with an on-site interaction parameter of \( U − J = 2.0 \) eV for Ru. As shown in ref 14, the total energy difference between NM and AFM-ordered RuO₂ increases with increasing value of \( U − J \), but for too large a value, RuO₂ becomes a semiconductor, rather than a metal. The value \( U − J = 2.0 \) eV has been selected such that the NM–AFM total energy difference is a few times \( k_B T \) (at room temperature) per formula unit, and RuO₂ is still metallic. As PAW potentials, we use the Ru_pW potential, which includes p semicore states, and standard potentials for O and H atoms. We employ a plane-wave kinetic energy cutoff of 500 eV and energy and force convergence criteria of \( 10^{-5} \) eV and 0.01 eV/Å, respectively. The optimized RuO₂ bulk lattice parameters are \( a = 4.53 \) Å and \( c = 3.12 \) Å, in good agreement with the experimental values, \( a = 4.49 \) Å and \( c = 3.11 \) Å.

To model the (110) surface, a seven-layer stoichiometric RuO₂ slab is constructed with (110) surfaces, a \( 3 \times 2 \) rectangular surface supercell (cell parameters 9.36 and 12.82 Å), and a 15 Å vacuum region. A \( 4 \times 3 \times 1 \) Monkhorst–Pack sampling of the reciprocal cell is used. The atomic positions of the four bottom layers of the RuO₂ slab are fixed, and all other atomic positions are relaxed to their minimum energy positions. The rutile structure allows for only one particular AFM ordering in bulk RuO₂ that does not enlarge the size of the (bulk crystal) unit cell with respect to the NM unit cell; see Figure S1. As this is the AFM ordering determined from spin-polarized neutron diffraction, we adopt it for our calculations. We transfer the spin arrangement found for bulk RuO₂ to the seven-layer RuO₂(110) slab, as indicated by down (orange) and up (blue) arrows at the Ru sites shown in Figure 1. The size of the magnetic moments on the Ru atoms changes during the (electronic) optimization, but this AFM ordering persists. Convergence tests regarding the size of the slab and supercell are presented in the Supporting Information. Table S1–S3 give the calculated magnetic moments on the Ru atoms of bulk RuO₂ and of RuO₂ slabs of varying thickness, and Figures S1–S3 show the corresponding atomic structures.

**RESULTS AND DISCUSSION**

**RuO₂(110) Surface. Magnetism.** Starting with bulk RuO₂, we find that the AFM state is 74 meV per formula unit lower in energy than the (non-spin-polarized) NM state, with magnetic moments on the Ru atoms of \( \pm 1.18 \mu_B \), which is in agreement with previous work. Proceeding with the surface, the slab used to model the (110) surface is shown in Figure 1. It has a fully O-terminated surface on one side, which is a stable surface termination under high pH and overpotential conditions; see below. This surface contains two structurally different Ru atoms, indicated by the labels 7 and 14 in Figure 1. We maintain the stoichiometry of RuO₂ in the slab, so the surface on the other side (Ru atoms 1 and 8) remains clean of O atoms.

The optimized magnetic moments of the Ru atoms in the slab are shown in Table 1. The AFM ordering persists throughout the slab, with the magnetic moments in the middle of the slab (Ru atoms 4 and 11) attaining values of around \( \pm 1.18 \mu_B \), which is similar to the bulk. Toward the surfaces of the slab, the absolute magnetic moments become somewhat positive/negative signs stand for spin-up/down.

<table>
<thead>
<tr>
<th>Ru atoms</th>
<th>magnetic moment (( \mu_B ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–7</td>
<td>−0.91, −0.91, −1.15, −1.17, −1.11, −1.12, −0.22</td>
</tr>
<tr>
<td>8–14</td>
<td>1.18, 1.09, 1.18, 1.18, 1.16, 1.16, 1.45</td>
</tr>
</tbody>
</table>

![Figure 1.](image-url)
smaller but stay close to their bulk value. The exceptions are the Ru atoms 14 and 7 at the O-terminated surface, which have magnetic moments of $1.45 \mu_B$ and $-0.22 \mu_B$ respectively, signifying that their absolute values are 0.27 $\mu_B$ larger, respectively, 0.95 $\mu_B$ smaller than the bulk value. Especially the latter large change likely indicates a significant change in the electronic structure of the surface atom.

A Ru ion in bulk RuO$_2$ has a nominal oxidation state of 4+, corresponding to a configuration of 5s$^2$4d$^4$. The partial density of states (PDOS) of Ru atom 4, which is in the middle of the slab and thus bulk-like, is shown in Figure 2a. In the rutile structure, a Ru atom is 6-fold coordinated by oxygen atoms in a distorted octahedral coordination with O–Ru–O angles of 78 and 102°. Perfect octahedral coordination gives a multiplet further, so that the energy ordering of the d-states on the surface atom.

Figure 2, which likely causes its increased oxidation. All other O atoms in the structure are bonded to two neighboring Ru atoms.

Ru atom 7 represents an active site for the OER, implying that over the course of the OER (to be discussed in detail below) the O atom adsorbed on top is replaced by an OH or OOH species, or becomes a vacancy, thereby creating a coordinatively unsaturated (CUS) surface Ru atom. Interestingly, replacing the O atom by OH or OOH or creating a vacancy restores the basic electronic configuration of the Ru atom. The calculated magnetic moments of CUS Ru and Ru with OH adsorbed on top are $-1.21 \mu_B$ and $-1.26 \mu_B$, respectively, close to the bulk value. The corresponding PDOSs, Figure 2c,d, are consistent with valency 4+, and are in fact very similar to that of a Ru atom in the middle of the slab, Figure 2a. In conclusion, from the PDOS and magnetic moments analysis, we find that the electronic configuration of the CUS Ru atom is affected by O adsorption but not much by OH adsorption.

Surface Termination. Though the RuO$_2$(110) surface is mostly thought of as O-terminated under OER conditions, experiments also find a mixed O/OH surface termination under certain conditions. The exact coverage by O or OH depends upon the applied potential, as is concluded from in situ surface X-ray scattering experiments combined with DFT calculations. Previous calculations have used a NM RuO$_2$ substrate and considered a small number of fixed O/OH terminations. Here, we focus on AFM RuO$_2$, consider a wide range of O/OH terminations, and incorporate the entropies of the O/OH coverages to calculate their free energies.

The relative stability of different terminations can be inferred from studying the adsorption of n water molecules on the N sites of an O/OH-free surface in the form of m OH groups and n – m O groups, as in the reaction

$$ n\text{H}_2\text{O}(l) \rightarrow (\text{OH})_m\text{O}_{n-m} + (2n-m)\text{H}^+ + (2n-m)e^- $$

where * indicates the O/OH-free surface and *(OH)$_m$O$_{n-m}$ with the surface mixed O/OH coverage. Applying the computational hydrogen electrode (CHE) approach, one refers the potential of the RuO$_2$ electrode with respect to the reversible hydrogen electrode (RHE), which sustains the equilibrium $H^+ + e^- \leftrightarrow \frac{1}{2}H_2$ under standard conditions ($T = 298$ K, $p_{H_2} = 1$ bar). In addition, an equilibrium between liquid and gaseous water is assumed, $H_2\text{O}(l) \leftrightarrow H_2\text{O}(g)$ ($T = 298$ K, $p_{H_2O} = 0.035$ bar).

The Gibbs free energy of reaction 1 can then be expressed as

$$ G(n, m) = E^\ast(\text{OH})_m\text{O}_{n-m} + ZPE - TS(n, m) $$

$$ + (2n - m) \left[ \frac{1}{2} \mu_{H_2(g)} - eU_{\text{RHE}} \right] - E^\ast $$

$$ - \frac{1}{2} \mu_{H_2O(g)} $$

where $E^\ast(\text{OH})_m\text{O}_{n-m}$ and $E^\ast$ are the DFT total energies of the O/OH-covered RuO$_2$(110) and the O/OH-free surface, respectively. ZPE $= ZPE_{\text{RHE}} - ZPE_{\text{OH}}$ is the zero-point energy correction, with $ZPE_{\text{OH}}$ being the zero-point vibrational energies of all species on the left and right sides of reaction 1, respectively. These vibrational energies can be calculated as
$\sum \frac{1}{2} \hbar \nu_i$, with $\nu_i$ being the vibrational frequency and $\hbar$ Planck’s constant. In principle, the sum runs over all vibrational modes of the system, but in practice, only the modes involving hydrogen have a frequency sufficiently high to give an appreciable contribution. In our case, the only hydrogen-containing species are the adsorbed species and the free water and hydrogen molecules, for which we then calculate the vibrational modes and the ZPE. Furthermore, $\mu_{H,O(g)}$ and $\mu_{H_2(g)}$ are the chemical potentials of hydrogen gas and water gas, obtained from the DFT total energies and ZPEs of the molecules and the tabulated properties of the gases; $U_{\text{RHE}}$ is the potential of the RuO$_2$ electrode with respect to the RHE. The entropy $S(n, m)$ is modeled as the sum of the vibrational entropy\(^{30,31}\) and the mixing entropy.

We find that mixed O/OH coverages are energetically favorable only on a fully covered surface ($n = N$) and the O/OH configurations at fixed OH concentration (fixed $m$) differ little in energy ($\leq 0.1$ eV), so we use the simple expression

$$S_{\text{mix}}(N, m) = -Nk_B \ln \left( \frac{m}{N} \right) + \frac{N - m}{N} \ln \left( \frac{N - m}{N} \right) \tag{3}$$

Creating uncovered Ru sites on the surface ($n < N$) is energetically favorable only in the case of a fully OH-covered surface ($n = m$), and then far more favorable CUS Ru atoms (Ru atom 7 in Figure 1). So, for that particular case, we use the mixing entropy

$$S'_{\text{mix}}(n, n) = -\frac{1}{2}Nk_B \left( 2n - N \right) \ln \left( \frac{2n - N}{N} \right) + 2N - 2n \ln \left( \frac{2N - 2n}{N} \right) \tag{4}$$

where the factors 2 originate from the fact that only half of the Ru sites on the (110) surface are CUS Ru atoms.

The pH dependence of the free energy, eq 2, can be made explicit by referring the RHE to the standard hydrogen electrode (SHE) (pH 0) by the standard expression

$$-\epsilon U_{\text{RHE}} = -\epsilon U_{\text{SHE}} + k_B T \ln a_{\text{H}^+}$$

$$= -\epsilon U_{\text{SHE}} - (\text{pH}) \times k_B T \ln 10 \tag{5}$$

The values $m, n$ that give the minimum $G(n, m)$ represent the most stable surface O/OH coverage.

Starting from the fully O-covered surface, we have studied mixed O/OH/vacancy coverages; a number of representative structures are shown in Figure 3. A Pourbaix diagram of the most stable coverages, as a function of $U_{\text{SHE}}$ and pH, is shown in Figure 4. A fully O coverage is most stable above $U_{\text{SHE}} \approx 1.3$ V at pH 0, dropping linearly to above $U_{\text{SHE}} \approx 0.5$ V at pH 14. Between $U_{\text{SHE}} \approx 0.4$ and 1.1 V, a full OH coverage is most stable at pH 0, and that interval drops linearly to $U_{\text{SHE}} \approx -0.4$ and 0.3 V at pH 14. In the intermediate voltage ranges (1.1 V $\leq U_{\text{SHE}} \leq 1.3$ V at pH 0 to 0.3 V $\leq U_{\text{SHE}} \leq 0.5$ V at pH 14), mixed O/OH coverages are stable. Below the line $U_{\text{SHE}} \approx 0.4$ V at pH 0 to $U_{\text{SHE}} \approx -0.4$ V at pH 14, it becomes increasingly advantageous to create uncovered Ru sites, but a surface configuration where all CUS Ru atoms are uncovered only becomes stable below the line $U_{\text{SHE}} \approx -0.5$ V at pH 0 to $U_{\text{SHE}} \approx -1.1$ V at pH 14.

In experiments, the OER on RuO$_2$ is typically measured in the interval $U_{\text{RHE}} = 0.2$–1.6 V, which translates into the same interval for $U_{\text{SHE}}$ at pH 0 to 0.6–0.8 V at pH 14; see eq 5. The lowest part of this interval corresponds to a OH-covered surface with a small number of uncovered CUS Ru atoms; see Figure 4. In the range $U_{\text{RHE}} = 0.4$–1.1 V, one has a fully OH-covered surface, from 1.1 to 1.3 V one has mixed O/OH coverage with an increasing O percentage, and above 1.3 V the fully O-covered surface is most stable. These results actually agree quite well with what has been found in an experimental study.

**OER Reaction.** We consider a four-electron reaction mechanism for OER under alkaline conditions.\(^{32,33}\) The
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oucomes are easily adapted to the reaction mechanism under acidic conditions.32 The overall water oxidation reaction is

\[ 4\text{OH}^- \rightarrow \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \]  
(6)

where (g) and (l) refer to the gas and liquid phases, respectively. The reaction proceeds in four steps32

\[ \begin{align*}
* + \text{OH}^- & \rightarrow \text{*OH} + e^- \\
\text{*OH} + \text{OH}^- & \rightarrow \text{O} + \text{H}_2\text{O}(l) + e^- \\
\text{O} + \text{OH}^- & \rightarrow \text{*OOH} + e^- \\
\text{*OOH} + \text{OH}^- & \rightarrow \text{*} + \text{O}_2(g) + \text{H}_2\text{O}(l) + e^-
\end{align*} \]

(7) (8) (9) (10)

where * represents the active site of the catalyst, in this case a CUS Ru site on the surface, and *OH, *O, and *OOH represent the species adsorbed on the active site. As in the previous section, we use the CHE approach, assuming the equilibrium \( \text{H}^+ + e^- \leftrightarrow \frac{1}{2}\text{H}_2 \) under standard conditions \((T = 298 \text{ K}, p_{\text{H}_2} = 1 \text{ bar})\),29 as well as equilibrium between liquid and gaseous water, \( \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{O}(g) \) \((T = 298 \text{ K}, p_{\text{H}_2\text{O}} = 0.035 \text{ bar})\). Referring the potential of the RuO\(_2\) electrode with respect to the reversible hydrogen electrode (RHE), the Gibbs free energies, \( \Delta G_n \), of reactions 6–10 are given by

\[ \begin{align*}
\Delta G_1 &= \text{E}_{\text{*OH}} - \text{E}_* - \text{E}_{\text{H}_2\text{O}} + \frac{1}{2}\text{E}_{\text{H}_2} + (\text{AZPE} - T\Delta S)_1 \\
- eU_{\text{RHE}} \\
\Delta G_2 &= \text{E}_{\text{O}} - \text{E}_{\text{*OH}} + \frac{1}{2}\text{E}_{\text{H}_2} + (\text{AZPE} - T\Delta S)_2 \\
- eU_{\text{RHE}} \\
\Delta G_3 &= \text{E}_{\text{*OOH}} - \text{E}_\text{O} - \text{E}_{\text{H}_2\text{O}} + \frac{1}{2}\text{E}_{\text{H}_2} \\
+ (\text{AZPE} - T\Delta S)_3 - eU_{\text{RHE}} \\
\Delta G_4 &= \Delta G_0 - \Delta G_1 - \Delta G_2 - \Delta G_3 - 4eU_{\text{RHE}}
\end{align*} \]

(11) (12) (13) (14)

where \( \Delta G_0 = 4.92 \text{ eV} \) is the Gibbs free energy of the overall reaction 1; \( \text{E}_*, \text{E}_{\text{*OH}}, \text{E}_\text{O}, \text{E}_{\text{*OOH}} \), and \( \text{E}_{\text{H}_2\text{O}} \) and \( \text{E}_{\text{H}_2} \) are the total energies of the surface and of surfaces with the single adsorbed species OH, O, and OOH, respectively, and \( \text{E}_{\text{H}_2\text{O}} \) and \( \text{E}_{\text{H}_2} \) are the total energies of the \( \text{H}_2\text{O} \) and \( \text{H}_2 \) molecules, all obtained from DFT calculations. Note that we use eq 14 to avoid having to calculate the total energy of the \( \text{O}_2 \) molecule, whose triplet ground state is described less accurately in the current approach. AZPE and \( T\Delta S \) are the changes in zero-point energies and entropy from the initial state to the final state, respectively, with \( T \) being the temperature. In addition, \( \Delta S \) contains the entropy contributions of the gas phases used in reactions 7–10.\(^{10,31}\)

For an ideal catalyst, the four reaction steps have an equally large \( \Delta G_n \)

\[ \frac{G_0}{4} = \Delta G_1 = \Delta G_2 = \Delta G_3 = \Delta G_4 = 1.23 \text{ eV} \]

(15)

such that a single potential \( U_0 = 1.23 \text{ V} \) drives all reaction steps. Normally, this is not the case, and an additional overpotential is required to drive the step with the largest \( \Delta G_n \).

The overpotential is then defined by

\[ \eta \approx \frac{1}{1} \max \left( \Delta G_n \right) - U_0 \]

(16)

**Free Energies and Overpotentials.** We start from the fully O-covered RuO\(_2\)(110) surface with one active Ru site, which either is uncovered or adsorbs one of the intermediate species, *OH, *O, and *OOH, according to reactions 7–10, as shown in Figure 5. Upon geometry optimization, the H atom of an adsorbed OOH species transfers spontaneously to an adjacent O–Ru site on the surface, leaving behind an OO species adsorbed on the active site (see Figure 5d), which agrees with the results obtained by Rao et al.\(^5\) In fact, such a spontaneous H transfer leaving behind an OO species also happens on mixed O/OH terminated surfaces, as long as there is an O-terminated Ru site neighboring the active Ru site. Only if such an O-terminated Ru site is not available, as on a fully OH-terminated surface, the OOH adsorbs without splitting off the \( \text{H}_2 \) as shown in Figure S4.

Figure 6 shows the Gibbs free energies of reactions 11–14, calculated at zero potential \( (U_{\text{RHE}} = 0) \), and the calculated overpotential, eq 16, for mixed O/OH-covered RuO\(_2\)(110) surfaces, with \( 0–100% \) fractions OH coverage, and an AFM RuO\(_2\)(110) substrate. In order to analyze the effects of magnetism on the RuO\(_2\)(110) surface for the OER, we have repeated the calculations switching off the spin polarization, which makes the RuO\(_2\) substrate NM. The fully O-terminated (0% OH) NM surface has an overpotential of 0.41 V, which agrees with literature results,\(^{37,42}\) where the potential determining step (PDS) is the final reaction step, eq 10, Figure 6a. Partially OH-covered surfaces display higher overpotentials between 0.63 and 0.73 V, where the third reaction step, eq 9, is the PDS. These higher overpotentials disagree with the experimental observations regarding the OER activity of RuO\(_2\). However, they agree with the fact that DFT calculations on NM RuO\(_2\) consistently predict larger overpotentials, as discussed in ref 35.

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**Figure 5.** Top and side views of the OER reaction cycle, eqs 7–10, for a O-covered surface, (a) the active CUS (uncovered) Ru atom highlighted in yellow, (b) with OH, (c) O, and (d) OOH adsorbed. The dashed line between O and H in part d indicates the transfer of H to a neighboring O site.
For the AFM configuration, the fully O-terminated (0% OH) surface has an overpotential of 0.49 V, which is close to the NM configuration but different from the latter; the PDS is the third reaction step, eq 9, Figure 6b. In addition, the overpotential calculated for AFM RuO$_2$ decreases slightly to 0.41 V, for increasingly OH-covered surfaces, the third reaction step remaining the PDS. These low overpotentials of diatomic OOH groups transfer to an O on an adjacent Ru site, Figure 5d, as discussed above. This route is blocked for a fully covered OH surface and forces OOH to adsorb as one species, which increases its energy.

Introducing magnetism in RuO$_2$ does not affect the OER on a fully O-covered (110) surface much, but it considerably reduces the overpotential on mixed O/OH-covered surfaces, Figure 6c. A fully O-covered surface is maximally oxidized, resulting in very small magnetic moments on the CUS Ru atoms (Ru atom 7 in Figure 1), where the difference in the electronic configuration between AFM and NM states is small, Figure 2b. As discussed in the Magnetism section, on mixed O/OH-covered surfaces, the average oxidation state of the CUS Ru atoms decreases, and the increased number of electrons prefer to be in a high-spin state, as is signaled by the magnetic moments on the CUS Ru atoms, Figure 2d. Whereas this is correctly taken into account in the AFM calculation, in a NM calculation, one enforces a low-spin configuration on these atoms, which introduces an error, as this is not the true ground state. The results discussed here are obtained with a 3 × 2 surface supercell. Using a smaller 2 × 1 supercell, as in ref S, for instance, the results are qualitatively similar but quantitatively a little different, as discussed in the Supporting Information; see Figures S5 and S6. Using a larger supercell increases the accuracy of the calculations.

**Adsorption Energies.** In order to interpret the trends in the calculated overpotentials, it is instructive to examine the adsorption free energies of the OER intermediates. These can be easily extracted from the Gibbs free energies of the reaction steps, eqs 11–14, setting $U_{RHE} = 0$

$$
\Delta G_{OH}^{*} = \Delta G_{1}
= E_{OH}^{*} - E_{a} - E_{H,O} + \frac{1}{2}E_{H_2} + (\Delta ZPE - T\Delta S)_1 \tag{17}
$$

$$
\Delta G_{O}^{*} = \Delta G_{1} + \Delta G_{2}
= E_{O}^{*} - E_{a} - E_{H,O} + E_{H_2} + (\Delta ZPE - T\Delta S)_{1+2} \tag{18}
$$

$$
\Delta G_{OOH}^{*} = \Delta G_{1} + \Delta G_{2} + \Delta G_{3}
= E_{OOH}^{*} - E_{a} - 2E_{H,O} - \frac{3}{2}E_{H_2} + (\Delta ZPE - T\Delta S)_{1+2+3} \tag{19}
$$

The free energies of the OER intermediates for adsorption on pure and mixed O/OH-covered surfaces are shown in Figure 7. The lower the adsorption free energy, the stronger the bonding of the species to the active site.

Starting with the OH adsorbate, we notice that $\Delta G_{OH}^{*}$ decreases with increasing OH coverage from 0.80 eV for a fully O-covered surface (0% OH) to nearly zero for the 92% OH-covered surface; see the bottom panel in Figure 7. This is consistent with the calculated stability of the fully OH-covered surface under zero-potential conditions; see Figure 4. For the ideal catalyst, the $\Delta G_{OH}^{*}$ should be close to the ideal value $\Delta G_{OH}/4 = 1.23$ eV, eqs 15 and 17. However, all of the O/OH coverages give a $\Delta G_{OH}^{*}$ that is significantly smaller than the ideal value, which means the OH binds to the surface too strongly. Because of the sum rule $\Delta G_{OH}^{*} + \Delta G_{2} + \Delta G_{3} + \Delta G_{4} = \Delta G_{0}$, eqs 14 and 17, if $\Delta G_{OH}^{*}$ is too small, then one or more of the remaining steps, $\Delta G_{i}$ ($i = 2, 3, 4$), have to be too large.

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Figure 6. Gibbs free energies of the four reaction steps, eqs 11–14, of (a) NM and (b) AFM systems with mixed O/OH coverages and different OH percentages. The values of the overpotentials are given in the legends. The potential determining steps are represented by the solid lines between the steps. (c) Summary plot of the overpotentials of the NM and AFM systems.
Defining the deviation from ideal as $\delta_1 = \frac{(\Delta G^*_G - \Delta G^*_{O})}{\epsilon}$, the overpotential $\eta$, eq 16, must be at least $\delta_1/3$ V, as the best scenario is to divide this deviation because of the OH overbinding equally over the three remaining reaction steps.

The next reaction step, following OH adsorption, involves an adsorbed O species. The middle panel in Figure 7 displays the adsorption free energy, $\Delta G^*_{O}$, of the O species, eq 18. $\Delta G^*_O$ decreases from 1.97 to 1.45 eV upon increasing the surface OH coverage from 0 to 92%, showing a similar trend in the increase of the O binding strength as for the OH species. Comparing to the ideal value $\Delta G^*_O/2 = 2.46$ eV, eqs 15 and 18, also the O atom is bonded too strongly. Defining a deviation from ideal by $\delta_2 = \frac{(\Delta G^*_O/2 - \Delta G^*_{O})}{\epsilon}$, we note that $\delta_2 \approx \delta_1$, so the second reaction step has not compensated for the deviation of the first step at all. On the contrary, following a reasoning similar to that in the previous paragraph, then because of the O overbinding, the overpotential must now be at least $\delta_2/2$ V, if the deviation is divided equally over the two remaining reaction steps.

Finally, the top panel in Figure 7 shows the adsorption free energy, $\Delta G^*_{OOH}$ of the OOH species, eq 19. The calculated values for $\Delta G^*_{OOH}$ decrease from 3.69 to 3.39 eV upon increasing the surface OH coverage from 0 to 92%. These values are in fact close to the ideal value $3\Delta G^*_O/4 = 3.69$ eV, eqs 15 and 19, which means that the systems bind OOH almost perfectly. We define as before the deviation from the ideal value as $\delta_3 = \frac{(\Delta G^*_O/4 - \Delta G^*_{OOH})}{\epsilon}$, where we note that numerically $\delta_3 < \frac{1}{2}\delta_2$. From eqs 18 and 19, we now obtain $\Delta G_3 = \frac{\Delta G^*_O}{4} + \epsilon(\delta_2 - \delta_3)$ and $\Delta G_3 = \frac{\Delta G^*_O}{4} + \epsilon\delta_3$. We conclude that $\Delta G_3 > \Delta G_0$, so the third reaction step, eq 9, determines the overpotential, which is $\eta = \delta_2 - \delta_3$. Notably, this number is fairly constant as a function of OH coverage; see Figure 6b and c. In summary, the overpotential is determined by the fact that the intermediate species O and OH bind to the substrate too strongly.

Repeating this analysis for the OER on NM RuO$_2$ shows that $\Delta G^*_O$ for AFM RuO$_2$ is consistently higher than that for NM RuO$_2$ by up to ~0.3 eV for all O/OH coverages, except for the 92% OH coverage; see Figure S7. In contrast, the difference in $\Delta G^*_{OOH}$ between AFM and NM RuO$_2$ alternates in sign as a function of increasing OH coverage, whereas $\Delta G^*_{OOH}$ is relatively unaffected. This suggests that the main effect of magnetism is to decrease the bonding strength of the O adsorption, which decreases $\delta_1$ and therefore reduces the overpotential, as caused by the third reaction step, to bring it in agreement with experiment. This finding is consistent with ref 35, where an overbinding of the O adsorbate in DFT calculations on NM RuO$_2$ has been suggested as a possible cause for the discrepancy in overpotential between these calculations and experiment.

We propose that the differences between the OER results on AFM and NM RuO$_2$ can be understood from the changes in the electronic structure that accompany the magnetism, Figure 2. As discussed above, switching on spin polarization creates a high-spin state (and magnetic moments) on the OER-active Ru atoms without adsorbate, or with OH/OOH adsorbates; see Figure 2c and d. This lowers the total energies $E_{Ru}$, $E^{OH}_{Ru}$, $E^{O}_{Ru}$, and $E^{OOH}_{Ru}$ with respect to their low-spin NM counterparts. The Ru atom with O adsorbate is low spin anyway (see Figure 2b), so the effect on the total energy $E_{Ru}$ of switching on spin polarization is minimal. In view of eqs 17–19, the largest effect of switching on spin polarization then should be an increase of $\Delta G^*_O$.

Previous computational studies on metal oxides have found that the O versus OH termination of a surface can strongly modify the overpotential of the OER. 37–40 For example, Calle-Vallejo et al. 39 have studied this for the NiO(001) surface and its hydroxylated modification NiOOH. Pristine NiO shows an overpotential of 0.3 V, while the overpotential increases to 0.6 V for the hydroxylated (NiOOH) surface, demonstrating that hydroxylation of the surface significantly decreases its OER activity. Sun et al. 40 have investigated the OER on clean, O- and OH-terminated spinel Co$_3$O$_4$(100) surfaces. The O-terminated surface gives an overpotential of 0.45 V, whereas OH-terminated and clean surfaces yield much higher overpotentials of 0.93 and 1.82 V, respectively.

Our calculations show that the overpotential obtained for the OER on the RuO$_2$(110) surface is remarkably insensitive to the exact mix of O versus OH coverage. This can be traced to the fact that the adsorption energies of the intermediate species, OH, O, and OOH, do not change very much upon varying the O/OH coverage mix. The exception to this rule is a significantly decreases its OER activity. The Pourbaix diagram shows that a fully OH-covered surface is unlikely to be present under typical OER conditions.

## SUMMARY

Although rutile RuO$_2$ is usually assumed to be non-magnetic (NM), it is in fact an anti-ferromagnetic (AFM) metal at room temperature according to the recent literature. By means of density functional theory (DFT) calculations, applying the DFT+$U$ formalism, we model the oxygen evolution reaction (OER) on the AFM RuO$_2$(110) surface and contrast our results with those obtained for NM RuO$_2$. Although magnetic ordering as such is not expected to play a role in chemical bonding, the presence of magnetic moments on the Ru atoms changes their electronic structure considerably, as compared with the low-spin NM state, which affects their bonding to adsorbed species.

The RuO$_2$(110) surface is known to be covered by O or OH groups, or a mixture of the two, depending on the pH and on
the applied potential. We model the thermodynamic stability of these possible coverages and the effect they have on the free energies of the OER steps. We find that different coverages have little effect on the overpotential calculated for the OER on an AFM RuO₂(110), with values between 0.41 and 0.49 V. The adsorption energies of the intermediate species involved in the OER (OH, O, and OOH) on the active Ru sites on the surface vary little with different O/OH coverages. This indicates that it is the local electronic structure of the active Ru site which determines the reaction energies and that this electronic structure does not change very much upon altering the surface coverage.

The exception is a 100% OH-covered surface, which gives a significantly higher overpotential of 0.71 V. This is due to blocking the proton transfer from the adsorbed OOH species to the surface in this particular case. However, such a coverage is not stable at the potentials required to drive the OER, where (part of) the surface is converted to O-coverage, which allows for the proton transfer, and lowers the overpotential.

In contrast, a NM RuO₂(110) surface gives significantly higher overpotentials of 0.63–0.67 V for mixed O/OH terminations. It demonstrates that representing the magnetic moments on the Ru atoms is necessary to describe their electronic structure properly and capture accurately the bonding to the intermediate species involved in the OER. The overpotential calculated for AFM RuO₂(110) is not only low but also remarkably insensitive to different surface terminations, which adds to the reasons why RuO₂ is an excellent OER catalyst.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c08700.

Figures S1–S3 and Tables S1–S3 describe the structure and magnetic structure of the RuO₂ bulk and (110) surface and the results of convergence tests regarding the size of the slab and supercell used to represent this surface. Figure S4 visualizes the OER reaction cycle on a fully OH-terminated RuO₂(110) surface. Figures S5 and S6 show the results of calculations using a smaller, 2 × 1 surface supercell. Figure S7 shows the adsorption energies of the intermediate species as calculated for NM RuO₂ (PDF)

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**Notes**

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