Ti atoms in $\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ mixed oxides form active and selective sites for electrochemical chlorine evolution

Rasmus K. B. Karlsson^a, Heine A. Hansen^b, Thomas Bligaard^c, Ann Cornell^a, Lars G. M. Pettersson^{d,*}

^a*Applied Electrochemistry, School of Chemical Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

^b*Department of Energy Conversion and Storage, Technical University of Denmark, DK-4000 Roskilde, Denmark*

^c*SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, USA*

^d*Department of Physics, AlbaNova University Center, Stockholm University, S-106 91 Stockholm, Sweden*

Abstract

The electrocatalytic properties of the (1 1 0) surface of Ru-doped TiO_2 , Ti-doped RuO_2 and the industrially important Dimensionally Stable Anode (DSA) composition $\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ have been examined using density functional theory. It is found that the oxygen adsorption energy on a Ti site is strongly affected by the presence of small amounts of Ru dopant, whereas oxygen adsorption is relatively unaffected by Ti dopants in RuO_2 . The calculations also indicate that coordinatively unsaturated Ti sites on Ru-doped TiO_2 and on $\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ could form active and selective sites for Cl_2 evolution. These results suggest a reason for why DSA shows a higher chlorine selectivity than RuO_2 and propose an experimental test of the hypothesis.

Keywords: Dimensionally stable anodes, electrolysis, oxygen, chlorine, selectivity, density functional theory

*Corresponding author. Tel: +468-5537-8712

Email addresses: rasmusk@kth.se (Rasmus K. B. Karlsson), lgm@fysik.su.se (Lars G. M. Pettersson)

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1 **1. Introduction**

2 Chlorine is a major industrial chemical, with uses in *e.g.* production of construction
3 materials, detergents, pesticides, and in water treatment. Chlorine is produced by elec-
4 trolysis of concentrated sodium chloride solutions. While the process has a high current
5 efficiency, part of the electrical energy is used in the unwanted side reaction of oxygen
6 evolution.[1, 2] The industrial production of chlorine is performed using so-called Di-
7 mensionally Stable Anodes (DSA), a trade name for mixed Ru-Ti oxide coatings with,
8 originally, the overall composition $\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$. These coatings exhibit high stability
9 and are more selective than pure RuO_2 for chlorine evolution over oxygen evolution.[2, 3]

10 There are numerous experimental studies of chlorine evolution and oxygen evolution on
11 Ru-Ti mixed oxides and RuO_2 (see *e.g.* [2, 4–9]). Studies of selectivity and activity trends
12 on electrodes where the coating composition (Ru:Ti ratio) has been varied in a systematic
13 way are particularly relevant for the present paper. Kuhn and Mortimer [10] found that
14 the anodic exchange current density in NaCl solution was approximately constant down
15 to 20 mol-% Ru content in the mixed coatings. Similar data was presented by Burrows
16 *et al.* [11]. Tilak *et al.* [12] found essentially constant voltammetric charge and kinetic
17 properties at Ru concentrations above 20%, although they did not study coatings with
18 higher than 40 mol-% Ru. More recently, Aromaa and Forsén [13] found that kinetics
19 (Tafel slopes and overpotentials) for chlorine evolution were essentially unchanged as
20 long as Ru concentrations were above 20%. The chlorine selectivity has been measured
21 directly in a number of studies. Buné *et al.* [3] studied the selectivity of $\text{RuO}_2\text{-TiO}_2$
22 electrodes, quantifying the gas compositions using gas chromatography. They found a
23 clear increase in oxygen selectivity as the Ru concentration in the coating was increased
24 from 5% to 100%. The increase was especially pronounced at Ru concentrations above
25 30%. As observed by Kuhn and Mortimer [10] and Burrows *et al.* [11], Tafel slopes were
26 essentially unchanged in the range from 30% Ru to 100% Ru. Arikawa *et al.* [14] used
27 differential electrochemical mass spectroscopy to study the selectivity for chlorine using
28 Ru-Ti oxide electrodes. They again concluded that the selectivity for chlorine evolution

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29 over oxygen evolution increased with decreasing Ru concentration. Overall, experimental
 30 results thus seem to agree that the activity for chlorine evolution is maintained even as
 31 the Ru content of the Ru-Ti mixed oxide is reduced to 20%. Furthermore, the selectivity
 32 studies that have been performed show that the chlorine selectivity increases as the
 33 Ru content is decreased, down to 20%. However, the fundamental reason behind the
 34 enhanced selectivity is still not fully elucidated. The traditional explanation has been
 35 that oxygen evolution requires two adjacent Ru surface sites, while chlorine evolution
 36 just needs one.[3] In that view, the Ti component of DSA is simply a stabilizing "filler"
 37 material, that serves to separate Ru atoms. This might also be expected from the
 38 observation that non-defected TiO_2 is very inert. In contrast to this explanation, we
 39 here present results that instead suggest that the Ti component is modified and becomes
 40 selective towards chlorine evolution through doping with Ru.

41 In addition to the experimental studies of chlorine and oxygen evolution using metal-
 42 oxide electrodes, theoretical studies have appeared more recently. Electrocatalytic pro-
 43 duction of chlorine and oxygen on pure RuO_2 , TiO_2 , IrO_2 and PtO_2 was studied by
 44 Hansen *et al.* [15]. It was found that the adsorption energy of O, $\Delta E(\text{O}^c)$, on the coor-
 45 dinatively unsaturated site (cus) of rutile (1 1 0) surfaces is a reasonable descriptor for
 46 the activity for both chlorine and oxygen evolution [15]. Although another descriptor
 47 ($G_{\text{O}^*}^\circ - G_{\text{OH}^*}^\circ$) for the oxygen evolution reaction is more generally applicable, for both
 48 rutiles, perovskites, anatases, Co_3O_4 and Mn_xO_y oxides, $\Delta E(\text{O}^c)$ is a reasonable descrip-
 49 tor for both the oxygen evolution reaction and the chlorine evolution reaction on rutile
 50 oxides [16]. Hansen *et al.* also presented a theoretical volcano plot for chlorine evolu-
 51 tion and oxygen evolution on rutile (1 1 0) surfaces (Fig. 5 in [15]). This volcano plot
 52 shows the minimum overpotentials needed for oxygen and chlorine evolution to occur, as
 53 a function of the $\Delta E(\text{O}^c)$ descriptor. The paper of Hansen *et al.* identifies three different
 54 intermediates which can all lead to chlorine evolution. These three intermediates, Cl^c ,
 55 ClO^c and $\text{Cl}(\text{O}^c)_2$, all bind to the cus of rutile oxides. The prevalence of each different
 56 intermediate varies between materials (as a function of $\Delta E(\text{O}^c)$). On the other hand,

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oxygen evolution was identified to occur via only a single intermediate for all materials. The existence of three different intermediates in the case of chlorine evolution is what makes it possible to alter the selectivity for chlorine evolution over oxygen evolution, even though both reactions are governed by the same $\Delta E(\text{O}^\text{c})$ descriptor. By examining the volcano plot of Hansen *et al.* one realizes that there is a minimum in the theoretical overpotential for chlorine evolution from rutile surfaces at the point where $\Delta E(\text{O}^\text{c}) = 3.2$ eV, corresponding to the lowest overpotential for chlorine formation via the Cl^c intermediate. At this point, the overpotential for oxygen evolution is more than 0.4 eV higher. At all other points, the overpotential difference between oxygen evolution and chlorine evolution is smaller. Thus, a rutile material which exhibits a value of approximately 3.2 eV for the O adsorption descriptor is predicted to be an active and selective electrocatalyst for chlorine evolution. While this conclusion was not mentioned in the paper by Hansen *et al.*, it is a direct consequence of the volcano plot.

The theoretical Pourbaix diagram for chlorine and oxygen on RuO_2 has been reexamined by Exner *et al.* [17], who found that their calculated Pourbaix diagram agreed well with that of Hansen *et al.* [15]. Both the study of Hansen *et al.* [15] and that of Exner *et al.* [17] considered all possible arrangements of oxygen, chlorine or chloroxy species on the RuO_2 (110) surface, so the agreement indicates that there is now a good understanding of the surface intermediates and configurations relevant for electrochemical oxygen and chlorine evolution. However, Exner *et al.* [17] also performed calculations where solvent effects were included in an approximate way. The adsorption energies were corrected by a solvation energy obtained from calculations using a cluster description of the adsorbate and surface, and a continuum description of the electrolyte. The adsorption energies were changed significantly by including solvation effects in this way. As an example, the inclusion of solvent effects made the adsorption energy difference between two considered adsorbate arrangements ($\text{ClO}^\text{c} + \text{O}^\text{c}$ versus $\text{Cl}(\text{O}^\text{c})_2$) 0.7 eV larger. This is in contrast with an earlier study, performed at the DFT level with explicit water molecules included and a periodic description of the surface, where it was instead found

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that inclusion of water changed the adsorption energies of O and OH on RuO₂ by less than 0.05 eV[18]. However, it should be noted that this earlier study did not examine the effects of explicit solvent molecules on the adsorption energies of any other species than O and OH.

In the present study, we use the same gas phase H₂ and H₂O reference states for the O^c adsorption energies as Hansen *et al.* [15] in order to directly relate to their predictions. We have performed calculations of O adsorption on the rutile (1 1 0) surface of a number of different pure and mixed RuO₂ and TiO₂ systems. The (1 1 0) surface is the most stable for TiO₂ [19], and is also prominent on the particles forming the coating of Ru_{0.3}Ti_{0.7}O₂ electrodes [20]. Additionally, experimental work on chlorine and oxygen evolution on RuO₂ (1 1 0) single-crystals shows that the (1 1 0) surface in many respects has a similar behavior as polycrystalline RuO₂ [21]. As in the study of Hansen *et al.*, we do not consider the effect of vacancies or interstitials in this study. However, according to the Pourbaix diagrams and scaling relations presented previously [15, 17], vacancies and interstitials are not necessary to explain the oxygen and chlorine evolution activity of rutile oxides. *Ab initio* analysis of mixed oxides of Ti and Ru has been performed in a number of earlier studies [22–25], but there is no first-principles study of the interaction between Ru doping of TiO₂ and the selectivity for electrolytic production of chlorine versus oxygen.

2. Computational methods

All density functional theory (DFT) calculations were performed using GPAW [26], version 0.9.1.258, and the GPAW atomic PAW setups version 0.9.9672. These setups include semicore electrons on the metal atoms, which has been shown to be important [27, 28]. For Ru and Ti, 16 and 11 electrons, respectively, were handled self-consistently in the calculations. These PAW setups have been found to be quite accurate [29] and are expected to improve the description of O, Ru and Ti compared to previous studies [15] (see section 1 of the Supplementary Information). The RPBE [30] exchange-correlation

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functional was used for all calculations.

The O^c adsorption energy is calculated in the following way, with H_2 and H_2O in vacuum as reference states [15]:

$$\Delta E(\text{O}^c) = E(\text{O}^c) - E(^c) - E(\text{H}_2\text{O}) + E(\text{H}_2), \quad (1)$$

where $E(\text{O}^c)$ is the energy of a surface with a relaxed O^c adsorbate and $E(^c)$ is the energy of a surface without the same adsorbate. Although using H_2O and H_2 in vacuum as reference states results in a consistent treatment of adsorption energies, they will not correspond directly to binding energies of O to the surface. The adsorption calculations were performed in the GPAW finite-difference mode using a grid spacing of 0.18 Å. All model systems used in the calculations consisted of 4-layer metal oxide slabs, the same number of layers as in the study of Hansen *et al.* [15] (more details about the convergence in adsorption energy with respect to the number of layers in the slab are found in section 2 of the Supplementary Information). All calculations were fully periodic. Each slab was separated from the next slab in the z direction by 32 Å of vacuum. The periodic oxide model systems consisted of unit cells of either a 1x1 surface with 2 surface sites (one bridge site and one cus site, see Figures 1 and 2b), a 1x2 surface with 4 surface sites, making it twice as wide in the y direction (two bridge and two cus sites), or a 2x1 slab with 4 surface atoms (four bridge and four cus sites), twice as wide in the x direction. The three-dimensional structure of a 1x1 surface slab is shown in Figure 1, for the optimized O^c adsorption geometry. For the 2x1 slab systems, the GPAW linear combination of atomic orbitals (LCAO) mode [31] with a double-zeta polarized basis set was first used to relax the systems, before final relaxation in the finite difference mode. In all calculations, the two bottom layers of the slab were fixed. Monkhorst-Pack k-point sampling with $4 \times 4 \times 1$ k-points was used for all adsorption calculations. Adsorbates, as well as the first two layers of the slab, were relaxed until the maximum force on any atom was less than 0.05 eV / Å.

The plane-wave (PW) mode, with a plane-wave energy cutoff of 900 eV and an $8 \times 8 \times 8$

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138 k-point sampling, was used to obtain the structures of bulk RuO_2 and TiO_2 . Optimization
139 of lattice parameters and atomic positions proceeded until the maximum force was less
140 than $0.01 \text{ eV} / \text{\AA}$. The lattice constants determined for pure oxides were used also for
141 doped systems, except for the $\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ (“DSA”) model system where (to reduce the
142 computational demands) the lattice constants were assumed to follow Vegard’s law [32]
143 (see section 4 of the Supplementary Information).

144 A Fermi smearing of 0.1 eV together with Pulay density mixing [33] was used in all
145 calculations.

146 Values for grid spacing, number of layers, k-point sampling, and vacuum distance
147 between layers were converged to better than 0.1 eV in the adsorption energies.

148 Dipole correction [34] was not included since it was found that including a dipole
149 correction changes the adsorption energy of O on the cus site of TiO_2 , RuO_2 or TiO_2
150 doped with Ru in the first-layer bridge site by less than 5 meV .

151 It is well known that DFT GGA functionals tend to overly delocalize electrons due to
152 the self-interaction error (SIE) [35, 36]. To gauge the size of the self-interaction error
153 for the mixed systems considered in this paper, Hubbard- U calculations were carried out
154 (see section 3 of the Supplementary Information). We have used U values between 1
155 and 6 eV on the Ti d orbitals, since these d -states are the states that would be affected
156 most significantly by the self-interaction error. We conclude that the self-interaction
157 errors appear small enough to ignore in the present study. All subsequently discussed
158 calculations are performed without the inclusion of a Hubbard- U parameter.

159 3. Results and discussion

160 3.1. Adsorption energies on pure oxides

161 As a starting point, we determined the adsorption energies on pure oxides of RuO_2
162 and TiO_2 . At full surface coverage of O^c , the O^c adsorption energies on pure TiO_2 and
163 RuO_2 were found to be 5.1 eV and 1.7 eV , respectively. The first value agrees well with
164 that found in a previous study [15], but the latter is about 0.8 eV lower than in previous

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studies [15, 17, 37]. The cause for this difference between the present work and the previous studies is that we here include semi-core states in the self-consistent description of Ru and Ti. To examine the effect of these semi-core states, the same O^c adsorption calculation on RuO_2 was repeated using a GPAW Ru setup which does not include semi-core states. This calculation yielded an adsorption energy of 2.4 eV, which is close to those reported previously [15, 17]. The remaining difference between the earlier and the present results can be attributed to the smaller 1x1 surface cell used in the present work. The main reason for the difference is thus the inclusion of semi-core states, yielding what we would expect to be a significantly more accurate description of the metal ion and therefore also a more accurate adsorption energy. The exchange interaction between same-shell sp - and d -states is large and cannot be easily described by a static potential as required if the sp -states are treated as core and d as valence [27, 28].

3.2. *Comparing adsorption energies on 1x1 and 1x2 surfaces*

In theoretical studies of surface reactions, proper description of the surface phenomena relies on using adequately large unit cells. Since we use small 1x1 surface cells in several parts of this paper, it is useful to consider differences between adsorption energies on the 1x1 and 1x2 slabs. The most critical effect of using 1x1 surface slabs is that they impose a more limited configurational freedom for the O^c adsorbate. This can lead to artificially increased adsorbate-adsorbate interactions, destabilizing the adsorbate. The trends observed in this study are similar for 1x1 and 1x2 cells (see below), but it is prudent to clarify the magnitude of the contribution from adsorbate-adsorbate interactions. Therefore, we calculated O^c adsorption energies on both 1x1 and 1x2 slabs of TiO_2 and RuO_2 . In case of the 1x2 surface systems, calculations were performed for both the case of adsorption of one oxygen with both cus sites empty initially (resulting in the surface cus configuration of $O^c + ^c$) and the case of adsorption of one oxygen with one cus site already occupied by oxygen (resulting in the surface cus configuration of $O^c + O^c$). Furthermore, we calculated the average adsorption energy of two O^c on two empty cus sites.

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3.3 Adsorption energies on doped TiO_2 , RuO_2 and mixed oxides

System	RuO_2	TiO_2
1x1 surface / eV	1.7	5.1
1x2 surface, 50% final coverage / eV	1.6	4.7
1x2 surface, 100% final coverage	1.7	5.6
1x2 surface, average of 2 O^c	1.6	5.1

Table 1: Surface coverage effects on adsorption energies (in eV) of O on the cus site of RuO_2 and TiO_2 and comparison of adsorption energies on 1x1 and 1x2 slabs.

The results are seen in Table 1. In the case of RuO_2 , the adsorption energies increase by about 0.1 eV as the O^c coverage is increased. The change for TiO_2 is significantly larger, at about 0.9 eV. In both cases, the value of the adsorption energy increases as the coverage increases, indicating an adsorbate interaction-induced destabilization of the O^c adsorbate. That the increased adsorption energy is associated with a destabilization of the O^c adsorbate is due to the formula for adsorption energy used (equation 1), where a decreased binding energy of oxygen (a numerically larger value of $E(\text{O}^c) - E(^c)$) will result in a larger (more positive) value for $\Delta E(\text{O}^c)$. The adsorption energy on the 1x1 surface is in both cases a good approximation for the mean adsorption energy for two O^c on a surface with two empty cus sites.

3.3. Adsorption energies on doped TiO_2 , RuO_2 and mixed oxides

We started the study of the doped oxides by performing calculations on 1x1 slabs of Ru-doped TiO_2 and Ti-doped RuO_2 . These calculations correspond to a full surface coverage of O. As was discussed above, adsorption energies on a 1x1 slab are a reasonable approximation of the mean adsorption energy of two O^c on two cus.

In each case, one metal atom of the pure oxide was replaced by Ru or Ti, respectively. Since only 1x1 surfaces of the oxide are used, this implies that every cus site atom in the periodic structure was replaced by a dopant atom. This dopant atom was then successively placed in each possible site of the slab structure (see Figures 2a and 3). In all cases, O was allowed to adsorb on the first layer cus site ("1cus").

The adsorption energy trends on Ru-doped TiO_2 , Ti-doped RuO_2 and a DSA model system (see below) are shown in Figure 5.

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3.1 Adsorption energies on doped TiO_2 , RuO_2 and mixed oxides

We will start our discussion with the case of Ru-doped TiO_2 . It is seen that Ti is activated by the Ru dopant, while Ru is relatively unaffected by the TiO_2 environment. When adsorption occurs directly on the Ru dopant atom (the "1cus" case), the adsorption energy is essentially the same as that on pure RuO_2 . This was seen also in the study of García-Mota *et al.* [23]. However, when the dopant Ru atom is placed in the first layer bridge site ("1br"), and O adsorption occurs on the 1cus Ti site, the O adsorption energy is close to the optimal one of $\Delta E(\text{O}^\text{c}) = 3.2 \text{ eV}$ (see Figure 4). It is clear that the Ti atom is strongly affected by the Ru dopant, while Ru is almost unaffected by the TiO_2 environment. Furthermore, as the Ru dopant is moved from the first layer and further down through the layers, the adsorption energy approaches that of pure TiO_2 . It seems that the effect of the Ru dopant on the adsorption energy is significantly diminished when the dopant is separated from the surface layer by two layers of TiO_2 .

The trends in O adsorption energy on Ti-doped RuO_2 are also seen in Figure 5. Again, Ru is not affected strongly by the Ti dopant. The situation when the O adsorption energy deviates most significantly from that on pure RuO_2 is when adsorption occurs on the Ti dopant (the "1cus" case). The Ti atom is thus affected strongly by the RuO_2 environment, whereas the Ru atoms are less affected by the Ti dopant. This effect of the dopant atom on its surroundings is expected to be present at even lower concentrations of dopant than the 12.5% (1/8) considered here, although it might not necessarily be important for the macroscopic properties of an electrode if the concentration is too low.

On a real electrode, adsorbate coverage will not necessarily be complete. To examine the effect of surface coverage, a similar calculation was performed on a 1x2 slab of Ru-doped TiO_2 . The overall stoichiometry in this slab is $\text{Ru}_2\text{Ti}_{14}\text{O}_{32}$, keeping the relative concentrations of Ru and Ti constant. O was placed over one of the cus sites before relaxing the system. This situation corresponds to 50% surface coverage of O^c . The trends are seen in Figure 6. The trend is plotted together with the line corresponding to the 1x1 surface of Ru-doped TiO_2 (Figure 5), enabling a direct comparison. Even in this situation, the O adsorption energy on Ru ("1cus") is similar to that on undoped RuO_2 .

Furthermore, the effect of the Ru dopant on the adsorption energy is significant even when the Ru atoms are located in the fourth layer. The adsorption energy difference between 50% surface coverage and 100% surface coverage of up to about 1 eV is similar to what has been seen before [15]. Even in the 1x2 surface case, there are surface sites which have oxygen adsorption energies close to the optimal one of $\Delta E(\text{O}^\circ) = 3.2$ eV. This indicates that the activating effect of Ru on Ti should be maintained also at lower surface coverages. It also indicates that the overall trend is still captured in the 1x1 cell, even if the adsorption energies are shifted somewhat due to additional adsorbate-adsorbate interactions.

A similar analysis as for Ru-doped TiO₂ and Ti-doped RuO₂ was also performed for 2x1 slabs of DSA composition, Ru_{0.3}Ti_{0.7}O₂. These slabs had an overall stoichiometry of Ru₅Ti₁₁O₃₂, yielding a Ru concentration of 31%. To allow this DSA model system to be compared with the doped RuO₂ and TiO₂ slabs, four of the five Ru dopants were placed in the bottom corner of the slab, enabling the fifth dopant to be moved in the same way as in the other systems (Fig. 2b). The O adsorption energy trends are again seen in Figure 5, where the trends on the DSA model system are compared with those on Ru-doped TiO₂ and Ti-doped RuO₂. Overall, the trends for Ru-doped TiO₂ and the DSA model system are quite similar. Although the calculated adsorption energies are likely shifted due to adsorbate-adsorbate interactions in the 2x1 surface cell used, the fact that the same overall trend was observed above for Ru-doped TiO₂ both in the 1x1 (100% surface coverage) and 1x2 (50% surface coverage) surface cases supports the claim that the trends are realistic.

This analysis indicates that there are arrangements of Ru and Ti in DSA which could result in active Ti cus sites with an O adsorption energy close to 3.2 eV, the value identified as yielding an especially high selectivity for chlorine evolution. This is an electronic effect, and not a result of Ru site separation. We are presently studying the details of the electronic effect, but donation of electronic density from the Ru atom to the surrounding Ti atoms is likely one aspect [38]. This electronic effect is a fundamental explanation for

the higher selectivity for chlorine evolution in comparison with pure RuO₂. The increase in Cl₂ selectivity with decreasing concentration of Ru in RuO₂-TiO₂ mixed oxides has been seen in a number of experimental studies, and thus supports our theoretical results. Several experimental studies have found that the Tafel slope of 40 mV /dec for anodic chloride brine electrolysis is essentially unaffected by a decrease in Ru content from 100% to 20-30%. Furthermore, the increase in overpotential when comparing coatings of 80% Ru and 20% Ru was found to be 5 mV in the study of Burrows *et al.* [11], while Buné *et al.* [3] found the increase to be 21 mV when comparing oxide coatings of 100% Ru with coatings of 20% Ru. The overpotential is logarithmically proportional to the current density, through the Tafel equation. Thus, if the current density per site were directly proportional to the number of Ru sites only, which would be the case if only the Ru sites were electrocatalytically active, a reduction of the Ru content from 80 to 20% would be expected to result in a difference in overpotential of 24 mV

$$\frac{\eta_{80\% \text{ Ru}}}{\eta_{20\% \text{ Ru}}} = \log (0.8/0.2) \times 0.040 = 24 \text{ mV} \quad (2)$$

while the expected difference for a reduction from 100 to 20% would be 28 mV

$$\frac{\eta_{100\% \text{ Ru}}}{\eta_{20\% \text{ Ru}}} = \log (1/0.2) \times 0.040 = 28 \text{ mV}. \quad (3)$$

This is not valid if the chlorine evolution reaction takes place by recombination of Cl[•] on adjacent Ru sites. However, a recombination mechanism would likely entail an even larger increase in overpotential when reducing the Ru concentration. Our simulations suggest that perhaps the measured overpotential differences are smaller than expected partly due to activation of Ti sites, so that the decrease in Ru (active site) concentration is made up for by activation of certain Ti sites by Ru. Certain Ti atoms could be both highly active and highly chlorine-selective sites on DSA. That an overpotential increase is still measured could indicate that not all Ti surface atoms are close enough to Ru dopants in real DSA.

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3.1 Adsorption energies on a dopant monolayer on pure oxides

3.4. Adsorption energies on a dopant monolayer on pure oxides

An atomic-level control of the synthetic arrangement of Ru and Ti in a mixed DSA-like oxide is presently not realistic. However, there are surfaces that could be prepared and used to confirm or refute the predictions made in the present work. Two such surfaces are a monolayer of TiO_2 on RuO_2 and the opposite situation, that of a monolayer of RuO_2 on TiO_2 . Such surfaces could be prepared using atomic layer deposition [8] and we have computed $\Delta E(\text{O}^\circ)$ for both 1x1 and 1x2 surfaces which allows us to indicate the expected effects in these situations. In the case of 1x2 surfaces, we simulated both the cases of O adsorption on $^\circ+^\circ$, giving 50% surface coverage, and $\text{O}^\circ+^\circ$, giving 100% surface coverage. We also calculated the average adsorption energy of 2 O° on 2 $^\circ$ -sites. The computed electronic adsorption energies of O° are seen in Table 2. The adsorption energy of O on a TiO_2 monolayer on RuO_2 is closer to the optimum in the volcano. It is clear that surface coverage has a significant effect on the adsorption energy of Ru-doped TiO_2 , resulting in $\Delta E(\text{O}^\circ)$ spanning the range from 2.7 eV-4.2 eV with an average at 3.5 eV. While the calculated surface coverage effects do suggest that the coverage will significantly change the selectivity and activity, the range is shifted to the optimal selectivity area around $\Delta E(\text{O}^\circ) = 3.2$ eV. It is possible that TiO_2 -covered RuO_2 would also exhibit a high corrosion resistance. On a RuO_2 monolayer, the adsorption should be similar to that on RuO_2 , spanning the range of 1.1 eV-1.6 eV with an average at 1.4 eV. We note again that the adsorption energy in the small 1x1 cell is a good approximation for the average adsorption energy of 2 O° on 2 $^\circ$ -sites. It can be noted that Novell-Leruth *et al.* [25] performed theoretical studies on the stability of overlayers of all combinations of IrO_2 , RuO_2 , SnO_2 or TiO_2 on substrates of the same materials, which indicate that the growth of the monolayers suggested in the present paper should be possible. It is not certain that such monolayers will be stable long term, but the calculations of Novell-Leruth *et al.* at least indicate that they could exhibit sufficient short-term stability to allow them to be prepared and tested. Experimental measurements on such monolayers of RuO_2 on TiO_2 or TiO_2 on RuO_2 could determine whether the selectivity for chlorine

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System	RuO ₂ monolayer on TiO ₂	TiO ₂ monolayer on RuO ₂
1x1 surface	1.4	3.5
1x2 surface, 50% final coverage	1.1	2.7
1x2 surface, 100% final coverage	1.6	4.2
1x2 surface, average of 2 O ^c	1.4	3.5

Table 2: Computed $\Delta E(\text{O}^c)$ (in eV) for O adsorption on overlayers.

evolution is higher on electrode coatings with a TiO₂ monolayer on RuO₂ than on the opposite case of an RuO₂ monolayer on TiO₂. It would be an experimental verification of both the predictions made in the present paper and those of the paper of Hansen *et al.* [15].

The fact that the O adsorption energy on Ru is the same in both pure RuO₂ and on Ru dopants in TiO₂ indicates that Ru sites in DSA should have the same overpotential and selectivity for chlorine evolution as Ru sites in pure RuO₂. They should thus be more selective for O₂ evolution than the Ti cus sites. This implies that another possible way to improve the selectivity of DSA electrodes would be to block the Ru surface sites, *e.g.* by introducing an electrolyte additive that adsorbs preferentially and strongly to the Ru sites. However, this could result in an increased overpotential, as not all Ti surface atoms are likely to be close to Ru dopants in a real DSA. Another possibility would be to replace Ru in the DSA electrode with one or more cheaper metals that activate Ti in the same way.

3.5. The chlorine evolution mechanism and the accuracy of the results

Before discussing the electrochemical chlorine evolution mechanism, some comparisons with the related heterogeneous non-electrochemical chlorine evolution reaction, the Deacon reaction, will be made. The Deacon process has been studied in detail, both experimentally and theoretically. An in-depth comparison between the two processes has recently appeared in the review of Over [9]. The differences are based on two fundamental differences between the processes: that of the reaction temperature and that of the charge transfer reactions possible only under electrochemical conditions. Elec-

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344 trochemical chlorine production takes place at significantly lower temperatures than the
345 Deacon process, which operates at temperatures above 500 K. This means that the
346 Langmuir-Hinshelwood step important for the Deacon process, the recombination of
347 adsorbed Cl° (which would be a Volmer-Tafel mechanism under electrochemical condi-
348 tions), is kinetically inaccessible under electrochemical chlorine evolution conditions. The
349 analogous situation holds for the oxygen evolution mechanism. Oxygen evolution under
350 electrochemical conditions occurs through an OOH^* intermediate [18]. Under Deacon
351 conditions, it must instead occur through a Langmuir-Hinshelwood mechanism. These
352 mechanistic details are obviously connected with the second fundamental difference, that
353 an electrochemical reaction can involve ionic adsorption with or without discharge of the
354 adsorbed ion. This opens up the possibility for surface oxidation under electrochemical
355 conditions through oxidation of H_2O rather than through dissociation of O_2 (the only
356 possibility under Deacon conditions). The driving force for this electrochemical process
357 is directly controlled by the electrochemical potential. Another, more specific, difference
358 between the electrochemical and Deacon processes is that, under Deacon process condi-
359 tions, bridge sites on RuO_2 (1 1 0) surfaces in the gas phase will be partly chlorinated
360 [9, 39]. This has significant kinetic consequences, as the chlorine evolution rate in the
361 Deacon process is limited by the re-oxidation of the catalyst at high chlorine coverages
362 [39]. However, the recent theoretical work of Exner *et al.* [17] examined this very issue
363 and concluded, in agreement with what was already found by Hansen *et al.* [15], that
364 such chlorination does not occur under electrochemical conditions and electrode poten-
365 tials above 1 V. Another example of such differences between reactions catalyzed by rutile
366 oxides under heterogeneous and electrochemical conditions is the case of heterogeneously
367 catalyzed Br_2 -production on rutile TiO_2 , which has recently been studied by Moser *et al.*
368 [40]. The mechanism in that case relies on the formation of bridge-oxygen bound Br
369 ($\text{O}^{\text{br}}\text{Br}$). The analogous mechanism for Cl_2 evolution under electrochemical conditions
370 is not possible, since bridge-oxygen bound chlorine ($\text{O}^{\text{br}}\text{Cl}$) is unstable under relevant
371 potentials [15, 17]. There are thus clear differences between the transition metal oxide

3 RESULTS AND DISCUSSION evolution mechanism and the accuracy of the results

surface configurations and the mechanisms relevant for studying the Deacon process and those relevant for studying electrochemical chlorine evolution.

The theoretical volcano plot of Hansen *et al.* [15] does not include activation energies for the different elementary steps. This is due to the application of the so-called Computational Hydrogen Electrode method of Nørskov *et al.* [41], in which the polarization of the electrode surface is not treated explicitly (e.g. by adding or removing electrons from the slab in the simulation cell), but instead standard thermodynamic relationships are applied to achieve a correct description of the free energies of reactions at a polarized electrode surface. Although the method decreases the complexity in modeling reactions at charged interfaces, it does mean that it is not possible to calculate activation barriers, as is possible within e.g. the approach of Filhol and Neurock [42]. Nevertheless, it has been found that in heterogeneous catalytic reactions, the reaction free energy of an elementary reaction step in general correlates with the activation energy for the same step (Brønsted-Evans-Polanyi relations) [43]. Although fewer detailed DFT calculations of activation barriers for electrochemical heterogeneous reactions have been performed, studies of *e.g.* electrochemical hydrogen evolution on Pt (1 1 1) have found that similar correlations can also be found for electrochemical heterogeneous reactions [44, 45]. If this is the case also for chlorine evolution from rutile oxide surfaces, the thermochemical barriers studied in Hansen *et al.* [15] will yield a qualitatively correct description of the complete electrochemical process including both free energies and activation energies.

One might question whether the treatment of Hansen *et al.* [15] is a correct description of the chlorine evolution reaction, given that the exact mechanism of electrochemical chlorine evolution from solution has yet to be determined experimentally. Several chlorine evolution mechanisms agreeing with the observed reaction order of 1 (at constant pH) and the Tafel slope of 40 mV have been proposed [6]. Three of these mechanisms are the Volmer-Tafel mechanism, involving chlorine evolution via recombination of two adsorbed Cl atoms, the Volmer-Heyrovsky mechanism, involving chlorine evolution via the reaction between a chloride ion and an adsorbed Cl atom, and the Krishtalik mecha-

4 CONCLUSIONS

nism, which is similar to the Volmer-Heyrovsky mechanism except that the adsorbate is thought to be a Cl atom with a net positive charge [6, 9, 15]. Hansen *et al.* [15] did not base their treatment on one particular mechanism. First, they determined the adsorption energies of the three different chlorine-containing intermediates ClO° , $\text{Cl}(\text{O}^\circ)_2$ and Cl° . The thermochemical barrier for forming these intermediates, as a function of pH and applied potential, was then determined. They found that these intermediates are stable (at different anodic potentials) at an anodically polarized rutile oxide surface. The volcano plots were then prepared by writing the chlorine evolution reaction as a Heyrovsky mechanism. It is important to point out that writing the reaction as a Heyrovsky mechanism will not affect the optimum of the thermochemical volcanos. No matter if the last step in Cl_2 formation is recombination of two Cl adsorbates, or the reaction between a chloride ion and a Cl adsorbate, a low free energy of formation of the Cl intermediate is a necessity. Since no transition state energy barriers were calculated, the volcano plots for reactions involving each of these three intermediates indicate a necessary precondition, of a small thermochemical barrier for formation of the intermediate, for chlorine evolution through any reaction mechanism. The treatment is valid no matter if the reaction actually proceeds through a Volmer-Tafel mechanism, a Volmer-Heyrovsky mechanism or a Krishtalik mechanism. Still, it must be noted that the RPBE GGA functional, as used both in Hansen *et al.* [15] and in the present work, does not achieve perfect chemical accuracy. Errors in adsorption energies of around 0.2 eV-0.3 eV could be expected (see also section 1 of the Supplementary Information) [30]. Nevertheless, these errors are small enough that trends in adsorption energies can be determined. Based on these considerations, we find it reasonable to use the volcano plot of Hansen *et al.* [15] as base for our discussion regarding activation (change in $\Delta E(\text{O}^\circ)$) of Ti sites in mixed Ru-Ti oxides and its effect on selectivity.

4. Conclusions

- Based on the volcano plot of Hansen *et al.* [15] and first-principles DFT calculations on the GGA and GGA+U level, Ru-doped TiO₂ should function as an active and selective electrocatalyst for chlorine evolution. This agrees with experimental evidence.
- Ti is activated by RuO₂ in both doped TiO₂ and in DSA-like mixed oxides.
- Ti sites activated by RuO₂ are predicted to be especially chlorine-selective.
- The oxygen adsorption energy on Ti sites is affected by Ru dopants more than the oxygen adsorption energy on Ru is affected by Ti dopants.
- This work indicates that a path towards higher selectivity for chlorine evolution could be to either expose only activated Ti sites, *e.g.* through a thin film of TiO₂ on RuO₂, or by blocking exposed Ru sites through a Ru-specific adsorbate. An alternative path would be to search for an unreactive metal that activates Ti the same way.

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Figure 1: The optimized structure of $\text{O}^\ominus$ adsorption on a 1×1 slab of Ru-doped TiO_2 . The Ru dopant is seen forming the surface layer bridge site. The unit cell used in the calculations is indicated by the dashed lines. The unit cell is repeated several times in the x and y directions to clarify the structure of the slab. The x direction is oriented from bridge site to bridge site across the cus sites, while the y direction is oriented along the lines of bridge (or cus) sites. The z direction is normal to the surface.

Figure 2: Two slabs pictured from the side, with the z surface direction being the vertical one. Unit cells are indicated by dashed lines. a) A relaxed Ru-doped TiO_2 system. The Ru dopant that is moved is seen here in the "1br" position. A relaxed O adsorbate, having moved down in the z direction to reach its relaxed state, is seen on top of the "1cus" position. The arrows indicate the position of the O adsorbate as well as the naming used for the different possible sites where Ru can be placed. This naming system is used in later figures showing trends in adsorption energy. This is the same system as in Figure 1. b) A relaxed DSA model system. The structure shown was chosen not because it is believed to be the most realistic structure of DSA, but rather to enable trends in activation of the Ti surface site by Ru to be analyzed in a simplified model system.

Figure 3: All Ru-doped TiO_2 1×1 slabs, with relaxed O^c . The naming for each system is shown above the respective slabs. The systems are seen from the same direction as in Figure 2.

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Figure 4: The volcano plot of Hansen *et al.* [15] together with $\Delta E(O^-)$ for the case of Ru doped into the 1br position of TiO_2 .

Figure 5: Oxygen adsorption energy trends as the dopant atom position is varied in Ru-doped TiO_2 , Ti-doped RuO_2 and in the DSA model system. The O adsorbate is allowed to adsorb on the “1cus” site in all cases, so that adsorption occurs directly on the dopant atom only in the “1cus” case.

Figure 6: The effect on the O^c adsorption energy on the cus site of Ru-doped TiO_2 . The position of the Ru atom is varied. The system is either a 1x1 system (100% surface coverage) or a 1x2 system with adsorption of O only on one cus site (50% surface coverage). The dashed lines for the adsorption energies on pure materials are from calculations on 1x1 surface systems.