

## Supplementary information

For construction of the surface phase diagrams, we need to calculate the free energy of adsorbates formed by water discharge, e.g.  $O^c$  or  $HO^c$ :



and from adsorption of chloride ions:



The free energy of formation of  $O^c$ , defined by (A.2), is

$$\Delta G(O^c)(U, a_{H^+}) = G(O^c) + 2 \mu(H^+) + 2 \mu(e^-) - \mu(H_2O(l)) - G^c, \quad (A.4)$$

Where  $G(O^c)$  and  $G^c$  is the free energy of the surface with and without  $O^c$  respectively.  $\mu(H^+) = \mu(H^+)^{\ominus} + k_B T \ln a_{H^+}$  is the chemical potential of protons and  $\mu(e^-) = \mu(e^-)^{\ominus} - e U$  is the chemical potential of electrons at the electrode at the potential  $U$ .  $\mu(e^-)^{\ominus}$  is an arbitrary reference energy determined by the potential scale.

Throughout this work we reference the potential relative to the standard hydrogen electrode (SHE), which means the hydrogen electrode reaction



is at equilibrium at zero potential and standard conditions ( $p_{H_2} = 1$  bar,  $pH = 0$ ), from which it follows, that

$$\frac{1}{2} \mu(H_2)^{\ominus} = \mu(H^+)^{\ominus} + \mu(e^-)^{\ominus}. \quad (A.6)$$

The chemical potential of liquid water is calculated from water vapor in equilibrium with liquid water at 298 K.

$$\mu(H_2O(l)) = \mu(H_2O(g)) @ 0.035 \text{ bar and } 298 \text{ K} \quad (A.7)$$

The formation energy of  $O^c$  can therefore be written as:

$$\begin{aligned} \Delta G(O^c)(U, a_{H^+}) &= G(O^c) - G^c - \mu(H_2O(g)) @ 0.035 \text{ bar} + \mu(H_2)^{\ominus} + 2 (k_B T \ln a_{H^+} - eU), \\ &= \Delta E_{O^*} + \Delta ZPE - T\Delta S^{\ominus} + 2 (k_B T \ln a_{H^+} - eU), \end{aligned} \quad (A.8)$$

Where  $\Delta E(O^c)$  is calculated as described in the section “scaling relations”,  $\Delta ZPE$  is the change in zero point energy upon adsorption and is calculated within the harmonic approximation for an adsorbate at the cus-site of  $RuO_2$ , and assumed to be constant from one rutile oxide to the next.  $\Delta S$  includes the loss of translational entropy of the gas phase molecules upon adsorption on the surface.

An equation similar to (A.8) may be derived for the adsorption of  $HO^c$ :

$$\Delta G(HO^c)(U, a_{H^+}) = \Delta E(HO^c) + \Delta ZPE - T\Delta S^{\ominus} + k_B T \ln a_{H^+} - eU. \quad (A.9)$$

The free energy of adsorption of chlorine by (A.3) is

$$\Delta G(\text{Cl}^\ominus)(U, a_{\text{Cl}^-}) = G(\text{Cl}^\ominus) - G^\ominus + \mu(e^-) - \mu(\text{Cl}^\ominus)^\ominus - k_B T \ln a_{\text{Cl}^-}. \quad (\text{A.10})$$

By considering a chlorine electrode at equilibrium at standard conditions



We see that

$$0 = \frac{1}{2} \mu(\text{Cl}_2)^\ominus + \mu(e^-)^\ominus - eU_{\text{Cl}^\ominus}^\ominus - \mu(\text{Cl}^\ominus)^\ominus, \quad (\text{A.12})$$

where  $U_{\text{Cl}^\ominus}^\ominus$  is the standard potential of the reversible chlorine electrode,  $U_{\text{Cl}^\ominus}^\ominus = 1.36$  V at 298 K. We then have

$$\begin{aligned} \Delta G(\text{Cl}^\ominus)(U, a_{\text{Cl}^-}) &= G(\text{Cl}^\ominus) - G^\ominus + \frac{1}{2} \mu(\text{Cl}_2)^\ominus - e(U - U_{\text{Cl}^\ominus}^\ominus) - k_B T \ln a_{\text{Cl}^-} \\ &= \Delta E(\text{Cl}^\ominus) + \Delta \text{ZPE} - T\Delta S^\ominus - k_B T \ln a_{\text{Cl}^-} - e(U - U_{\text{Cl}^\ominus}^\ominus). \end{aligned} \quad (\text{A.13})$$

For simplicity we consider the standard conditions  $a_{\text{H}^+} = a_{\text{Cl}^-} = 1$ , and define for notational convenience  $\Delta G(\text{Cl}^\ominus) = \Delta G(\text{Cl}^\ominus)(U=0, a_{\text{Cl}^-}=1)$ ,  $\Delta G(\text{HO}^\ominus) = \Delta G(\text{HO}^\ominus)(U=0, a_{\text{H}^+}=1)$  etc., so that all free energies of adsorption are referenced to the standard hydrogen electrode.

In Table S1,  $\Delta \text{ZPE}$  and  $T\Delta S$  for all the relevant reactions are listed at  $T = 298\text{K}$ . ZPE are obtained from a vibrational calculation within the harmonic approximation. For the adsorbed species the ZPE have been calculated for an adsorbate at the cus-site of  $\text{RuO}_2$ .

	TS	TΔS	ZPE	ΔZPE	ΔZPE - TΔS
<b>H<sub>2</sub>O(l)</b>	.67	0	.56	0	0
<b>H<sub>2</sub>O → <sup>c</sup>OH + 1/2H<sub>2</sub></b>	.20	-.47	.50	-.06	.41
<b>H<sub>2</sub>O → <sup>c</sup>O + H<sub>2</sub></b>	.41	-.27	.34	-.22	.05
<b>H<sub>2</sub>O → 1/2O<sub>2</sub> + H<sub>2</sub></b>	.73	.05	.32	-.24	-.29
<b>1/2Cl<sub>2</sub> → Cl<sup>c</sup></b>	-	-.34	-	0.02	.37
<b>Cl<sub>2</sub></b>	.69	-	.06	-	
<b>H<sub>2</sub></b>	.41	-	.27	-	
<b>1/2O<sub>2</sub></b>	.32	-	.05	-	
<b>Cl<sup>c</sup></b>	0	-	.05	-	
<b>O<sup>c</sup></b>	0	-	.07	-	
<b>OH<sup>c</sup></b>	0	-	.36	-	
<b>H<sup>c</sup></b>	0	-	.17	-	

Table S1: Zero point energies and entropic corrections at 298 K.

### Adsorption energies:

Adsorption Energy (eV)	O on $2^c$	O on $O^c + ^c$	O on $Cl^c + ^c$	O on $ClO^c + ^c$	Average of 2 O on $2^c$
RuO <sub>2</sub>	2,30	2,71	2,73	2,8772	2,51
IrO <sub>2</sub>	1,32	1,63	1,66		1,48
TiO <sub>2</sub>	4,57	5,53	4,94		5,05
PtO <sub>2</sub>	3,59	3,20	3,24		3,39

Table S2: Adsorption energy of O at a free cus site ( $^c$ ) for different surface terminations. In all cases the bridge sites are covered with oxygen. The adsorption energy is calculated according to equation (2).

Adsorption Energy (eV)	Cl on $2^c$	Cl on $Cl^c + ^c$	Cl on $O^c + ^c$	Average of 2 Cl on $2^c$
RuO <sub>2</sub>	-0,91	-0,38	-0,48	-0,64
IrO <sub>2</sub>	-1,62	-1,06	-1,28	-1,347
TiO <sub>2</sub>	0,71	0,59	1,08	0,65
PtO <sub>2</sub>	-0,40	-0,54	-0,75	-0,47

Table S3: Adsorption energy of Cl at a free cus site ( $^c$ ) for different surface terminations. In all cases the bridge sites are covered with oxygen. The adsorption energy is calculated according to equation (1).

Adsorption Energy (eV)	ClO on $2^c$	ClO on $ClO^c + ^c$	ClO on $O^c + ^c$	Average of 2 ClO on $2^c$
RuO <sub>2</sub>	1,73	2,63	2,30	2,18
IrO <sub>2</sub>			1,40	1,42
TiO <sub>2</sub>	3,18	3,49		3,33
PtO <sub>2</sub>	1,99	2,76		2,38

Table S4: Adsorption energy of ClO at a free cus site ( $^*$ ) for different surface terminations. In all cases the bridge sites are covered with oxygen. The adsorption energy is calculated according to equation (3).

Adsorption Energy on top $O^c$ (eV)	Cl on $O^c + ^c$	Cl on $2 O^c$	Cl on $ClO^c + O^c$	Average of 2 Cl on $2 O^c$
RuO <sub>2</sub>	-0,58	-0,41	-0,24	-0,33
IrO <sub>2</sub>		-0,11	0,00	-0,06
TiO <sub>2</sub>	-1,40			-1,72
PtO <sub>2</sub>	-1,60			-1,02

Table S5: Adsorption energy of Cl on top O at a cus site ( $O^c$ ) for different surface terminations. In all cases the bridge sites are covered with oxygen. The adsorption energy is calculated according to equation (4).

## Linear Relations:

In constructing the generalized phase diagram and the Sabatier volcanoes we have used the linear relations below. The mean absolute error (MAE) of the fits is also listed.

$$\Delta E(Cl^c) = 0.59 * \Delta E(O^c) - 2.26 \text{ eV}, MAE = 0.17 \text{ eV}$$

$$\Delta E(ClO^c) = 0.52 * \Delta E(O^c) + 0.62 \text{ eV}, MAE = 0.16 \text{ eV}$$

$$\Delta E(O_2^{cc}) = 0.94 * \Delta E(O^c) + 1.96 \text{ eV}, MAE = 0.02 \text{ eV}$$

$$\Delta E(Cl(O^c)_2) = 0.56 * \Delta E(O^c) + 2.51 \text{ eV}, MAE = 0.21 \text{ eV}$$

and the scaling relation between O\* and OH\* from reference **Error! Bookmark not defined.:**

$$\Delta E(HO^c) = 0.61 * \Delta E(O^c) - 0.90 \text{ eV}$$