Supplemental Section A

Table A1 Dominant species present at each sample's pH_{PZC} in Table I **[1a, 2a-4a].**

Sample	*Dominant Species*	*Experimental Point of Zero Charge (pH)*
BeO	BeO	10.2
ZnO	ZnO	9.3
$Zn(OH)_2$	$Zn(OH)_2$	7.8
$Al(OH)_3$	$Al(OH)_3$	5.0 – 5.2
α-Fe_2O_3	α-Fe_2O_3	9.04
α- FeO(OH)	α- FeO(OH)	7.4
γ- FeO(OH)	γ- FeO(OH)	6.7
ThO_2	ThO_2	9.0 – 9.3
PuO_2	PuO_2	9.0
HgO	HgO	7.3
SnO_2	SnO_2	6.6
TiO_2	TiO_2	6.7
WO_3	WO_3	~ 0.5
SiO_2	SiO_2	1.8

Table A2 Dominant species present at each sample's pH_{PZC} in **Table II [1a, 2a-6a]** with the presence of nonzero crystal field splitting effect**.**

Sample	*Dominant Species*	*Experimental Point of Zero Charge*

		(pH)
$Co(OH)_2$	$Co(OH)_2$	11.4
CuO	CuO	9.4 ± 0.4
Cr_2O_3	Cr_2O_3	7.0

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Supplemental Section B

Table B1 Structure parameters, pH_{PZC} and $pH_{PPZC,}$ values for the metal-oxide/-hydroxide examples in **Table I [1b, 2b $^{€}$].**

Dominant Species	**C.N.**	**Z_M**	**L (Å)**	$^{€}f_{I\%}$ (%)	f_i	$= f_i \times I_{\%}$	**Exp. pH_{PZC}**	**Cal. pH_{PPZC}**	**Ref.**
BeO	4	+2	1.49	0.6321	1	0.6321	7.10	7.01	**1b, 3b, 4b**
ZnO	4	+2	1.978	0.5944	1	0.5944	10.20	10.31	**1b, 5b**
$Zn(OH)_2$	4	+3	1.95	0.5944	1	0.5944	10.3	10.19	**1b, 6b**
α-Al_2O_3	6	+3	1.91	0.6321	1	0.6321	9.5	9.49	**1b, 7b**
α-$Al(OH)_3$	6	+3	1.935	0.6321	1	0.6321	9.50	9.49	**1b, 8b-10b**
α-Fe_2O_3	5	+3	1.966	0.5145	1	0.5145	9.80	9.91	**1b, 11b, 12b, 13b**
γ- FeO(OH)	4	+3	1.89	0.5145	1	0.5145	7.40	7.47	**1b, 11b, 12b**
α- FeO(OH)	5	+3	1.97	0.5145	1	0.5145	9.80	9.92	**1b, 11b, 14b, 15b**

ThO_2	8	+4	2.425	0.7018	1	0.7018	11.00	10.58	**1b, 16b**
PuO_2	8	+4	2.094	0.7083	1	0.7083	9.00	9.28	**1b, 17b**
HgO	2	+2	2.231	0.4727	1	0.4727	7.30	7.18	**1b, 11b, 18b**
SnO_2	5	+4	1.84	0.5145	1	0.5145	6.60	6.50	**1b, 11b, 19b**
TiO_2	6	+4	1.969	0.6321	1	0.6321	6.97	7.15	**1b, 20b**
WO_3	6	+6	1.943	0.5551	1	0.5551	3.53	3.26	**1b, 21b, 22b**
SiO_2	4	+4	1.64	0.5145	1	0.5145	2.00	1.77	**1b, 23b, 24b**

Beryllium Oxide: (BeO)

The pH_{PZC} value used by Yoon et al. **[1b]** is for beryllium hydroxide ($Be(OH)_2$) **[25b]**, not BeO. Therefore, the pH_{PZC} value for the oxide phase had to be obtained from the literature (pH_{PZC} = 7.10) **[3b]**. In addition, the average surface bond length for this oxide was incorrect. Typically, surface bond lengths contract by 3% to 4% from those found in the interior bulk structure, for coordination numbers 4 thru 8 **[26b]**. BeO surface bonds are anomalous, as they have been found to contract by 10% from its bulk bond length **[27b]**. Therefore, the surface bond length, adjusted for this contraction, reduced $\mathbf{L}$ = 1.65 Å **[1b]** to $\mathbf{L}$ =1.49Å. Entering these structural changes resulted in a predicted pH_{PPZC} = 7.01, a difference of 0.09 pH units from its pH_{PZC}.

Gibbsite (γ-$Al(OH)_3$/α-$Al(OH)_3$)

There are multiple phases of aluminium hydroxide, with the gibbsite (hydrargillite) structure being the most thermodynamically stable phase **[28b]**. Examination of the Pourbaix diagrams supports the presence of only γ-$Al(OH)_3$/α-$Al(OH)_3$ **[29b-31b]** as the dominant structure across the pH range for the PZC values of each aluminium hydroxide structure in **Table I [1b]**. Therefore γ-$Al(OH)_3$/α-$Al(OH)_3$ was the only structure modelled in **Table I**.

The most basic pH_{PZC} for this material is pH = 9.5. It was obtained from a source where the gibbsite structure measured had also been confirmed **[32b]**. The average bond length given in **Table I [1b]** is shorter (**L** = 1.89 Å) than that obtained by Saalfeld, Wedde, and Megaw **[8b, 9b]** (**L** = 1.902 Å) for gibbsite. Use of the longer bond length in the model resulted in the pH_{PPZC} value closest to the experimental PZC value. The modelled value **[Eq. 6]** is for a $pH_{PPZC} = 9.45$, a difference of only 0.05 pH units.

Hematite (α-Fe_2O_3)

The bulk structure for hematite is corundum **[33b]**, where the C. N. = 6. When the structure factors from **Table I [1b]** were placed in **Eq. 6** the $pH_{PPZC} = 11.46$. This resulted in a pH_{PPZC} of 1.66 pH units above the most basic PZC value found in the literature, a $pH_{PZC} = 9.80$ **[12b].**

Work by Kraushofer et al. **[13b]** though determined that surface Fe^{+3} atoms are all 5-coordinated. Therefore a C. N. = 5 was placed in the model **[Eq. 6]**, along with the calculated bond length for this coordination using Shannon's ionic radii table **[11b].** The pH_{PPZC} was found to be a pH = 9.91, within 0.11 pH units of the experimental value.

Lepidocrocite (γ-$FeO(OH)$)

Based on the Pourbaix diagram FeO(OH) compounds are the **[29b-31b]** stable structures from a pH = 6 thru 14**.** Work by Navaro et al. **[34b]** though determined that the stability range for lepidocrocite is within a temperature range of **10^{oC} to 60^{oC}**, from a pH = 4.0 thru a pH = 8.0. The most basic PZC value found within this range is pH_{PZC} = 7.4 **[35b]**. Placing the structure factors from **Table I [1b]** into the model **[Eq.6]**, the pH_{PPZC} = 11.36 more than 3 pH units above the range where this structure is stable. Placing a C.N. = 5 and a calculated bond length **L** = 1.97 **[11b]** gives a pH_{PPZC} = 9.92, slightly less than 2.0 pH units above its stability range.

Work by Otte et al. **[14b]** though determined that the Fe2 sites on the [0 1 0] face of this structure exhibit a four-fold coordination. This suggested that the coordination number should be reduced to 4, with a calculated **L** = 1.89 **[11b].** These structure factors resulted in a pH_{PPZC} = 7.46, only 0.06 pH units different from the experimental value. These modeling results **[Eq. 6]** support Otte et al.'s **[14b]** findings indicate that the global coordination number for **γ-FeO(OH)** surface Fe^{+3} atoms have a C.N. = 4.

Goethite (α-FeO(OH))

The surface anomaly at the hematite surface is also present for goethite. Modelling of the bulk and the [0 1 0] face of the goethite crystal determined that, like hematite, the surface has a C. N. = 5 **[14b]**. The most basic pH_{PZC} located in the literature was for a pH_{PZC} = 9.80 **[15b]**. Therefore, the Fe – OH bond calculated from ionic radii gave an **L** = 1.97 Å **[11b].** When placed in the model **[Eq. 6]** the pH_{PPZC} = 9.92, only 0.12 pH units different from the experimental pH_{PZC} value.

Thorium Dioxide (ThO_2)

Thorium dioxide has a wide range of measured PZC values in the literature. Parks **[36b]** identified a range of values for pH_{PZC} = 4.2 – 11.0. The most basic value for thorium dioxide identified, was derived from an ion exchange experiment at its equilibrium pH point. This is where the material's surface reverses charge, and no further ions are adsorbed. The equilibrium point is also defined as the material's PZC, which for thorium dioxide is a pH_{PZC} = 11.0 **[35b].** An examination of both individual and compiled PZC values **[3b 36b-40b]** found no other values above this pH_{PZC}. Results of the modelled value gave a pH_{PPZC} = 10.58, a difference of only 0.46 pH units.

Mercuric Oxide (HgO)

In Yoon et al.'s **[1b]** work they modelled the pH_{PPZC} using the cinnabar structure for HgS, which has a C.N. = 6 and **L** = 2.57 Å **[1b, 41b].** The two common structures for HgO though are montroydite and cinnabar which consist of planar O-Hg-O zigzag chains that form these phases, both with a C.N. = 2 **[19b]**. Using the cinnabar structure (HgS) in **Table I** results in a pH_{PPZC} = 13.14, almost double the cited experimental pH_{PZC} = 7.3 **[1b]**. Using the structure factors for HgO in the model with a C.N. = 2 and bond length = 2.231 Å **[11b]** in **Eq. 6** results in a pH_{PPZC} = 7.18 a difference of 0.12 pH units.

Tin Oxide (SnO_2)

Using the global structure factors in Yoon et al. **[6]** with a C.N. = 6 for the Sn atom and a bond length = 2.053, gave a pH_{PPZC} = 9.73, a difference 3.13 pH units, above the experimental pH_{PZC} = 6.60 **[6]**. Work by Merte et al. **[19b]** though determined that Sn atoms have a C.N. = 5 at the surface. The Sn – O bond length for a five coordinated Sn atom ≅ 1.84 **[11b]**, giving a predicted pH_{PPZC} = 6.84, a difference of 0.28 pH units**.**

Tungsten Trioxide (WO_3)

There are seven **[42b]** different structures of tungsten Trioxide (WO_3). At ambient temperature and pressure WO_3 exhibits the monoclinic structure **[37b]**. Therefore, to model the surface structure of WO_3 it was necessary to choose the most basic PZC value for this crystal structure. The PZC identified for this structure is a pH_{PZC} = 3.53 **[43b]** with an average bond length of **L** = 1.943 Å **[42b].** The modelled pH_{PPZC} = 3.26, a difference of only 0.26 pH units.

Quartz (α-SiO_2)

An examination of the PZC values presented in Parks **[36b]** work revealed a wide range of results for SiO_2 with no indication as to whether they were obtained in either Region I or II. Therefore, the structure chosen to model was for α-SiO_2, as there is a substantial body of literature for its PZC value and possess a C.N. = 4. Work by Alves Jr. And Baldo **[24b]** was chosen, as they determined the PZC values for multiple α-SiO_2 structures with a C.N. = 4. All their results were highly reproducible ($pH_{PZC} \cong 2.0 \pm 0.1$).

To confirm the surface structure (i.e. average bond lengths), modelling work based on experimental values were examined. Work by Wang et al. **[23b]** provided the average surface bond length for α-SiO_2 as **L** = 1.64 Å, slightly longer than the value in **Table I [1b]** of **L** = 1.61**.** The results of this new structure information resulted in a pH_{PPZC} = 1.77, a difference of 0.23 pH units.

Table B2 Structure parameters for metal-oxides/hydroxide samples in Table II **[1b,** 2b$^{€}$**]**with the presence of nonzero crystal field splitting effect**.**

Dominant Species	**C.N.**	**Z_M**	**L (Å)**	**f_i (%)**	**$I_{\%}^{€}$**	**$= f_i \times I_{\%}$**	**Exp. pH_{PZC}**	**Cal. pH_{PPZC}**	**Ref.**
$Co(OH)_2$	4	+2	1.92	1.0	0.5145	0.5145	11.40	11.07	**1b, 11b, 18b**
Cr_2O_3	5	+3	1.850	1.0	0.5944	0.5944	7.90	8.01	**1b, 44b-46b**

Cobalt Hydroxide ($Co(OH)_2$)

The pH_{PPZC} = 13.68, using the original structure factors (i.e. C.N. = 6) from **Table II [6]** in **Eq. 6** which is two pH units above the experimental pH_{PZC} = 11.40 **[1b].** There are two known cobalt hydroxide structures, α-$Co(OH)_2$ with a tetrahedral (C.N. = 4) coordination and β-$Co(OH)_2$ which exhibits an octahedral (C.N. = 6) coordination **[47b]**. The most common coordination number for cobalt (Co^{+2}) is tetrahedral (C.N. = 4) **[18b, 47b]**. Using the structure factors for a tetrahedral coordinated Co - OH and calculated bond length, **L** = 1.93 Å **[11b]** resulted in a pH_{PPZC} = 11.68, a difference of 0.28 pH units.

Chromium Oxide (Cr_2O_3)

The most basic value for Cr_2O_3 in the literature is for a pH_{PZC} = 8.3 **[3b].** Entering the materials bulk structure factors **[1b]** into **Eq. 6** gives a pH_{PPZC} = 10.80, 2.5 pH units above the most basic pH_{PZC} found in the literature. Shortening or lengthening the bond length to allow the model to converge on the experimental pH_{PZC} resulted in a non-viable structure.

As Cr_2O_3 is the stable structure (i.e.$\mathbf{Z_M}$ = +3) in each of the Pourbaix diagrams **[29b-31b]** examined, it eliminated varying the oxidation state as well. To be sure, though the oxidation states of +2 and +4 were modelled resulting in a pH_{PPZC} = 12.80 and 7.73, respectively. While the +4-oxidation state is within a half pH unit, the increase in the oxidation state results in a calculated bond length of approximately 1.79Å **[11b]** which reduces the pH_{PPZC} = 6.52, approximately 1.8 pH units below the materials experimental pH_{PZC}.

Therefore, the final factor which could be varied was the C.N. number. Chromium, with an $\mathbf{Z_M}$ = +3 has only one common coordination number (C.N. = 6) in the Shannon table of ionic radii **[11b]**. A search of the literature on Cr_2O_3 though revealed its surface structure is an exception, it possesses a C.N. = 5 **[44b].** Density Functional Theory modelling of a Cr_2O_3 monolayer surface generating hydrogen gave a surface bond length **L** = 1.85 Å **[45b]**. When entered the model **[Eq. 6]**, a calculated value of pH_{PPZC} = 8.01 was obtained, a difference of 0.11 pH units below its most basic average pH_{PZC} value **[46b].**

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Supplemental Section C

Table C1 Model structure factors, experimental pH_{PZC} and calculated pH_{PPZC} values for C.N.= 3 => C.N.= 4 => C.N.= 5 **[**1c€, Avg. of A site bond lengths **[2cθ]**

Intervals (Minutes)	C.N.	M	L (Å)	f_i	$I_{\%}$ €	$= f_i \times I_{\%}$	Exp. pH_{PZC}	Cal. pH_{PPZC}	References
Freshly Fractured Surface	3	+3	1.88	1.0	0.5145	0.5145	3.85	3.89	**3c, 4c-7c**

80	3	+3	1.88	0.55	0.5145	0.283	5.60	5.65	**3c, 4c-7c,8c, 2c, 9c-10c**
	4	+3	1.93$^{\theta}$	0.45	0.5145	0.232			
120	3	+3	1.88	0.16	0.5145	0.082	7.15	7.16	**3c, 4c-7c, 2c, 9c,10c**
	4	+3	1.93$^{\theta}$	0.84	0.5145	0.432			
280	4	+3	1.93$^{\theta}$	0.54	0.5145	0.278	8.80	8.82	**3c, 4c, 2c, 9c-13c**
	5	+3	1.966	0.46	0.5145	0.237			
480	4	+3	1.93$^{\theta}$	0.11	0.5145	0.0772	9.80	9.79	**3c, 14, 2c, 9c-13c**
	5	+3	1.966	0.89	0.5145	0.437			

Table C2 Model structure factors, experimental pH_{PZC} and calculated pH_{PPZC} values for C.N.= 3 => C.N.= 5 [1c$^{\text{€}}$].

Intervals (Minutes)	**C.N.**	**M**	**L (Å)**	f_i	$I_{\%}^{\text{€}}$	$= f_i \times I_{\%}$	**Exp. pH_{PZC}**	**Cal. pH_{PPZC}**	**References**
Freshly Fractured Surface	3	+3	1.88	1.0	0.5145	0.5145	3.85	3.89	**3c, 4c-7c**
80	3	+3	1.88	0.715	0.5145	0.368	5.60	5.65	**3c, 4c-7c, 9c-13c**
	5	+3	1.966	0.285	0.5145	0.147			
120	3	+3	1.88	0.470	0.5145	0.242	7.15	7.16	**3c, 4c-7c, 9c-13c**
	5	+3	1.966	0.530	0.5145	0.273			
280	3	+3	1.88	0.200	0.5145	0.103	8.80	8.82	**3c, 4c-7c, 9c-13c**
	5	+3	1.966	0.80	0.5145	0.412			
480	3	+3	1.88	0.04	0.5145	0.0283	9.80	9.80	**3c, 14c, 4c-7c, 9c-13c**
	5	+3	1.966	0.96	0.5145	0.486			

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Supplemental Section D

Table D1: Surface Bond Lengths for Decreasing Particle Size in Region II of anatase titania [**1d**, **2d**].

Particle Diameter (nm)	**Surface Bond Length (Å)**	**Ionic Content of Surface Bonds (%)**	**Point of Zero Charge (pH)**
3.30	2.1000	99.5	1.54
5.307	2.0897	97.6	1.73
12.69	2.0521	91.6	3.04
16.13	2.0345	87.6	4.25
21.11	2.0091	79.8	5.47

23.52	1.9968	72.5	7.15
29.00[Ψ]	1.9689	62.1	7.19

[Ψ] Projected Intercept point of Regions I and II

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