Supporting Information

On the concept of metal–hydrogen peroxide batteries: Improvement over metal-air batteries?

Kai S. Exner[1,2,3,*]

[1] *University Duisburg-Essen, Faculty of Chemistry, Theoretical Inorganic Chemistry, Universitätsstraße 5, 45141 Essen, Germany*

[2] *Cluster of Excellence RESOLV, Bochum, Germany*

[3] *Center for Nanointegration (CENIDE) Duisburg-Essen, Duisburg, Germany*

* Corresponding author: kai.exner@uni-due.de ORCID: 0000-0003-2934-6075
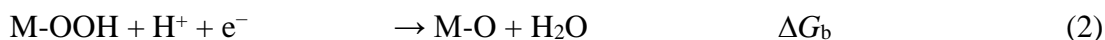
Keywords

metal-air batteries; oxygen evolution reaction; oxygen reduction reaction; hydrogen peroxide; selectivity; descriptor approach; volcano plot
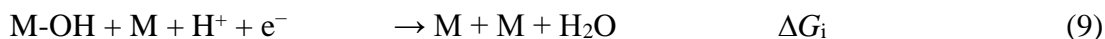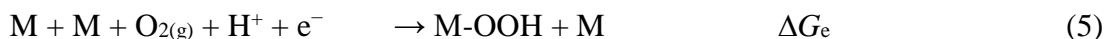
1 Reaction mechanisms

The volcano model in the main text consists of the reaction mechanisms denoted in the following. Various pathways via the *OOH, *O, and *OH intermediates consisting of both electrochemical and chemical steps are taken into account.

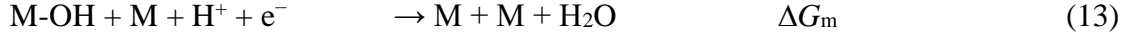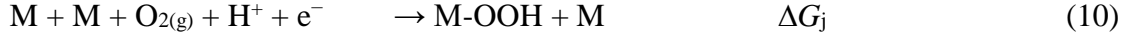1.1 Four-electron oxygen reduction reaction (ORR)

a) Mononuclear mechanism

$$M + O_{2(g)} + H^+ + e^- \rightarrow M\text{-}OOH \qquad \Delta G_a \qquad (1)$$
$$M\text{-}OOH + H^+ + e^- \rightarrow M\text{-}O + H_2O \qquad \Delta G_b \qquad (2)$$
$$M\text{-}O + H^+ + e^- \rightarrow M\text{-}OH \qquad \Delta G_c \qquad (3)$$
$$M\text{-}OH + H^+ + e^- \rightarrow M + H_2O \qquad \Delta G_d \qquad (4)$$

b) Chemical *OOH dissociation mechanism

$$M + M + O_{2(g)} + H^+ + e^- \rightarrow M\text{-}OOH + M \qquad \Delta G_e \qquad (5)$$
$$M\text{-}OOH + M \rightarrow M\text{-}O + M\text{-}OH \qquad \Delta G_f \qquad (6)$$
$$M\text{-}O + M\text{-}OH + H^+ + e^- \rightarrow M\text{-}OH + M\text{-}OH \qquad \Delta G_g \qquad (7)$$
$$M\text{-}OH + M\text{-}OH + H^+ + e^- \rightarrow M\text{-}OH + M + H_2O \qquad \Delta G_h \qquad (8)$$
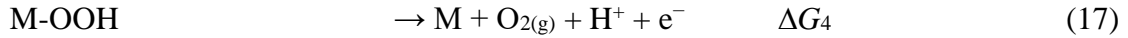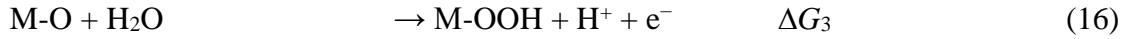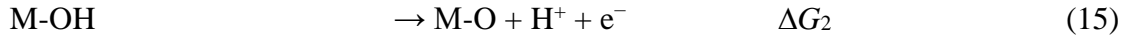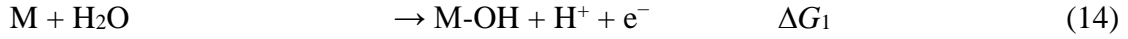$$M\text{-}OH + M + H^+ + e^- \rightarrow M + M + H_2O \qquad \Delta G_i \qquad (9)$$

c) Electrochemical *OOH dissociation mechanism

$$M + M + O_{2(g)} + H^+ + e^- \quad \rightarrow M\text{-}OOH + M \qquad \Delta G_j \qquad (10)$$

$$M\text{-}OOH + M + H^+ + e^- \quad \rightarrow M\text{-}OH + M\text{-}OH \qquad \Delta G_k \qquad (11)$$

$$M\text{-}OH + M\text{-}OH + H^+ + e^- \quad \rightarrow M\text{-}OH + M + H_2O \qquad \Delta G_l \qquad (12)$$

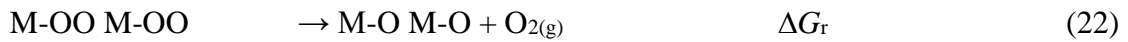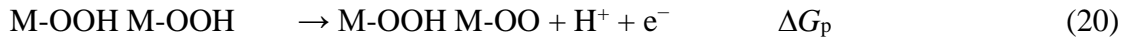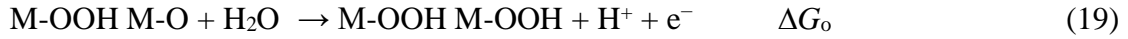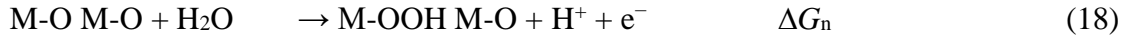$$M\text{-}OH + M + H^+ + e^- \quad \rightarrow M + M + H_2O \qquad \Delta G_m \qquad (13)$$
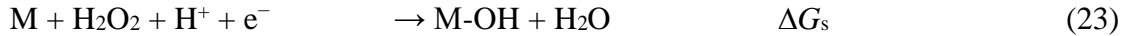
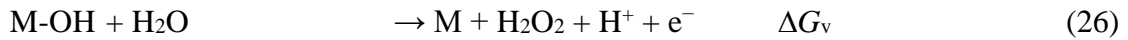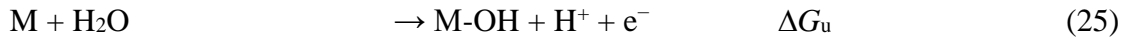1.2 Four-electron oxygen evolution reaction (OER)

a) Mononuclear mechanism

$$M + H_2O \quad \rightarrow M\text{-}OH + H^+ + e^- \qquad \Delta G_1 \qquad (14)$$

$$M\text{-}OH \quad \rightarrow M\text{-}O + H^+ + e^- \qquad \Delta G_2 \qquad (15)$$

$$M\text{-}O + H_2O \quad \rightarrow M\text{-}OOH + H^+ + e^- \qquad \Delta G_3 \qquad (16)$$

$$M\text{-}OOH \quad \rightarrow M + O_{2(g)} + H^+ + e^- \qquad \Delta G_4 \qquad (17)$$

b) *OO··OO* recombination mechanism

$$M\text{-}O\ M\text{-}O + H_2O \quad \rightarrow M\text{-}OOH\ M\text{-}O + H^+ + e^- \qquad \Delta G_n \qquad (18)$$

$$M\text{-}OOH\ M\text{-}O + H_2O \quad \rightarrow M\text{-}OOH\ M\text{-}OOH + H^+ + e^- \qquad \Delta G_o \qquad (19)$$

$$M\text{-}OOH\ M\text{-}OOH \quad \rightarrow M\text{-}OOH\ M\text{-}OO + H^+ + e^- \qquad \Delta G_p \qquad (20)$$

$$M\text{-}OOH\ M\text{-}OO \quad \rightarrow M\text{-}OO\ M\text{-}OO + H^+ + e^- \qquad \Delta G_q \qquad (21)$$

$$M\text{-}OO\ M\text{-}OO \quad \rightarrow M\text{-}O\ M\text{-}O + O_{2(g)} \qquad \Delta G_r \qquad (22)$$

1.3 Two-electron peroxide reduction reaction (PRR)

$$M + H_2O_2 + H^+ + e^- \quad \rightarrow M\text{-}OH + H_2O \qquad \Delta G_s \qquad (23)$$

$$M\text{-}OH + H^+ + e^- \quad \rightarrow M + H_2O \qquad \Delta G_t \qquad (24)$$

1.4 Two-electron peroxide formation reaction (PFR)

$$M + H_2O \quad \rightarrow M\text{-}OH + H^+ + e^- \qquad \Delta G_u \qquad (25)$$

$$M\text{-}OH + H_2O \quad \rightarrow M + H_2O_2 + H^+ + e^- \qquad \Delta G_v \qquad (26)$$

1.5 Two-electron ORR

$$M + O_{2(g)} + H^+ + e^- \quad \rightarrow M\text{-}OOH \qquad \Delta G_w \qquad (27)$$

$$M\text{-}OOH + H^+ + e^- \quad \rightarrow M + H_2O_2 \qquad \Delta G_x \qquad (28)$$

1.6 Two-electron OER

$$M + H_2O_2 \quad \rightarrow M\text{-}OOH + H^+ + e^- \qquad \Delta G_y \qquad (29)$$

$$M\text{-}OOH \quad \rightarrow M + O_{2(g)} + H^+ + e^- \qquad \Delta G_z \qquad (30)$$
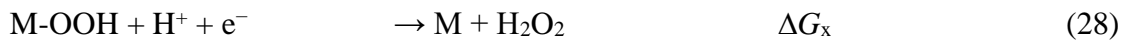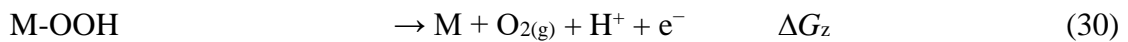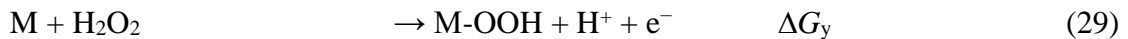
2 Thermodynamic theory of the elementary steps

The sum of the free-energy changes for all ORR mechanisms needs to fulfill the criterion of equations (31) – (33):

$$\Delta G_a + \Delta G_b + \Delta G_c + \Delta G_d = -4.92 \text{ eV } @ U = 0 \text{ V } vs. \text{ RHE} \tag{31}$$

$$\Delta G_e + \Delta G_f + \Delta G_g + \Delta G_h + \Delta G_i = -4.92 \text{ eV } @ U = 0 \text{ V } vs. \text{ RHE} \tag{32}$$

$$\Delta G_j + \Delta G_k + \Delta G_l + \Delta G_m = -4.92 \text{ eV } @ U = 0 \text{ V } vs. \text{ RHE} \tag{33}$$

The sum of the free-energy changes for all OER mechanisms needs to fulfill the criterion of equations (34) – (35):

$$\Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 = +4.92 \text{ eV } @ U = 0 \text{ V } vs. \text{ RHE} \tag{34}$$

$$\Delta G_n + \Delta G_o + \Delta G_p + \Delta G_q + \Delta G_r = +4.92 \text{ eV } @ U = 0 \text{ V } vs. \text{ RHE} \tag{35}$$

The sum of the free-energy changes for the PRR mechanism adheres to equation (36):

$$\Delta G_s + \Delta G_t = -3.52 \text{ eV } @ U = 0 \text{ V } vs. \text{ RHE} \tag{36}$$

The sum of the free-energy changes for the PFR mechanism adheres to equation (37):

$$\Delta G_u + \Delta G_v = +3.52 \text{ eV } @ U = 0 \text{ V } vs. \text{ RHE} \tag{37}$$

The sum of the free-energy changes for the two-electron ORR is given by equation (38):

$$\Delta G_w + \Delta G_x = -1.40 \text{ eV } @ U = 0 \text{ V } vs. \text{ RHE} \tag{38}$$

The sum of the free-energy changes for the two-electron OER is given by equation (39):

$$\Delta G_y + \Delta G_z = +1.40 \text{ eV } @ U = 0 \text{ V } vs. \text{ RHE} \tag{39}$$

2.1 Four-electron oxygen reduction reaction (ORR)

A detailed overview of how to derive the reaction intermediates' free energies for the ORR mechanisms is given in references [1,2]. We conclude:

a) Mononuclear mechanism

$$G_{M+O2}(U) = 0 \tag{40}$$

$$G_{M\text{-}OOH}(U) = \Delta G_1 + \text{SRI} - 4.92 \text{ eV} + 1 \times e \times U \tag{41}$$

$$G_{M\text{-}O}(U) = 3 \times \Delta G_1 - 4.92 \text{ eV} + 2 \times e \times U \tag{42}$$

$$G_{M\text{-}OH}(U) = \Delta G_1 - 4.92 \text{ eV} + 3 \times e \times U \tag{43}$$

$$G_M(U) = -4.92 \text{ eV} + 4 \times e \times U \tag{44}$$

b) Chemical *OOH dissociation mechanism

$$G_{M+M+O2}(U) = 0 \tag{45}$$

$$G_{M\text{-}OOH+M}(U) = \Delta G_1 + \text{SRI} - 4.92 \text{ eV} + 1 \times e \times U \tag{46}$$

$$G_{M\text{-}O+M\text{-}OH}(U) = 4 \times \Delta G_1 - 4.92 \text{ eV} + 1 \times e \times U \tag{47}$$

$$G_{\text{M-OH+M-OH}}(U) = 2 \times \Delta G_1 - 4.92 \text{ eV} + 2 \times e \times U \tag{48}$$

$$G_{\text{M-OH+M}}(U) = \Delta G_1 - 4.92 \text{ eV} + 3 \times e \times U \tag{49}$$

$$G_{\text{M+M}}(U) = -4.92 \text{ eV} + 4 \times e \times U \tag{50}$$

c) Electrochemical *OOH dissociation mechanism

$$G_{\text{M+M+O2}}(U) = 0 \tag{51}$$

$$G_{\text{M-OOH+M}}(U) = \Delta G_1 + \text{SRI} - 4.92 \text{ eV} + 1 \times e \times U \tag{52}$$

$$G_{\text{M-OH+M-OH}}(U) = 2 \times \Delta G_1 - 4.92 \text{ eV} + 2 \times e \times U \tag{53}$$

$$G_{\text{M-OH+M}}(U) = \Delta G_1 - 4.92 \text{ eV} + 3 \times e \times U \tag{54}$$

$$G_{\text{M+M}}(U) = -4.92 \text{ eV} + 4 \times e \times U \tag{55}$$

2.2 Four-electron oxygen evolution reaction (OER)

A detailed overview of how to derive the reaction intermediates' free energies for the OER mechanisms is given in references **[3]**. We conclude:

a) Mononuclear mechanism

$$G_{\text{M}}(U) = 0 \tag{56}$$

$$G_{\text{M-OH}}(U) = \Delta G_1 - 1 \times e \times U \tag{57}$$

$$G_{\text{M-O}}(U) = 3 \times \Delta G_1 - 2 \times e \times U \tag{58}$$

$$G_{\text{M-OOH}}(U) = \Delta G_1 + \text{SRI} - 3 \times e \times U \tag{59}$$

$$G_{\text{M+O2}}(U) = +4.92 \text{ eV} - 4 \times e \times U \tag{60}$$

b) *OO··OO* recombination mechanism

$$G_{\text{M-O M-O}}(U) = 0 \tag{61}$$

$$G_{\text{M-OOH M-O}}(U) = \text{SRI} - 2 \times \Delta G_1 - 1 \times e \times U \tag{62}$$

$$G_{\text{M-OOH M-OOH}}(U) = 2 \times \text{SRI} - 4 \times \Delta G_1 - 2 \times e \times U \tag{63}$$

$$G_{\text{M-OOH M-OO}}(U) = 2 \times \text{SRI} - 2 \times \Delta G_1 - 3 \times e \times U \tag{64}$$

$$G_{\text{M-OO M-OO}}(U) = 2 \times \text{SRI} - 4 \times e \times U \tag{65}$$

$$G_{\text{M-O M-O + O2}}(U) = +4.92 \text{ eV} - 4 \times e \times U \tag{66}$$

2.3 Two-electron peroxide reduction reaction (PRR)

$$G_{\text{M+H2O2}}(U) = 0 \tag{67}$$

$$G_{\text{M-OH}}(U) = \Delta G_1 - 3.52 \text{ eV} + 1 \times e \times U \tag{68}$$

$$G_{\text{M+O2}}(U) = -3.52 \text{ eV} + 2 \times e \times U \tag{69}$$

2.4 Two-electron peroxide formation reaction (PFR)

$$G_{\text{M+H2O}}(U) = 0 \tag{70}$$

$$G_{\text{M-OH}}(U) = \Delta G_1 - 1 \times e \times U \tag{71}$$

$$G_{\text{M+H2O2}}(U) = +3.52 \text{ eV} - 2 \times e \times U \tag{72}$$

2.5 Two-electron ORR

$$G_{M+O2}(U) = 0 \tag{73}$$
$$G_{M\text{-}OOH}(U) = \Delta G_1 + SRI - 4.92 \text{ eV} + 1 \times e \times U \tag{74}$$
$$G_{M+H2O2}(U) = -1.40 \text{ eV} + 2 \times e \times U \tag{75}$$

2.6 Two-electron OER

$$G_{M+H2O2}(U) = 0 \tag{76}$$
$$G_{M\text{-}OOH}(U) = \Delta G_1 + SRI - 3.52 \text{ eV} - 1 \times e \times U \tag{77}$$
$$G_{M+O2}(U) = +1.40 \text{ eV} - 2 \times e \times U \tag{78}$$

3 Free-energy spans relating to the descriptor $G_{max}(U)$

The concept of the descriptor $G_{max}(U)$, based on the notion of a free-energy span model, is discussed in depth in references [4-6].

3.1 Four-electron oxygen reduction reaction (ORR)

a) Mononuclear mechanism

The following free-energy spans are assessed:

$$G_{M\text{-}OOH}(U) - G_{M+O2}(U); \; G_{M\text{-}O}(U) - G_{M+O2}(U); \; G_{M\text{-}OH}(U) - G_{M+O2}(U);$$
$$G_{M\text{-}O}(U) - G_{M\text{-}OOH}(U); \; G_{M\text{-}OH}(U) - G_{M\text{-}OOH}(U); \; G_{M}(U) - G_{M\text{-}OOH}(U);$$
$$G_{M\text{-}OH}(U) - G_{M\text{-}O}(U); \; G_{M}(U) - G_{M\text{-}O}(U); \; G_{M}(U) - G_{M\text{-}OH}(U) \tag{79}$$

The activity measure $G_{max}(U)$ is defined by the largest free-energy difference among the set of available spans (cf. equation (79)):

$$G_{max}(U) = \max\{G_{M\text{-}OOH}(U) - G_{M+O2}(U); \; G_{M\text{-}O}(U) - G_{M+O2}(U); \; G_{M\text{-}OH}(U) - G_{M+O2}(U);$$
$$G_{M\text{-}O}(U) - G_{M\text{-}OOH}(U); \; G_{M\text{-}OH}(U) - G_{M\text{-}OOH}(U); \; G_{M}(U) - G_{M\text{-}OOH}(U);$$
$$G_{M\text{-}OH}(U) - G_{M\text{-}O}(U); \; G_{M}(U) - G_{M\text{-}O}(U); \; G_{M}(U) - G_{M\text{-}OH}(U)\} \tag{80}$$

The same procedure is conducted for the other ORR mechanisms. Please note that the ORR volcano curve is based on the energetically favored mechanistic description: for all three mechanisms, the largest free-energy span is extracted, but among these three free-energy spans the smallest one governs the volcano [1,2].

3.2 Four-electron oxygen evolution reaction (OER)

a) Mononuclear mechanism

$G_{max}(U)$ is determined by equation (81):

$$G_{max}(U) = \max\{G_{M\text{-}OH}(U) - G_{M}(U); \; G_{M\text{-}O}(U) - G_{M}(U); \; G_{M\text{-}OOH}(U) - G_{M}(U);$$
$$G_{M\text{-}O}(U) - G_{M\text{-}OH}(U); \; G_{M\text{-}OOH}(U) - G_{M\text{-}OH}(U); \; G_{M+O2}(U) - G_{M\text{-}OH}(U);$$
$$G_{M\text{-}OOH}(U) - G_{M\text{-}O}(U); \; G_{M+O2}(U) - G_{M\text{-}O}(U); \; G_{M+O2}(U) - G_{M\text{-}OOH}(U)\} \tag{81}$$

The same procedure is conducted for the *OO··*OO recombination pathway. For both mechanisms, the largest free-energy span is extracted, but among these two free-energy spans the smaller one governs the volcano [3].

3.3 Two-electron peroxide reduction reaction (PRR)

$$G_{max}(U) = \max\{G_{M\text{-}OH}(U) - G_{M+H2O2}(U); G_{M+O2}(U) - G_{M\text{-}OH}(U)\} \qquad (82)$$

3.4 Two-electron peroxide formation reaction (PFR)

$$G_{max}(U) = \max\{G_{M\text{-}OH}(U) - G_{M+H2O}(U); G_{M+H2O2}(U) - G_{M\text{-}OH}(U)\} \qquad (83)$$

3.5 Two-electron ORR

$$G_{max}(U) = \max\{G_{M\text{-}OOH}(U) - G_{M+O2}(U); G_{M+H2O2}(U) - G_{M\text{-}OOH}(U)\} \qquad (84)$$

3.6 Two-electron OER

$$G_{max}(U) = \max\{G_{M\text{-}OOH}(U) - G_{M+H2O2}(U); G_{M+O2}(U) - G_{M\text{-}OOH}(U)\} \qquad (85)$$

All volcano curves in the main text can be reproduced based on the introduced framework, using $\Delta G_1 = [-0.50, 2.50]$ eV with a step size of 0.01 eV, and SRI = [2.80, 3.20] eV with a step size of 0.20 eV [1-3]. There are no qualitative differences in the volcano plots independent if SRI = 2.8 eV, 3.0 eV, or 3.2 eV is used. Therefore, the volcano curves in the main text are constructed for either SRI = 3.2 eV (cf. **Figure 2**) or SRI = 3.0 eV (cf. **Figure 3**).

4 Sensitivity analysis of scaling relation

As discussed in section 2 of the main text, the main limitation of the compiled volcano curves refers to the assumption of a scaling relation between the *OH and *O intermediates (cf. equation (86)):

$$\Delta G_2 = 2 \times \Delta G_1 \qquad (86)$$

To quantify the robustness of the volcano plots, the above scaling relation is systematically modified to a reasonable extent. The following scenarios are discussed in the remainder:

$$\Delta G_2 = 2.3 \times \Delta G_1 \qquad (87)$$

$$\Delta G_2 = 1.7 \times \Delta G_1 \qquad (88)$$

$$\Delta G_2 = 2 \times \Delta G_1 + 0.3 \text{ eV} \qquad (89)$$

$$\Delta G_2 = 2 \times \Delta G_1 - 0.3 \text{ eV} \qquad (90)$$

We select the example of the competing four-electron and two-electron ORR (cf. **Figure 3a** in the main text) to quantify that an alteration of the *OH *vs.* *O scaling relation does not impact the obtained results. The four different cases are illustrated in **Figures S1-S2**.

a)

G_{max}(U = 0.70 V vs. RHE) [eV]
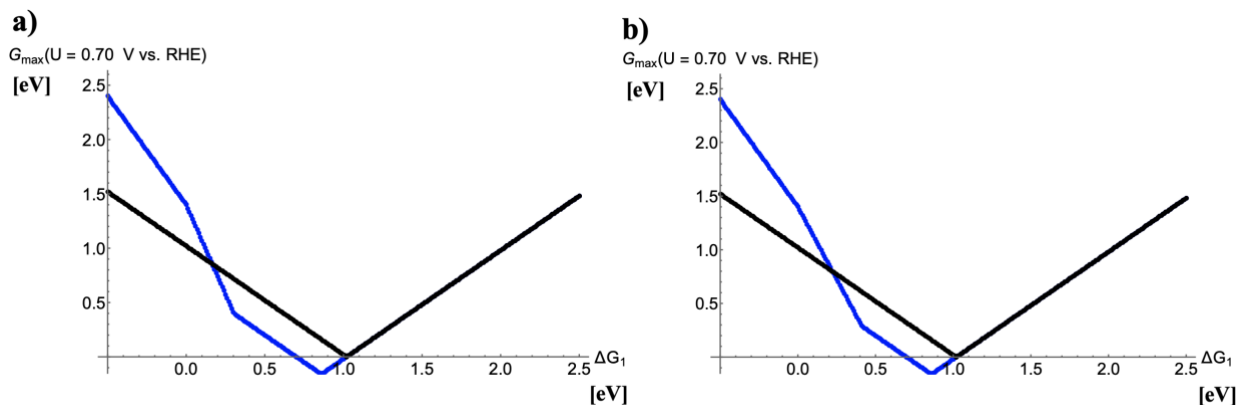
b)

G_{max}(U = 0.70 V vs. RHE) [eV]

Figure S1. Volcano plot for the four-electron (blue) and two-electron (black) oxygen reduction reactions (ORR), adopting a scaling-relation intercept of 3.2 eV, at $U = 0.7$ V *vs.* RHE. The following scaling relations have been chosen to connect the *O and *OH intermediates: a) $\Delta G_2 = 2.3 \times \Delta G_1$; b) $\Delta G_2 = 1.7 \times \Delta G_1$.
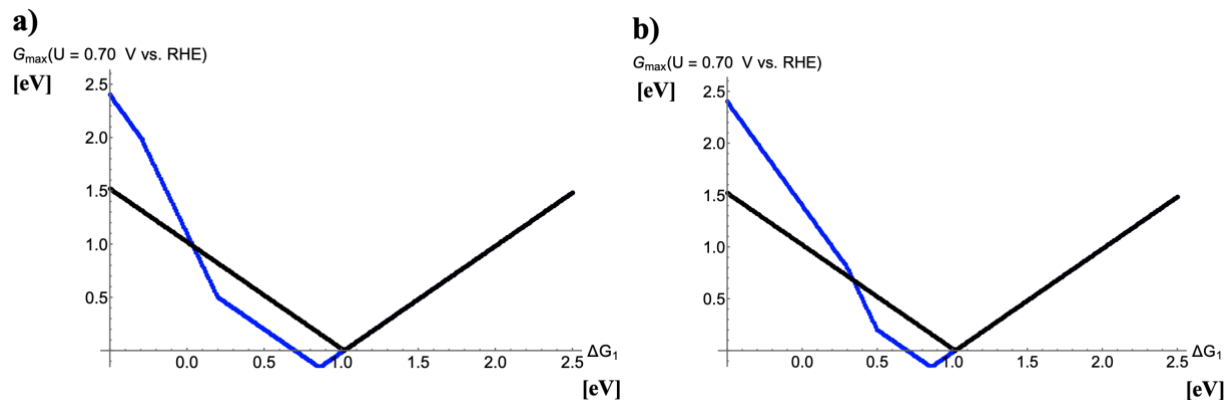
a)

G_{max}(U = 0.70 V vs. RHE) [eV]

b)

G_{max}(U = 0.70 V vs. RHE) [eV]

Figure S2. Volcano plot for the four-electron (blue) and two-electron (black) oxygen reduction reactions (ORR), adopting a scaling-relation intercept of 3.2 eV, at $U = 0.7$ V *vs.* RHE. The following scaling relations have been chosen to connect the *O and *OH intermediates: a) $\Delta G_2 = 2 \times \Delta G_1 + 0.3$ eV; b) $\Delta G_2 = 2 \times \Delta G_1 - 0.3$ eV.

Figures S1-S2 demonstrate that in each case, a trade-off between activity and selectivity for the electrochemical peroxide formation is observed, independent of the chosen scaling relation between the *OH and *O intermediates. This finding underpins the robustness of the presented approach, and it can be shown analogously for the competing PFR and OER (cf. **Figure 2a** in the main text) that a change in the *OH *vs.* *O scaling relation does not affect the general trend of the volcano curve.

5 Potential dependence of volcano curves

As discussed in section 2 of the main text, electrocatalytic turnover can only be obtained if an overpotential is applied. We select the example of the competing four-electron and two-electron ORR (cf. **Figure 3a** in the main text) to quantify that the discussion of volcano plot in a potential-dependent fashion does not alter the obtained results. **Figure S3** indicates the selectivity problem of the four-electron and two-electron oxygen reduction reactions (ORR) at applied electrode potentials of 0.6 V and 0.5 V *vs*. RHE.
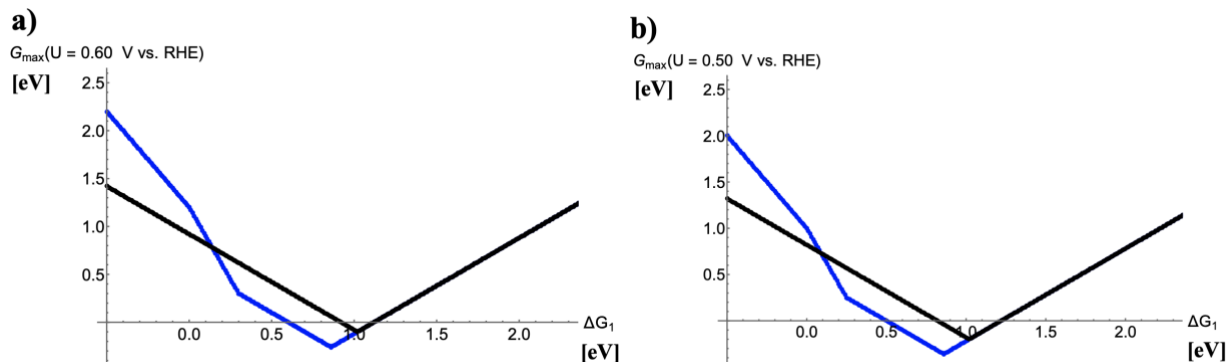

Figure S3. Volcano plot for the four-electron (blue) and two-electron (black) oxygen reduction reactions (ORR), adopting a scaling-relation intercept of 3.2 eV, at a) $U = 0.6$ V *vs*. RHE and b) $U = 0.5$ V *vs*. RHE. The following scaling relation for connection of the *O and *OH intermediates is used: $\Delta G_2 = 2 \times \Delta G_1$. Potential dependency does not alter the main result of this study in that selective peroxide formation is observed at the left or right volcano legs.

Figure S3 underpins that the obtained result of high selectivity toward peroxide formation at the volcano legs does not change when the applied overpotential is included into the discussion of the volcano plot. It can be shown analogously for the competing PFR and OER that the potential-dependent volcano curve reveals the same qualitative features as the volcano plot under equilibrium conditions (cf. **Figure 2a** in the main text).

References

[1] Exner, K. S. Rapid Screening of Mechanistic Pathways for Oxygen-Reduction Catalysts. ChemCatChem 2022, e202201222.

[2] Exner, K. S. Steering Selectivity in the Four-Electron and Two-Electron Oxygen-Reduction Reactions: On the Importance of the Volcano Slope. ACS Phys. Chem. Au 2023, DOI: 10.1021/acsphyschemau.2c00054.

[3] Exner, K. S. Implications of the M-OO··OO-M recombination mechanism on materials screening and the oxygen evolution reaction. J. Phys. Energy 2023, 5, 014008.

[4] Exner, K. S. A Universal Descriptor for the Screening of Electrode Materials for Multiple-Electron Processes: Beyond the Thermodynamic Overpotential, ACS Catal. 2020, 10, 12607-12617.

[5] Exner, K. S. Why approximating electrocatalytic activity by a single free-energy change is insufficient. Electrochim. Acta 2021, 375, 137975.

[6] Razzaq, S.; Exner, K. S. Materials Screening by the Descriptor $G_{max}(\eta)$: The Free-Energy Span Model in Electrocatalysis. ACS Catal. 2023, 13, 1740-1758.