Thermodynamic explanation of the universal correlation between oxygen evolution activity and corrosion of oxide catalysts

Tobias Binninger, Rhiyaad Mohamed, Kay Waltar, Emiliana Fabbri, Pieter Levecque, Rüdiger Kötz, and Thomas J. Schmidt

Supplementary Information

In the following, we will reformulate the three basic (electro)chemical processes (1)-(3) for acidic conditions with $H_3O_{aq}^+$ species.

Acidic conditions

1.) Chemical dissolution of the metal oxide without change of the cation oxidation state

$$\mathrm{M}^{2\mathrm{n}+}\mathrm{O}^{2-}_{\mathrm{n}}$$
 + $2\mathrm{n}\,\mathrm{H}_{3}\mathrm{O}^{+}_{\mathrm{aq}}$ \longleftrightarrow $\mathrm{M}^{2\mathrm{n}+}_{\mathrm{aq}}$ + $3\mathrm{n}\,\mathrm{H}_{2}\mathrm{O}$

2.) Oxygen evolution reaction (OER) from the electrolyte (water splitting)

$$3 \operatorname{H}_2 O \quad \longleftrightarrow \quad \frac{1}{2} \operatorname{O}_2 \quad + \quad 2 \operatorname{H}_3 \operatorname{O}_{\mathrm{aq}}^+ \quad + \quad 2 \operatorname{e}^- ,$$

3.) Lattice oxygen evolution reaction (LOER) directly from the metal oxide

$$\mathbf{M}^{2\mathbf{n}+} \mathbf{O}_{\mathbf{n}}^{2-} \longleftrightarrow \mathbf{M}_{\mathbf{aq}}^{2\mathbf{n}+} + \frac{1}{2} \mathbf{n} \mathbf{O}_{2} + 2\mathbf{n} \mathbf{e}^{-}$$

The consequent derivation of the thermodynamic instability of the metal oxide under OER conditions in acidic environment is exactly analogous to the one for alkaline environment.