

Supplementary Material for the Oxygen Evolution Reaction Mechanism at $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$ Powders Produced by Hydrolysis Synthesis

Anita Hamar Reksten, Heidi Thuv, Frode Seland, and Svein Sunde*

Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

April 5, 2018

S.1 Rietveld Refinements

Overview of the Rietveld refinement carried out of the $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$ samples obtained by hydrolysis synthesis are shown in Table S.1. The R_{wp} factor is defined as

$$R_{wp} = \sqrt{\frac{\sum w_m (Y^{exp} - Y^{th})^2}{\sum w_m (Y^{exp})^2}} \quad (\text{S.1})$$

where Y^{exp} and Y^{th} are the observed and calculated data, respectively, and w_m is the weighting given to the data point which for counting statistics is given by $w_m = 1/\sigma(Y^{exp})^2$ where $\sigma(Y^{exp})$ is the error in Y^{exp} [1].

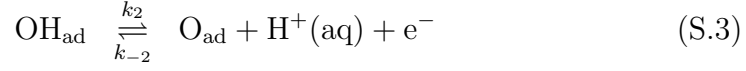
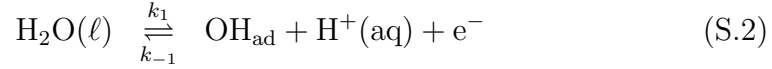
*Corresponding author. Tel.: +47 73594051; fax: +47 73591105, *E-mail address*: Svein.Sunde@material.ntnu.no

Table S.1: Overview of Rietveld refinement of the $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$ hydrolysis samples. The unit cell lengths, a and c , crystallite size, d , and the R_{wp} value of the refinements are summarized.

\mathbf{X}_{Ru}	$\mathbf{a} /$	$\mathbf{c} /$	\mathbf{d} / nm	\mathbf{R}_{wp}
0	4.5003(3)	3.1507(3)	8.5(1)	4.89
0.4	4.4954(5)	3.1383(4)	5.18(2)	6.18
0.7	4.994(5)	3.1160(2)	16.4(4)	7.57
1	4.5102(2)	3.0976(1)	9.5(1)	4.73

S.2 Electrochemical Oxide Path without Assumption of Quasi-Equilibrium

The electrochemical oxide path may be written



where surface sites are implicit in the equations and the area specific rate constants for reactions (S.2) and (S.3) are potential-dependent

$$k_1 = k_1^0 \exp \left[(1 - \alpha_1) F(E - E^0) / RT \right] \quad (\text{S.5})$$

$$k_{-1} = k_{-1}^0 \exp \left(\frac{-\alpha_1 F}{RT} (E - E^0) \right) \quad (\text{S.6})$$

$$k_2 = k_2^0 \exp \left[(1 - \alpha_2) F(E - E^0) / RT \right] \quad (\text{S.7})$$

$$k_{-2} = k_{-2}^0 \exp \left(\frac{-\alpha_2 F}{RT} (E - E^0) \right) \quad (\text{S.8})$$

The rates of reactions (S.2) and (S.3) are given by

$$v_1 = \Gamma k_1 (1 - \theta_1 - \theta_2) - \Gamma k_{-1} \theta_1 a_{\text{H}^+} \quad (\text{S.9})$$

and

$$v_2 = \Gamma k_2 \theta_1 - \Gamma k_{-2} \theta_2 a_{\text{H}^+} \quad (\text{S.10})$$

where the activity of water has been assumed equal to one, and θ_1 and θ_2 are the fractional coverages of OH_{ad} and O_{ad} , respectively. Γ is the maximum possible number of adsorbates per surface area, taken to be the same for the two adsorbates.

Solving Eq. (S.10) for θ_1 gives

$$\theta_1 = K_2 a_{\text{H}^+} \exp \left[-F(E - E^0)/RT \right] \theta_2 + v_2/k_2 \Gamma \quad (\text{S.11})$$

with $K_2 = k_{-2}^0/k_2^0$. Inserting Eq. (S.11) into Eq. (S.9) gives

$$\begin{aligned} v_1 = \Gamma k_1 \left[1 - \left(K_2 a_{\text{H}^+} \exp \left[-F(E - E^0)/RT \right] \theta_2 + v_2/k_2 \Gamma \right) - \theta_2 \right] \\ - \Gamma k_{-1} \left(K_2 a_{\text{H}^+} \exp \left[-F(E - E^0)/RT \right] \theta_2 + v_2/k_2 \Gamma \right) a_{\text{H}^+} \end{aligned} \quad (\text{S.12})$$

and assuming steady state ($v_2 = v_1$), we obtain

$$v_1 = \frac{\Gamma (k_1 - \theta_2 N_1)}{1 + k_1/k_2 + a_{\text{H}^+} k_{-1}/k_2} \quad (\text{S.13})$$

with

$$\begin{aligned} N_1 = k_1 \left\{ 1 + K_2 a_{\text{H}^+} \exp \left[-F(E - E^0)/RT \right] \right\} \\ + k_{-1} K_2 a_{\text{H}^+}^2 \exp \left[-F(E - E^0)/RT \right] \end{aligned} \quad (\text{S.14})$$

For reaction (S.4) we write,

$$v_3 = \Gamma k_3^0 \theta_2 - \Gamma k_{-3}^0 \sqrt{a_{\text{O}_2}} (1 - \theta_1 - \theta_2) \quad (\text{S.15})$$

and by substitution of Eq. (S.11)

$$\theta_2 = \frac{v (1 - k_{-3}^0 \sqrt{a_{\text{O}_2}}/k_2) + \Gamma k_{-3}^0 \sqrt{a_{\text{O}_2}}}{\left[\Gamma k_3^0 + \Gamma k_{-3}^0 \sqrt{a_{\text{O}_2}} (1 + K_2 a_{\text{H}^+} \exp \left[-F(E - E^0)/RT \right]) \right]} = Av + B \quad (\text{S.16})$$

again assuming steady state and $v_1 = v_2 = v_3 = v$ and where

$$A = \frac{(1/k_3^0 - K_3 \sqrt{a_{\text{O}_2}}/k_2)}{\Gamma \left[1 + K_3 \sqrt{a_{\text{O}_2}} (1 + K_2 a_{\text{H}^+} \exp \left[-F(E - E^0)/RT \right]) \right]} \quad (\text{S.17})$$

$$B = \frac{K_3 \sqrt{a_{\text{O}_2}}}{1 + K_3 \sqrt{a_{\text{O}_2}} (1 + K_2 a_{\text{H}^+} \exp \left[-F(E - E^0)/RT \right])} \quad (\text{S.18})$$

with $K_3 = k_{-3}^0/k_3^0$. By combination of Eq. (S.13) and (S.16)

$$v = \frac{\Gamma \{1 - BN_2\}}{1/k_1 + 1/k_2 + (a_{H^+}K_1/k_2) \exp[-F(E - E^0)/RT] - \Gamma AD_1} \quad (\text{S.19})$$

with

$$N_2 = 1 + K_2 a_{H^+} \exp[-F(E - E^0)/RT] + K_1 K_2 a_{H^+}^2 \exp[-2F(E - E^0)/RT] \quad (\text{S.20})$$

$$D_1 = 1 + K_2 a_{H^+} \exp[-F(E - E^0)/RT] + K_1 K_2 a_{H^+}^2 \exp[-2F(E - E^0)/RT] \quad (\text{S.21})$$

and $K_1 = k_{-1}^0/k_1^0$.

If $k_3^0 \gg 1$, $K_3 \ll 1$ (corresponding to $\theta_2 \rightarrow 0$) then $A \rightarrow 0$ and $B \ll 1$. Therefore the current density, i , becomes,

$$i \approx \frac{2F\Gamma k_2}{1 + k_2/k_1 + a_{H^+}K_1 \exp[-F(E - E^0)/RT]} \quad (\text{S.22})$$

or for $\alpha_1 = \alpha_2$

$$i \approx \frac{2F\Gamma k_2}{1 + k_2^0/k_1^0 + a_{H^+}K_1 \exp[-F(E - E^0)/RT]} \quad (\text{S.23})$$

and

$$i \approx \frac{2F\Gamma k_2^0 \exp[(1 - \alpha_2)F(E - E^0)/RT]}{(1 + k_2^0/k_1^0) + K_1 a_{H^+} \exp[-F(E - E^0)/RT]} \quad (\text{S.24})$$

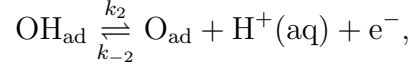
S.3 Double Layer Correction

Rates of reaction will be influenced by the potential distribution in the double layer structure at the electrode through its influence on the potential dependence of the rate constants and through its influence on the concentration (or activity) of the reacting species at the site at which electron transfer can take place [2].

For redox reactions involving charged species the equilibrium between a reactant in the bulk and that at the position at which the electron transfer may take place is governed by a Boltzmann factor in the difference between the potential at these two locations. However, reaction (S.3) assumes that the species involved in the reaction are either surface species that may not

exist in the bulk (OH_{ad} and O_{ad}) or species not adsorbed during the reaction (H^+). We are therefore left with the correction for the effects of the double layer on the rate constants.

The forward area-specific rate constant for the reaction in Eq. (S.3),



now written in terms of the difference between the potential in the electrode and the potential at the position of the adsorbate is

$$k_2 = k_2^0 \exp [(1 - \alpha_2) F (\phi_M - \phi_{\ddagger}) / RT] \quad (\text{S.25})$$

where M is used to denote the electrode surface and \ddagger the locus of OH_{ad} , i.e. the position of the adsorbate at which the electron transfer from it to the electrode may take place. We associate \ddagger with the inner Helmholtz plane, and may write Eq. (S.25) in terms of the potential difference across the entire double layer [as implied by Eq. (S.7)] as

$$k_2 = k_2^0 \exp [(1 - \alpha_2) FE / RT] \exp [(1 - \alpha_2) F (\phi_S - \phi_{\ddagger}) / RT] \quad (\text{S.26})$$

where $E = \phi_M - \phi_S$ with ϕ_S being the solution potential and

$$k_2^0 = k_2^{0'} \exp [-(1 - \alpha_2) FE^0 / RT].$$

The last factor in Eq. (S.26),

$$f_{DL} = \exp [(1 - \alpha_2) F (\phi_S - \phi_{\ddagger}) / RT] \quad (\text{S.27})$$

may be taken as a double-layer correction factor so that Eq. (S.26) becomes

$$k_2 = k_2^0 \exp [(1 - \alpha_2) FE / RT] f_{DL} \quad (\text{S.28})$$

We now assume \ddagger to be incident with the plane of proton adsorption in surface acid-base reactions [3]. Assuming equilibrium for $\text{H}_*^+ \rightleftharpoons \text{H}_{\ddagger}^+$ so that $\mu_{\text{H}_*^+} = \mu_{\text{H}_{\ddagger}^+}$, where $*$ is used to denote the bulk solution and μ denotes electrochemical potential,

$$\mu_{\text{H}_*^+} = \mu_{\text{H}^+}^0 + RT \ln a_{\text{H}_*^+} + F\phi_S = \mu_{\text{H}^+}^0 + RT \ln a_{\text{H}_{\ddagger}^+} + F\phi_{\ddagger} = \mu_{\text{H}_{\ddagger}^+} \quad (\text{S.29})$$

gives a Nernst-type relationship,

$$\phi_S - \phi_{\ddagger} = \frac{RT}{F} \ln \left(\frac{a_{H_{\ddagger}^+}}{a_{H_*^+}} \right) \quad (\text{S.30})$$

and

$$f_{DL} = \exp \left\{ \frac{(1 - \alpha_2) F}{RT} \left[\frac{RT}{F} \ln \left(\frac{a_{H_{\ddagger}^+}}{a_{H_*^+}} \right) \right] \right\} = \left(\frac{a_{H_{\ddagger}^+}}{a_{H_*^+}} \right)^{(1 - \alpha_2)} \quad (\text{S.31})$$

Eq. (S.28) can thus be written

$$k_2 = k_2^0 \left(\frac{a_{H_{\ddagger}^+}}{a_{H_*^+}} \right)^{(1 - \alpha_2)} \exp \left[\frac{(1 - \alpha_2) F}{RT} E \right] \quad (\text{S.32})$$

If the activity of the proton in the solid (i.e. H_{\ddagger}^+) is assumed constant with pH [3], it can be absorbed in the preexponential constant k_2^0 , and thus

$$k_2 = k_2^0 a_{H_*^+}^{-(1 - \alpha_2)} \exp [(1 - \alpha_2) FE/RT] \quad (\text{S.33})$$

We assume that the double-layer correction is the same for both reverse and forward directions [2, p. 41] so that it will not affect the ratio between the rate constants for the steps (S.3) and (S.2), i.e. the factor

$$K_1 a_{H^+} \exp [-F(E - E^0)/RT]$$

Eq. (S.33) introduces a factor $a_{H_*^+}^{-(1 - \alpha_2)}$ into the numerator of the rate equation, for example for the CC mechanism, so that the current now becomes

$$\begin{aligned} i_2 &\approx 2F \frac{\Gamma k_2^0 a_{H^+}^{-(1 - \alpha_2)} \exp [(1 - \alpha_2) F(E - E^0)/RT]}{1 + K_1 a_{H^+} \exp [-F(E - E^0)/RT]} \\ &\sim 2F \Gamma k_2^0 K_1^{-1} a_{H^+}^{-(2 - \alpha_2)} \exp [(2 - \alpha_2) F(E - E^0)/RT] \end{aligned} \quad (\text{S.34})$$

where we have set $a_{H_*^+} = a_{H^+}$ to make the notation consistent and let

$$k_2^0 \rightarrow k_2^0 \exp [-(2 - \alpha_2) FE^0/RT] \quad (\text{S.35})$$

References

- [1] B. A. GmbH, DIFFRAC^{plus} TOPAS 4.2 Technical Reference. Technical report (2009).
- [2] J. Albery, Electrode Kinetics, Clarendon Press, Oxford, 1975.
- [3] C. Angelinetta, M. Falciola, S. Trasatti, Heterogenous acid-base equilibria and reaction order of oxygen evolution on oxide electrodes, Journal of Electroanalytical Chemistry 205 (1-2) (1986) 347–353. doi:10.1016/0022-0728(86)90248-2.
URL <http://www.scopus.com/inward/record.url?eid=2-s2.0-0000630752&partnerID=40&md5=f1ef9d3f198b78fc09322346b0f10c10>