# The determination of the HOR/HER reaction mechanism from experimental kinetic data

Hector Prats<sup>†</sup> and Karen Chan<sup>\*,†</sup>

<sup>†</sup> Catalysis Theory Center, Department of Physics, Technical University of Denmark, 2800 Kogens Lyngby, Denmark

\* Corresponding author: kchan@fysik.dtu.dk

## S1. Rate equations

HOR/HER consists of three steps:

V

$$\begin{array}{c} k_T \\ H_2 + 2 * \underset{k_-T}{\leftrightarrow} 2H_{ads} \\ \text{Tafel:} \\ \end{array} \begin{array}{c} r_T = k_T^0 p_{H_2} (1-\theta)^2 \\ r_{-T} = k_{-T}^0 \theta^2 \end{array} \tag{1}$$

$$r_{H} = k_{H}^{0} p_{H_{2}} (1 - \theta) e^{\beta_{H} f \eta_{H}}$$
(3)

$$H = \kappa_{-H} u_{H}^{+} \theta \theta$$

$$(4)$$

$$H_{ads} \underset{k_{-V}}{\overset{k_{V}}{\leftrightarrow}} H^{+} + e^{-} + *$$
olmer:
$$r_{-V} = k_{-V}^{0} a_{H^{+}}^{0} (1 - \theta) e^{-(1 - \beta_{V}) f \eta_{V}}$$
(5)
(6)

where  $r_i$ ,  $k_i^0$ ,  $\beta_i$  and  $\eta_i$  are the reaction rate, rate constant, symmetry factor and the overpotential for step *i* (i.e., *i* = *T*,*H*,*V* for Tafel, Heyrovsky and Volmer, respectively; for  $r_i$  and  $k_i$  a minus sign indicates backward direction),  $p_{H_2}$  is the partial pressure of  $H_2$ ,  $\theta$  is the potential-dependent coverage of active H\* species,  $a_{H^+}$  is the activity of the protons and f denotes F/RT (F: the Faraday's constant, R: the universal gas constant, T: the temperature).

# S1.1. HOR

## Tafel - Volmer mechanism

If Tafel is the rate-determining step (RDS),  $\theta$  is close to zero, and the rate expression is obtained from Eq. 1:

$$r_{HOR} = k_T^0 p_{H_2} \tag{7}$$

Since Eq. 7 has no potential dependence, the anodic transfer coefficient  $\alpha_a$  is 0.

If Volmer is the RDS, Tafel step is equilibrated  $(r_T = r_{-T})$ , leading to the follow expression for  $\theta$ :

$$\theta = \frac{\sqrt{K_T^0 p_{H_2}}}{1 + \sqrt{K_T^0 p_{H_2}}}$$
(8)

where  $K_T^0 = k_T^0 / k_{-T}^0$  is the equilibrium constant for Tafel step. Then, the rate expression is obtained by combining Eqs. 5 and 8:

$$r_{HOR} = k_V^0 \frac{\sqrt{K_T^0 p_{H_2}}}{1 + \sqrt{K_T^0 p_{H_2}}} e^{\beta_V f \eta_V}$$
(9)

Only the exponential term in Eq. 9 depends on the applied potential. Therefore,  $\alpha_a = \beta_V$  and is between 0 and 1. <u>Heyrovsky</u> - <u>Volmer mechanism</u>

If Heyrovsky is the RDS,  $\theta$  is close to zero, and the rate expression is obtained from Eq. 3:

$$r_{HOR} = k_H^0 p_{H_2} e^{\beta_H f \eta_H}$$
(10)

Similar to the previous case,  $\alpha_a = \beta_H$  and is between 0 and 1.

If Volmer is the RDS, Heyrovsky step will be equilibrated  $(r_H = r_{-H})$ , leading to the follow expression for  $\theta$ :

$$\theta = \frac{K_H^0 p_{H_2}}{K_H^0 p_{H_2} + a_{H^+} e^{-f\eta_H}}$$
(11)

where  $K_H^0 = k_H^0 / k_{-H}^0$  is the equilibrium constant for Heyrovsky step. Then, the rate expression is obtained by combining Eqs. 5 and 11:

$$r_{HOR} = k_V^0 \frac{K_H^0 p_{H_2}}{K_H^0 p_{H_2} + a_{H^+} e^{-f\eta_H}} e^{\beta_V f\eta_V}$$
(12)

In this case, if  $K_H^0 p_{H_2} \gg a_{H^+} e^{-f\eta_H}$ ,  $\theta$  is saturated and the only potential dependence corresponds to the exponential term, so  $\alpha_a = \beta_V$  and is between 0 and 1. Otherwise, the H\* coverage vary exponentially with potential, giving rise to an effective  $\alpha_a$  that is between 1 and 2.

# S1.2. HER

# <u>Volmer</u> - <u>Tafel mechanism</u>

If Volmer is the RDS,  $\theta$  is close to zero, and the rate expression is obtained from Eq. 6:

$$r_{HER} = k_{-V}^{0} a_{H^{+}} e^{-(1-\beta_V)f\eta_V}$$
(13)

Only the exponential term in Eq. 13 depends on the applied potential. Therefore,  $\alpha_c = 1 - \beta_V$  and is between 0 and 1. If Tafel is the RDS, Volmer step will be equilibrated ( $r_V = r_{-V}$ ), leading to the follow expression for  $\theta$ :

$$\theta = \frac{a_{H^{+}}}{a_{H^{+}} + K_{V}^{0} e^{f \eta_{V}}}$$
(14)

where  $K_V^0 = k_V^0 / k_{-V}^0$  is the equilibrium constant for Volmer step. Then, the rate expression is obtained by combining Eqs. 2 and 14:

$$r_{HER} = k_{-T}^{0} \left( \frac{a_{H^+}}{a_{H^+} + K_V^0 e^{f\eta_V}} \right)^2$$
(15)

In this case, if  $a_{H^+} \gg K_V^0 e^{f\eta_V}$ ,  $\theta$  is saturated and the rate is independent of the applied potential, so  $\alpha_c = 0$ . Otherwise, the H\* coverage vary with potential as  $e^{2f\eta_V}$ , giving rise to an effective  $\alpha_c = 2$ . <u>Volmer - Heyrovsky mechanism</u>

If Volmer is the RDS, the rate is governed by Eq. 13, as for the Volmer - Tafel mechanism.

If Heyrovsky is the RDS, Volmer step will be equilibrated (i.e., Eq. 14). Then, the rate expression is obtained by combining Eqs. 4 and 14:

$$r_{HER} = k_{-H}^{0} \frac{\left(a_{H^{+}}\right)^{2}}{a_{H^{+}} + K_{V}^{0} e^{f\eta_{V}}} e^{-(1-\beta_{H})f\eta_{H}}$$
(16)

In this case, if  $a_{H^+} \gg K_V^0 e^{f\eta_V}$ ,  $\theta$  is saturated and the only potential dependence corresponds to the exponential term, so  $\alpha_c = 1 - \beta_H$  and is between 0 and 1. Otherwise, the H\* coverage vary exponentially with potential, giving rise to an effective  $\alpha_c$  that is between 1 and 2.

#### S2. Derivation of the concentration overpotential curve for HOR/HER

Mass transport limitations generate a concentration polarization at the interface, meaning that the surface concentrations of the reduced and oxidized species ( $c_R^{s}$  and  $c_0^{s}$ , respectively) and are different than the bulk concentrations of the reduced and oxidized species ( $c_R^{\infty}$  and  $c_0^{\infty}$ , respectively). For a chemical reaction completely governed by mass transport (i.e., when reaction kinetics can be considered infinitely fast) and under steady-state, the electrode potential and the surface concentrations of the initial reactant and the final product are in Nernstian equilibrium at all times:<sup>1</sup>

$$E = E_{eq} + \frac{RT}{nF} ln \frac{c_R^{\infty} c_0^{s,eq}}{c_R^{s,eq} c_0^{\infty}}$$
(17)

where E and  $E_{eq}$  are the electrode potential and the equilibrium potential, respectively ( $\eta = E - E_{eq}$ ) and  $C_R^{s,eq}$  and  $C_O^{s,eq}$  are the equilibrium surface concentrations of the reduced and oxidized species, respectively. Note that, for acidic HOR/HER,  $R \equiv H_2$  and  $O \equiv H^+$ . From mass conservation, the diffusion limited current density  $j_d$  is equivalent to the fluxes of O to and R species at the interface:

$$j_d = n_R F k_{d,R} \left( c_R^{\infty} - c_R^{s,eq} \right) \tag{18a}$$

$$j_{d} = n_{0} F k_{d,0} \left( c_{0}^{s,eq} - c_{0}^{\infty} \right)$$
(18b)

where  $n_i$  is the number of electrons transferred per species *i* and  $k_{d,i}$  is the mass transport coefficient for species *i*. At sufficiently high anodic or cathodic overpotentials,  $j_d$  converges to the limiting anodic  $(j_{l,a})$  and cathodic  $(j_{l,c})$  currents, respectively:

$$j_{l,a} = n_R F k_{d,R} c_R^{\infty} \tag{19a}$$

$$j_{l,c} = -n_0 F k_{d,0} c_0^{\infty} \tag{19b}$$

By dividing Eqs. 18a and 18b by Eqs. 19a and 19b, respectively, the following relations are obtained:

$$\frac{c_R^{s,eq}}{c_R^{\infty}} = 1 - \frac{j_d}{j_{l,a}}$$
(20a)

$$\frac{c_0^{s,eq}}{c_0^{\infty}} = 1 - \frac{j_d}{j_{l,c}}$$
(20b)

Finally, substituting Eqs. 20a and 20b into the Nernst equation (i.e., Eq. 17) and rearranging, we obtain

$$j_{d} = \frac{1 - e^{-nF\eta/RT}}{\frac{1}{j_{l,a}} - \frac{e^{-nF\eta/RT}}{j_{l,c}}}$$
(21)

which is known as the *concentration overpotential curve*. For acidic or alkaline HOR/HER, the transport of  $H^+$  or  $OH^-$  species is much faster than that of  $H_2$ , so mass transport limitations arise from limited solubility of  $H_2$  (i.e.,  $\leq 1 \text{ mmol/L}$  at 298 K).<sup>2</sup> Then, Eq. 21 can be simplified by assuming  $j_{l,c} \rightarrow \infty$ :

$$j_d = j_{l,a} \left( 1 - e^{-2F\eta/RT} \right)$$
(22)

If the kinetics of the reaction is fast enough, j will be completely determined by the transport of  $H_2$  from the bulk to the electrode surface in the HOR branch and from the electrode surface to the bulk in the HER branch. For instance, the measured polarization curve for acidic HOR/HER on Pt-based electrodes using rotating disk electrodes (RDEs) overlaps with Eq. 22.<sup>2,3</sup>

#### S3. The apparent Tafel slope of 30 mV/dec for acidic HER on Pt

Eq. 22 can be rearranged as follows:

$$\eta = -\frac{RT}{2F} \ln\left(1 - \frac{j_d}{j_{l,a}}\right) \tag{23}$$

Figure S1 shows the concentration overpotential curve for acidic HOR/HER under typical RDE conditions. In the HER branch,  $|j_d|$  is orders of magnitude higher than  $j_{l,a}$ , meaning that in the Tafel region for HER the logarithm in Eq. 23 can be approximated by:

$$ln\left(1 - \frac{j_d}{j_{l,a}}\right) \approx ln(|j_d|) - ln(j_{l,a})$$
(24)

Combining Eqs. 23 and Eq. 24, it is possible to see that the slope of a  $\eta$  vs  $\log |j_d|$  plot is just  $-RT \ln 10/2F$ . At room temperature, this corresponds to a Tafel slope of 30 mV/dec, as shown also in the inset plot in Figure S2. A true Tafel slope that arises from intrinsic kinetics, however, can only be obtained from  $j_k$ .

**Figure S1.** Concentration overpotential curves for acidic HER/HOR when considering the mass transport limitation from both H<sup>+</sup> and H<sub>2</sub> (dotted blue line, Eq. 21), and when only mass transport limitation from H<sub>2</sub> is considered (dashed purple line, Eq. 22). The limiting currents used in the plot are  $j_{l,a} = 2.2 \text{ mA/cm}^2$  and  $j_{l,c} = -1700 \text{ mA/cm}^2$ , which correspond to a RDE experiment in 0.5M H<sub>2</sub>SO<sub>4</sub>,  $p_{H_2} = 1 \text{ atm}$  and  $\omega = 1600 \text{ rpm}$ .



S4. Imposing  $\alpha_a + \alpha_c = 1$  as a constrain when fitting experimental data

Figure S2 shows that imposing  $\alpha_a + \alpha_c = 1$  as a constrain when fitting polarization curves in the overpotential range [-0.05 V, 0.05 V] always leads to a good fit, even when the true  $\alpha_a + \alpha_c$  is ~0 or 2. This is because in the range of  $\eta$  considered the manifestations of  $\alpha_a$  and  $\alpha_c$  are not very pronounced. The kinetic parameters obtained by imposing such constrain, however, are significantly different, which can ultimately result in different mechanistic interpretation.

Figure S2. Simulated polarization curves (black dots) for kinetic limited systems with  $j_0 = 1$  a.u. and  $\alpha_a + \alpha_c =$  (a) 0.01, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1 and their fits to the Butler-Volmer equation (Eq. 1 in the main text, red lines) imposing  $\alpha_a + \alpha_c = 1$ .



Similarly, different assumptions in the value of  $\alpha_a + \alpha_c$  can lead to discrepancies in the values of  $j_0$  when it is obtained from the slope of the micropolarization region. Indeed, at very small overpotentials (i.e.,  $|\eta| < 0.03$  V if  $\alpha_a + \alpha_c = 1$  and  $|\eta| < 0.02$  V if  $\alpha_a + \alpha_c = 2$ , see Figure S3) the Butler-Volmer equation can be linearized by the Taylor expansion  $e^x \approx 1 + x_i$ .

# Supporting Information

$$\eta = \frac{1}{j_0(\alpha_a + \alpha_c)F} j \tag{25}$$

Since the slope is proportional to  $1/j_0(\alpha_a + \alpha_c)$ ,  $j_0$  cannot be determined from the slope of the micropolarization region alone and the original Butler-Volmer equation (i.e., Eq. 1 in the main text) must be used. Nevertheless, several studies have used Eq. 25 to determine  $j_0$  for acidic HOR/HER on Pt by assuming that  $\alpha_a + \alpha_c$  is either one<sup>4,5</sup> or two.<sup>6789</sup> **Figure S3.** Simulated polarization curves (black dots) for kinetic limited systems with  $j_0 = 1$  a.u. and  $\alpha_a + \alpha_c =$  (a) 0.01, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1 and their fits to the Butler-Volmer equation (Eq. 1 in the main text, red lines) imposing  $\alpha_a + \alpha_c = 1$ .



## S5. Reversible vs. irreversible Koutecky-Levich equation

Table S1 show the kinetic parameters obtained from the polarization curves for Pt/C in 0.1 M KOH at 293 K using a RDE setup taken from Zheng et al.<sup>2</sup> using:

• (i) the *reversible* Koutecky-Levick equation in the HOR branch and the HER branch:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}$$
(26)

• (ii) the *irreversible* Koutecky-Levick equation only in the HOR branch, assuming that the HER branch is free of mass transport effects

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_{l,a}}$$
(27)

The differences between the kinetic parameters obtained from methods (i) and (ii) become more pronounced as the range of overpotential considered for the fitting is narrower, due to a strong dependence of these with the range of overpotential when using (ii). In the range  $-0.03 \le \eta \le 0.03$ , the transfer coefficients obtained from the irreversible Koutecky-Levich equation are so overestimated that can result in misleading mechanistic interpretations. Figure S4 plots the kinetic currents estimated with both methods.

It is hard to give a general estimate about the magnitude of the error when using the irreversible Koutecky-Levich equation for HOR/HER, since it depends on how strong mass transport effects are and also on the overpotential range considered for the fitting. For most electrochemical reactions where the offset potential is relatively large using the irreversible Koutecky-Levich equation is fine because  $j_d$  will be very close to the limiting anodic or cathodic current densities. However, it might lead to significantly different kinetic parameters when applied to the highly reversible HOR/HER simply because the overpotentials can be really small.

Overpotential range (V)	j <sub>0 (mA/cm<sup>2</sup><sub>disk</sub>)</sub>		α <sub>a</sub>		α <sub>c</sub>	
	(i) Rev. KL	(ii) Irrev. KL	(i) Rev. KL	(ii) Irrev. KL	(i) Rev. KL	(ii) Irrev. KL
$-0.05 < \eta < 0.05$	$2.1 \pm 0.1$	$1.5 \pm 0.1$	$0.51 \pm 0.02$	$0.66 \pm 0.02$	$0.56 \pm 0.02$	$0.71 \pm 0.02$
$-0.04 < \eta < 0.04$	$1.9 \pm 0.1$	$1.2 \pm 0.1$	$0.55 \pm 0.04$	$0.78 \pm 0.03$	$0.62 \pm 0.04$	$0.85 \pm 0.03$
$-0.03 < \eta < 0.03$	$1.9 \pm 0.3$	$1.0 \pm 0.1$	$0.5 \pm 0.1$	$0.87 \pm 0.06$	$0.6 \pm 0.1$	$0.97 \pm 0.06$

**Table S1.** Differences between the kinetic parameters obtained from Eqs. 26 and 27 for RDE measurements of alkaline HOR/HER taken from Zheng et al.<sup>2</sup> Three different overpotential ranges have been considered for the fitting.

**Figure S4.** RDE polarization curve for alkaline HOR/HER on Pt/C taken from Zheng et al.<sup>2</sup> (black dots), diffusion limited current ( $j^{d}$ , blue triangles), and kinetic current estimated from the reversible ( $j^{k,rev}$ , red squares) and irreversible ( $j^{k,irrev}$ , magenta rhombuses) Koutecky-Levich equations.



## S6. Lower limit for the scan rate in CV/LSV experiments

The lower limit for the scan rate is determined by the mass transport boundary layer. Electrode reactions lead to natural convection in the solvent due to temperature gradients and density changes. Bockris suggests that the thickness of the natural convection boundary layer is around  $5 \cdot 10^{-4}$  m.<sup>10</sup> When the electrode reaction starts, a diffusion layer will be formed at the electrode-solution interface. The thickness of this layer,  $\delta_i$ , is:<sup>1</sup>

$$\delta_i \approx 2\sqrt{D_i t} \tag{28}$$

where  $D_i$  is the diffusion coefficient of species i and t is the time. For the CV/LSV analysis to be correct,  $\delta_i$  needs to be small compared with 5·10<sup>-4</sup> m. This means that, for a scan of 1 V and assuming  $D_i = 1.10^{-9} \text{ m}^2/\text{s}$ , the scan rate should be faster than ~16 mV/s so that the measurements are not affected by convection.

#### S7. Fitting of experimental data

**Figure S5.** H<sub>2</sub>-pump PEMFC polarization curve for low loading Pt/C at 353 K taken from Neyerlin et al.<sup>11</sup> (black dots, Figure 4 in the original work) and fit to the Butler-Volmer equation (red line).



**Figure S6.** Black dots show RDE polarization curves for a) Pt/C in 0.1 M KOH at 294 K taken from Sheng et al.<sup>3</sup> (Figure 7b in the original work), b) Pt(pc) disk in 0.1 M KOH at 293 K taken from Rheinländer et al.<sup>12</sup> (Figure 2a in the original work) and c) Pt/C in 0.1 M KOH at 293 K taken from Zheng et al.<sup>2</sup> (Figure 3 in the original work). Blue dots show the corresponding concentration overpotential curves (i.e., jd). Red dots show the calculated kinetic current jk from the reversible Koutecky-Levich equation. Red lines show the fits of jk to the Butler-Volmer equation. Only values in the range [-0.05, 0.05 V] are considered for the fitting.



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