

Supporting Information

Fluorine-Free Pt-Nanocomposites for Three-Phase Interfaces in Fuel Cell Electrodes

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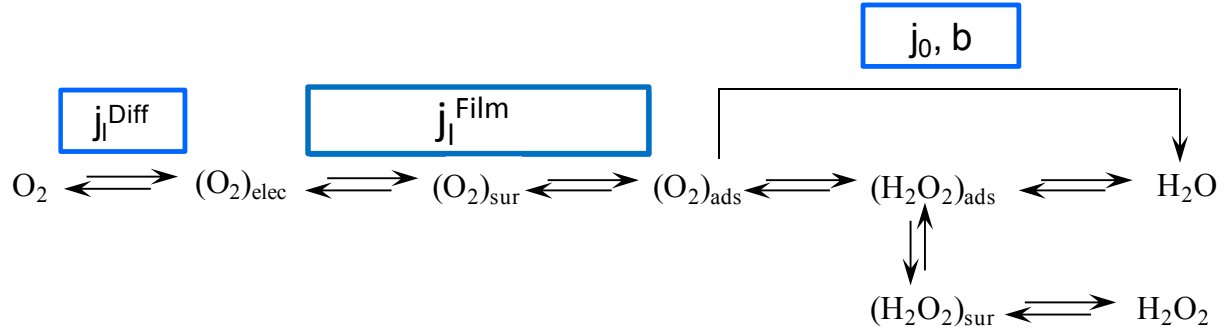
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Mathematical treatment of the generalized Koutecky-Levich (KL) equation

A more general analysis of data was carried out by separating the contribution of the diffusion of molecular dioxygen from that of the electrode processes involved in the oxygen reduction reaction using the $1/j$ vs $1/\omega^{1/2}$ Koutecky–Levich plots. For that purpose the more detailed reaction mechanism considered, involving the formation of H_2O_2 ,¹ is represented by the following scheme:



where j_l^{Diff} is the limiting diffusion current density of O_2 in the bulk electrolyte, j_l^{Film} is the diffusion limiting current density of O_2 in the porous catalytic film, j_0 is the exchange current density and b is the Tafel slope.

Assuming the rate determining step (rds) is the charge transfer, and therefore that the adsorption process is more rapid than the electron transfer, the Koutecky-Levich equation can be expressed as follows²:

$$\frac{1}{j} = \frac{1}{j_e} + \frac{1}{j_l^{\text{Diff}}} = \frac{1}{j_k} + \frac{1}{j_l^{\text{Film}}} + \frac{1}{j_l^{\text{Diff}}} = \frac{1}{j_0 e^{(\eta/b)}} + \frac{1}{j_l} + \frac{1}{j_l^{\text{Diff}}}$$

with $\eta = E - E_{\text{eq}}$, the overvoltage and E_{eq} , the equilibrium potential.

The diffusion limiting current density of molecular oxygen in the bulk electrolyte, j_l^{Diff} , is controlled by the electrode rotation rate ω , whereas the limiting current density due to the diffusion inside the film, j_l^{Film} , is independent on ω . The diffusion limiting current density in the electrolyte is given by the Levich's law:

$$j_l^{\text{Diff}} = 0.20nFD_{\text{O}_2}^{2/3} \nu^{-1/6} C_{\text{O}_2} \omega^{1/2}$$

and can be calculated using the following data: n the number of exchanged electron per reduced oxygen molecule, F the Faraday constant ($96,485 \text{ C mol}^{-1}$), D_{O_2} the diffusion coefficient of oxygen in 0.1 M HClO_4 ($1.7 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν the kinematic viscosity of the electrolyte ($1.0 \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$), C_{O_2} the oxygen concentration in the considered electrolyte ($1.3 \cdot 10^{-3} \text{ mol dm}^{-3}$)^{3,4}, ω the

rotation rate of the electrode in revolution per minute (rpm), and 0.2 the coefficient used when ω is expressed in rpm.

The slopes of the Koutecky-Levich plots $1/j = f(\omega^{-1/2})$ give the number of exchanged electrons per reduced oxygen molecule at different electrode potentials, whereas the intercepts at origin of the KL plots with the Y-axis give the values of $1/j_e$. The determination of $1/j_l^{\text{Film}}$ is made by determining the limit of $1/j_e$ vs η (or E) when $|\eta|$ tends towards $+\infty$:

$$\frac{1}{j_e} = \frac{1}{j_k} + \frac{1}{j_l^{\text{Film}}} = \frac{1}{j_0 e^{(|\eta|/b)}} + \frac{1}{j_l}$$

now, knowing j_e , and j_l^{Film} , the Tafel slope, b , and exchange current density, j_0 , can be determined by using the following equation:

$$\eta = E - E_{\text{eq}} = -b \left[\ln \left(\frac{j_l}{j_0} \right) + \ln \left(\frac{j_e}{j_l - j_e} \right) \right]$$

and further, the values of j_k @ 0.9 V are determined thanks to the following equation:

$$j_k = j_0 e^{(|\eta|/b)}$$

Figure S1 presents, as an example, the quasi-stationary current vs potential curves recorded on a Pt catalyst modified with PSSA (DP_n of 2500 and grafting density of ca. $2.82 \cdot 10^{-7} \text{ mol}_{\text{PSSA}} \text{ g}_{\text{Pt}}^{-1}$), as an example during slow negative potential sweeps (scan rate of 1 mV s^{-1}) between 1.05 and 0.3 V vs RHE for different rotation rates ω from 500 to 2500 rpm of the rotating disc electrode (RDE) in O_2 -saturated 0.1 M HClO_4 supporting electrolyte. Figure 1b gives the Koutecky-Levich plots drawn from Figure 1a at different potentials, Figure 1c gives the current densities related to phenomena occurring at the electrode (j_e) for the ORR as a function of the electrode potential and at last Figure 1d shows the resulting Tafel plots.

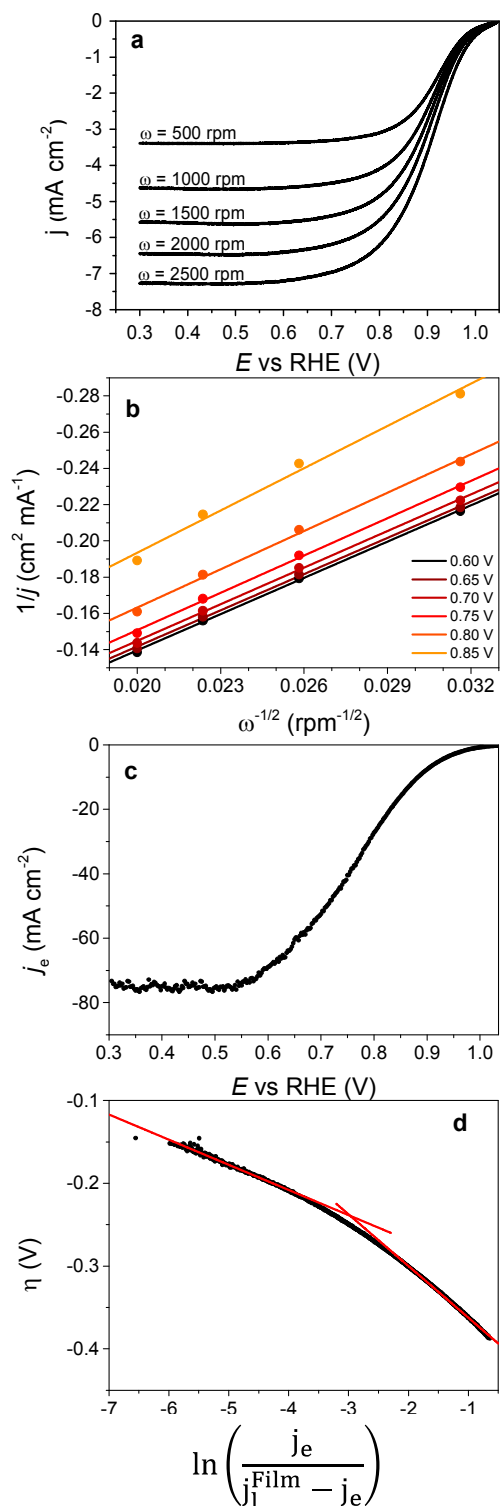


Figure S1. (a) Hydrodynamic polarization curves recorded for different electrode rotation rates ω (in rpm) on a Pt-NP(PSSA)/C ($DP_n = 2500$, grafting density = $2.82 \cdot 10^{-7} \text{ mol}_{\text{PSSA}} \text{ g}_{\text{Pt}}^{-1}$) at 25 °C in O₂-saturated 0.1 M HClO₄ electrolyte with a scan rate $s = 1 \text{ mV s}^{-1}$; (b) Koutecky-Levich plots drawn at different potentials from the polarization curves; (c) Current densities related to phenomena occurring at the electrode (j_e) for the ORR as a

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