Electronic Supplementary Information

1. Linearity of the system for ORR

The applied voltage step has a height of 100 mV for the investigations of the ORR. This step is rather small and may therefore be regarded as pseudo-linear perturbation. The pseudo-linear behavior is examined with contrary voltage steps but same size of amplitude. The maximum amplitude examined was a 200 mV step. Two measurements starting from 1.3 V to 1.4 V and 1.3 V to 1.2 V, respectively, are shown in Figure 1ESI. The resulting currents show the same characteristic in different directions indicating a pseudo-linear behavior in this voltage range. The two measurements are compared within an increment of 200 mV (two times 100 mV) and a pseudo-linear behavior is much more reasonable in a 100 mV interval as conducted in the measurements from our recent work. We therefore assume that the non-linear behavior for this voltage step is very small and is not influencing our impedance spectra in a significant way.

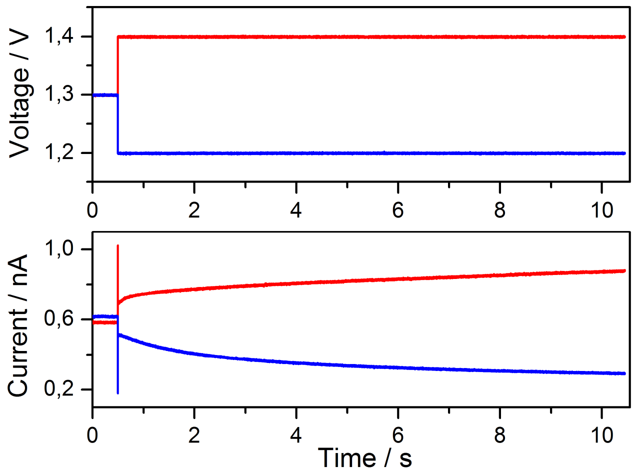

Figure 1ESI: Two chronoamperometric experiments starting from 1.3 V with voltage jumps to 1.4 V (red) and to 1.2 V (blue) with the corresponding current signals.

2. Calculation of the stoichiometric ratio S_{O_2} :

From Faraday's First Law one gets:

$I = z \cdot F \cdot \frac{n}{t}$, and with $\dot{n} = \frac{n}{t}$ one obtains $\dot{n} = \frac{I}{z \cdot F}$

Where I denotes the current and F the Faraday constant. The time is labeled as t and the number of electrons transferred per molecule as z. A dot above a symbol marks the flux of this physical quantity.

Substituting $\dot{n} = \frac{\dot{m}}{M}$ and $\dot{m} = \dot{V} \cdot \rho$ the volume flow in dependence of the current is observed. m denotes the mass, M the molecular weight and ρ the density of the substance. The ratio M/ρ is identical to the molar volume v_M which is 24.45 l mol^{-1} at 298 K and 1 atm.

$$\dot{V} = \frac{I}{z \cdot F} \cdot \frac{M}{\rho} = \frac{I}{z \cdot F} \cdot v_M$$

Calculating the volume flow for a typical current of 10 nA with four electrons transferred per oxygen molecule yields $\dot{V}_{O_2} = 2.28 \cdot 10^{-9}\ \text{l h}^{-1}$

The real mass flow is $1.05\ \text{l h}^{-1}$ leading to a stoichiometric ratio of

$$S_{O_2} = \frac{1.05\,\mathrm{l\,h^{-1}}}{2.28 \cdot 10^{-9}\ \mathrm{l\,h^{-1}}} \approx 0.46 \cdot 10^{9}$$

3. Constant Phase Element:

The impedance of a constant phase element is described by an extension through a normalization factor ω/ω_0 [1]. The parameter C_{CPE} is put in as Farad. ω_0 was chosen to be 1000 Hz. The exponent α is dimensionless. For α=1 the impedance is identical to a pure capacitor.

$$Z(\omega) = \frac{1}{\omega_0 \cdot C_{CPE} \left(\frac{i\omega}{\omega_0}\right)^{\alpha}} \xrightarrow{\alpha=1} \frac{1}{i\omega C} \text{ (pure capacitor)}$$

4. Nernst Element:

$$N = \frac{W}{\sqrt{i\omega}} \cdot tanh\sqrt{\frac{i\omega\, d^2}{D}} \qquad k = \frac{D}{d^2}$$

D: diffusion constant, d: thickness of Nernst layer, ω: frequency, W: Warburg coefficient

References

[1] C. A. Schiller, W. Strunz, *Electrochimica Acta* **2001**, *46*, 3619.