Electronic Supplementary Information

Fuelling electrocatalysis at single nanoparticle by ion flow in a nanoconfined electrolyte layer

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Optical evaluation of the thin electrolyte film (Figure 2)

Optical images recorded at 532 ± 4 nm (green) and at 450 ± 10 nm (blue) of the same droplet were converted into relative reflectivity ($1+\frac{\Delta R}{R}$) images. Noteworthy, the farthest ITO region of interest, ROI, is bare ITO and therefore its relative reflectivity is 1 (see orange ROIs in Figure 2, and Materials and methods). The reflectivity image obtained at 532±4 nm (Figure 2a) is the most sensitive to the thin electrolyte film, which is directly detected as a brighter (more reflective) region surrounding the droplet. This more reflective region extended ca. 4 µm from the droplet reservoir's edge. Compared to bare ITO, this region is 4% more reflective, with a relative reflectivity of 1.04 (see the red ROI in Figure 2a) assigned to the presence of a thin precursor layer of water. Changing the illumination to 450±10 nm (Figure 2b), the thin electrolyte film could not be distinguished from the background or the bare ITO surface (red ROI with relative reflectivity ≈ 1).

The local intensity of a pixel in the optical image accounts for the reflectivity of the illuminated ITO surface and is therefore sensitive to the composition of the ITO/thin precursor film/air dielectric assembly. Using an s-CMOS monochrome 16-bit sensitive camera (Photometrics) and band-pass filtering the illumination source, monochromatic images of the bare ITO surface (absence of Pt NPs) were recorded before and after landing of a micrometric electrolyte droplet.

Converting the images into reflectivity images not only enhanced the contrast, but also allowed to quantify the apparent thickness of the thin electrolyte film using a simple optical model based on the Fresnel formalism summarized in Figure 2c (detailed below). In brief, the reflectivity of a sandwiched layer of water between an ITO layer and a semi-infinite air medium can be evaluated at both illumination wavelengths for different thicknesses of water layer (respectively green and blue curves in Figure 2c) at a given ITO layer thickness.

This mean-field optical analysis of the relative reflectivity of 1.04 in the green and 1.00 in the blue further provides a unique couple of water and ITO layer thicknesses. This means 1) that the equivalent water layer thickness can be evaluated without prior exact knowledge about the actual ITO layer thickness and 2) that the latter can be evaluated indirectly simultaneously. It turned out to be equal to 274±1 nm, which is very different from the 350 nm indicated by the supplier. This significant mismatch was confirmed by imaging a cross section of the same ITO-coated coverslip by SEM (Figure S1) and by profilometry after dissolution of a portion of the ITO layer in 1 M HCl solution (comparison in Table S1).

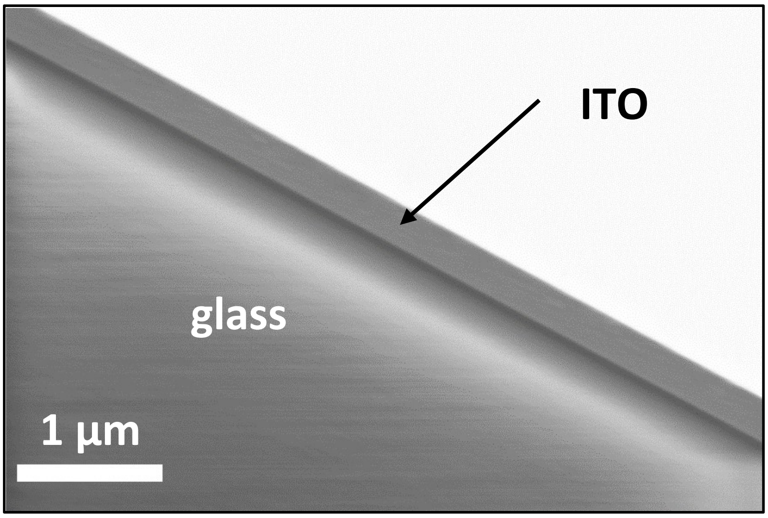

Figure S1: *Cross-sectional view of the same ITO-coated coverslip obtained by SEM for evaluation of the ITO layer thickness.*

Method	Optical model	SEM cross section	Profilometry
ITO layer thickness / nm	274±1	272±2 (N=6, 95%)	272±6 (N=4, 95%)

Table S1. *Comparison of the ITO layer thickness, δ_{ITO}, determined by the optical model, SEM and profilometry. The value indicated by the supplier (see Materials and Methods) for a 15-30 Ω cm resistivity is 350 nm.*

Fresnel mean-field evaluation of reflectivity

The optical model used to determine the thickness of the thin electrolyte film is based on the Fresnel equations describing the reflection of light at an interface and was implemented in Python. The idea is to calculate the reflection coefficient of the interface defined by the first two media in the optical path (glass|ITO, see inset of Figure 2c), and then to recursively add the following media (in order water and air) into the optical path and calculate the new reflection coefficient of the ensemble.

In the case of normal incidence, the reflection coefficient, $r_{i,i+1}$, of an electromagnetic wave reflecting at the interface between medium **i** (of refractive index n_i) and medium **i+1** (of refractive index n_{i+1}) is given by the Fresnel equation:

$$r_{i,i+1} = \frac{n_i - n_{i+1}}{n_i + n_{i+1}} \tag{S1}$$

If medium **i+1** is a thin film so that the electromagnetic wave crosses another medium (**i+2**), the new reflection coefficient of the ensemble, $r_{i,i+2}$, can be expressed as follows:

$$r_{i,i+2} = \frac{r_{i+1,i+2} + r_{i,i+1}\exp(2i\phi_{i+1})}{1 + r_{i+1,i+2}r_{i,i+1}\exp(2i\phi_{i+1})} \tag{S2}$$

where $\phi_{i+1} = 2\pi n_{i+1}\delta_{i+1}/\lambda$ is the phase shift induced by crossing medium **i+1**, δ_{i+1} the thickness of medium **i+1** and λ the wavelength of the incident light.

Following this principle, the reflection coefficient of a stack composed of several thin films can be calculated recursively. The absolute reflectivity, R, of an electromagnetic wave propagating through media 1 to k (>1) is then given by the following equation:

$$R = |r_{1,k}|^2 \tag{S3}$$

If the intensity of the incident light remains constant throughout the experiment, the variations of the intensity of the reflected light, I_{opt}, can be compared to its initial value. The relative reflectivity, $\Delta R/R$, is then linked to I_{opt} *via* the following equation:

$$1 + \frac{\Delta R}{R} = \frac{I_{opt}(t)}{I_{opt}(0)} \tag{S4}$$