Supporting Information

The Interface Peak

Here, we shortly discuss the behavior of the interface layer with its separate XPS doublet which is visible for most 5-ML-thick tetragonal zirconia films.

The interface peak shifts in the opposite direction than the main peak (described in section 3.1 of the main paper); at high $E_B (\gtrsim 183$ eV) of the main peak, it is a distinct peak with $E_B$ between 180.7 eV–181.0 eV. At lower $E_B$ of the main peak, it is a less distinct shoulder as in Figure 1a of the main paper, and becomes invisible when the main peak is located at $\approx 182.6$ eV.

In summary, the Zr 3d doublet of the interface peak shifts to lower binding energies when the main peak's binding energy increases, i.e. with increasing reduction level. So, with an increased number of oxygen vacancies, the distance between main peak and interface peak increases, with a lower number of $V_{Os}$ it decreases.

It is likely that the shift of the interface peak results from a changing number of oxygen vacancies at the interface. DFT calculations indicate that substrate–Zr bonds lead to the different binding energy of the interface layer [1]. Therefore, a higher number of $V_{Os}$ can lead to a stronger bond between Rh and the Zr atoms surrounding the vacancy, thereby decreasing the binding energy further. (The Zr $E_B$ at the interface becomes more metal-like.) A varying number of oxygen vacancies at the interface could also explain variations in the interface peak area observed by us (though near the confidence limit of peak fitting); with a lower number of $V_{Os}$ present at the interface, less Zr atoms encounter a strong bond to Rh, and thus, a lower amount of Zr contributes to the interface peak.