Operando X-ray Investigation of Electrode/Electrolyte Interfaces in Model Solid Oxide Fuel Cells

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Supplementary material

The supplementary material summarizes the following complementary fit results: from an area on the surface several mm away from the LSC electrode for three different conditions and for the UHV prepared clean YSZ (100) surface (see Table 1). In Figure 1 the corresponding occupancy profiles are shown. Figure 2 and 3 show the corresponding experimental data

(open circles) together with the fits (lines). In Figure 4 the CTR data and fits are shown for condition 2 (775 K, p=$1.0 \cdot 10^{-7}$ mbar) and condition 5 (775 K, p(O$_2$)=18mbar, U=+250 mV) from the main text. The goodness of all the fits presented in this manuscript is given by normalized χ^2 parameter listed in Table 2.

Table 1: Refined out-of-plane values of atomic displacements (Δ) and Debye-Waller factors (B) at three different conditions for away from the electrode (area "a" on Figure 1) and for pristine YSZ(100) sample at reducing conditions.

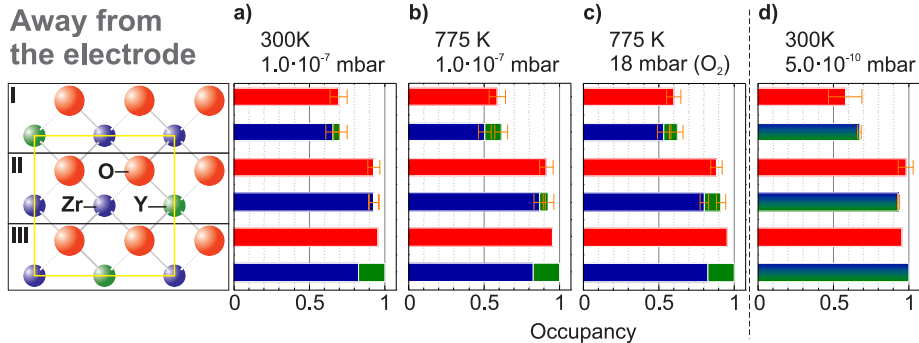| Atomic dilayer	Atom	300 K $1.0 \cdot 10^{-7}$ mbar		775 K $1.0 \cdot 10^{-7}$ mbar		775 K 18 mbar (O$_2$)		UHV prepared YSZ(100) 300 K $5.0 \cdot 10^{-10}$ mbar	
		Δ [Å]	B [Å^2]	Δ [Å]	B [Å^2]	Δ [Å]	B [Å^2]	Δ [Å]	B [Å^2]
1	O	-0.005(13)	2.29	-0.085(15)	2.29	-0.115(15)	2.29	-0.11(2)	5(3)
	Zr/Y	-0.036(4)	1.41	-0.003(4)	1.41	-0.016(4)	1.41	-0.082(3)	1.6(1)
2	O	0.002(13)	2.29	0.004(13)	2.29	0.005(14)	2.29	0.002	2.29
	Zr/Y	0.027(3)	1.41	0.008(3)	1.41	0.010(3)	1.41	0.027	1.41
3	O	0	2.29	0	2.29	0	2.29	0	2.29
	Zr/Y	0	1.41	0	1.41	0	1.41	0	1.41

Figure 1: a)-c): occupancy profiles of 3 first atomic dilayers of YSZ away from the LSC electrode, where 3rd layer represents bulk values as a reference and 1st and 2nd layers occupancies were fitted with ANA-ROD. Side view of the unit cell and first three atomic layers (I, II, III) are presented on the left, where oxygen is red, Yttrium is green and Zirconium is blue. The unit cell is marked with yellow. The colour code of the bar plots corresponds to the one for the atoms. d): occupancy profile of UHV prepared clean YSZ(100) surface. Since no anomalous diffraction data were taken, only the combined sum of the Y and Zr occupancies could be refined.
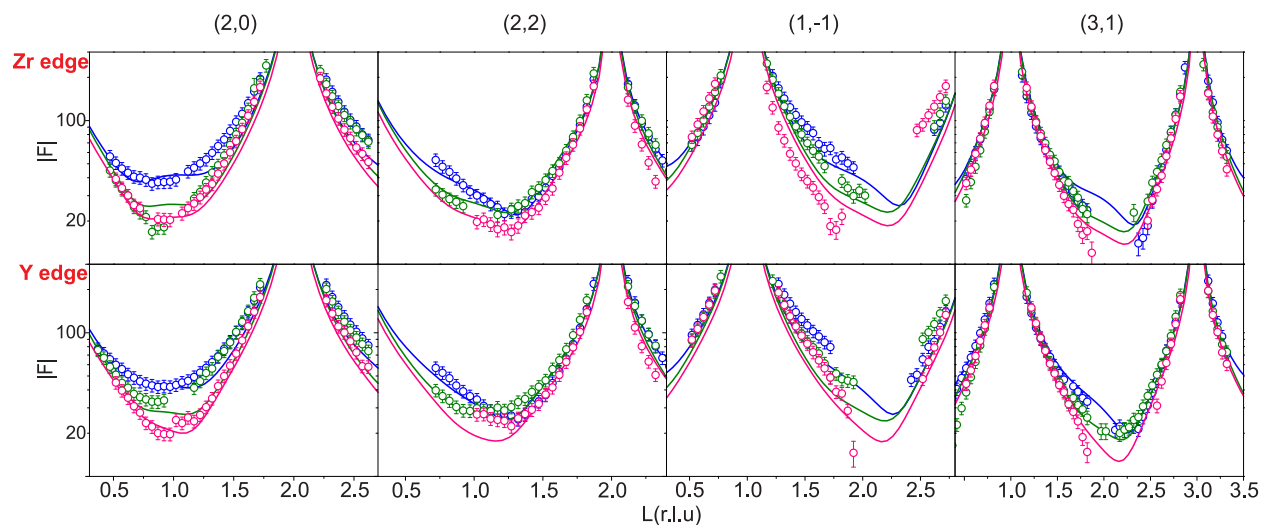
Figure 2: The CTR data and fits for 3 different conditions from free surface away from the electrode: 300 K, p=$1.0 \cdot 10^{-7}$ mbar (blue line); 775 K, p=$1.0 \cdot 10^{-7}$ mbar (pink line); 775 K, p(O_2)=18 mbar (green line). One data set consists of 8 CTRs - 4 taken at Zr K-edge, and other 4 taken at Y K-edge. All 8 CTRs taken under each particular condition are fitted simultaneously. On the (1, -1) rod the signal was cut by one of the supporting rods of the Be window.
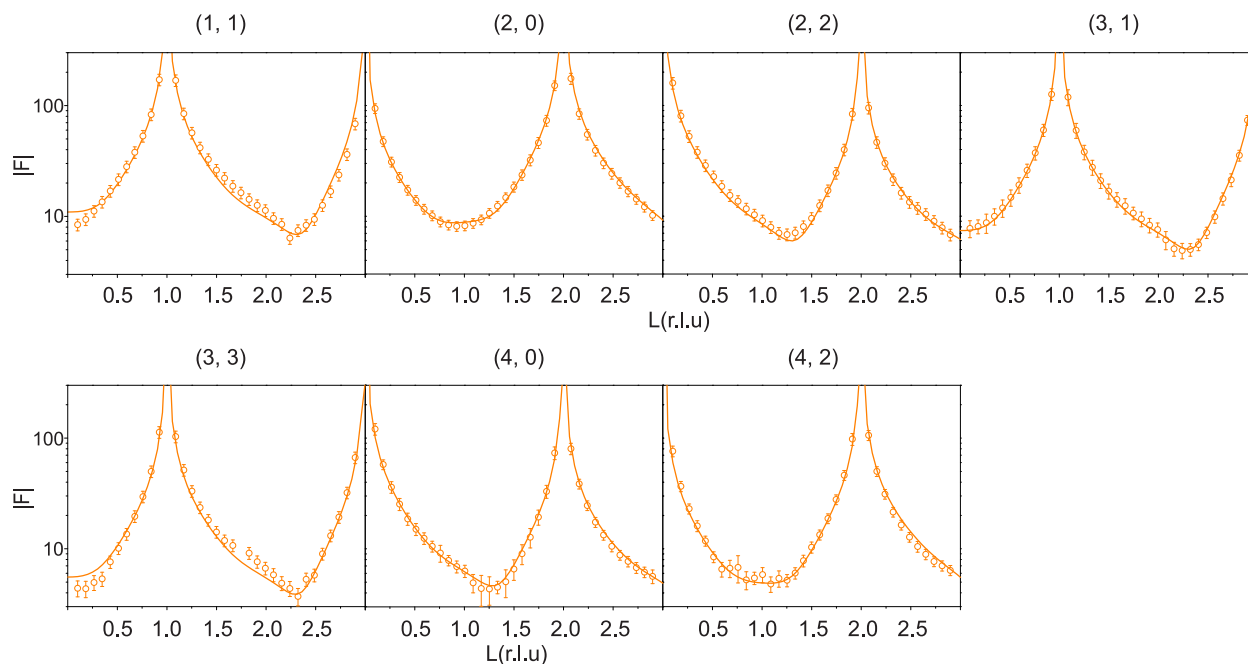

Figure 3: The CTR data and fits for the UHV prepared YSZ(100) sample taken at 300 K, p=$5.0 \cdot 10^{-10}$ mbar.
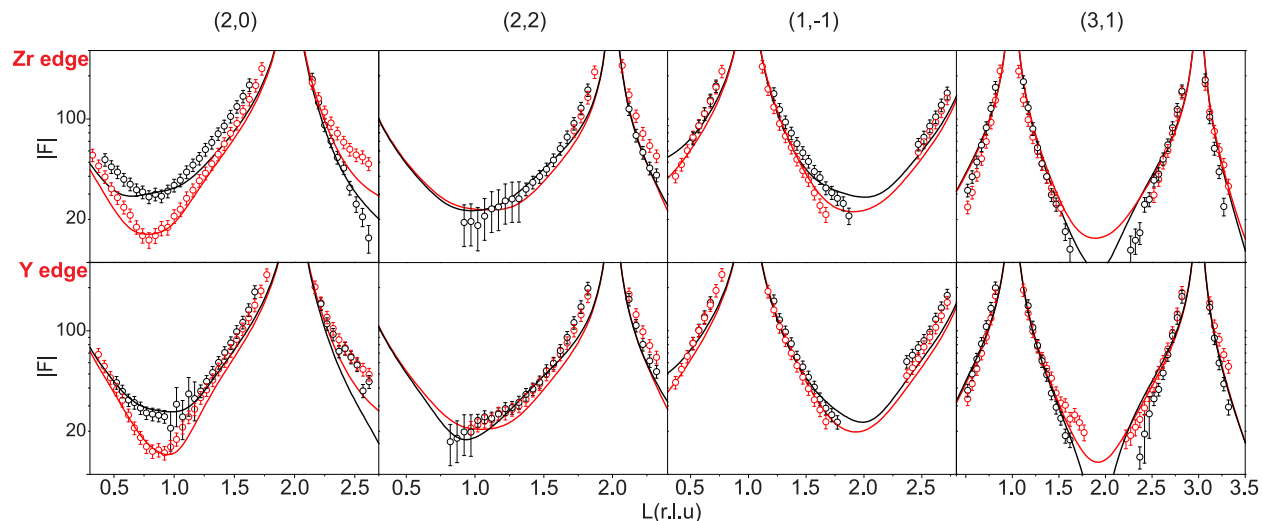
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Figure 4: The CTR data and fits for 2 different conditions from electrode/electrolyte interface: 775 K, p=$1.0 \cdot 10^{-7}$ mbar (black line), 775 K, p(O$_2$)=18 mbar, U=+250 mV (red line). One data set consists of 8 CTRs - 4 taken at Zr K-edge, and other 4 taken at Y K-edge. All 8 CTRs taken under each particular condition are fitted simultaneously. On the (1, -1) rod the signal was cut by one of the supporting rods of the Be window.

Table 2: The agreement factor for all refinement procedures computed in ANA-ROD (see ref. 12, 13).

Condition	Agreement factor, normalized χ^2		
	Below the electrode	Away from the electrode	UHV prepared YSZ(100)
T=300 K, p=$5.0 \cdot 10^{-10}$ mbar	–	–	0.6
T=300 K, p=$1.0 \cdot 10^{-7}$ mbar	4.3	2.1	
T=775 K, p=$1.0 \cdot 10^{-7}$ mbar	3.7	3.6	
T=775 K, p(O$_2$)=18 mbar	3.5	3.9	
T=775 K, p(O$_2$)=18 mbar, U=-500 mV	4.2		
T=775 K, p(O$_2$)=18 mbar, U=+250 mV	3.9		

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