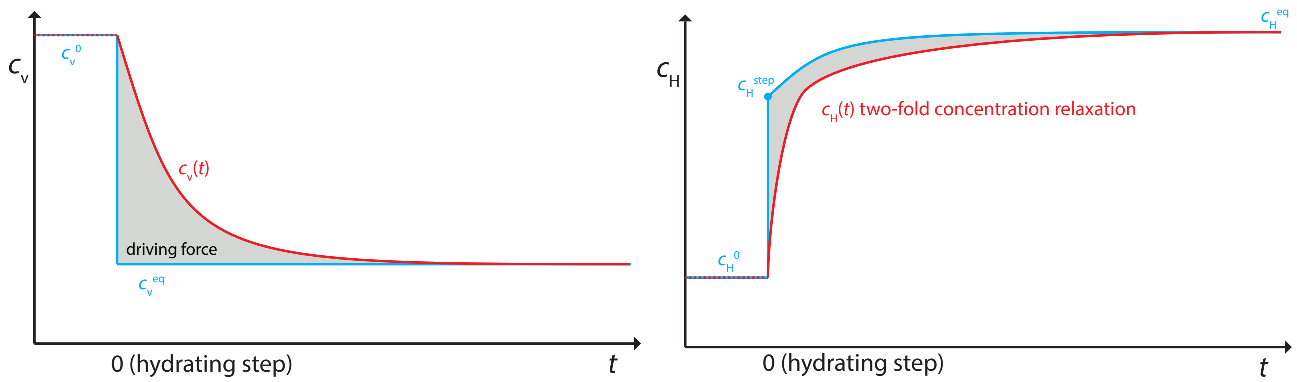
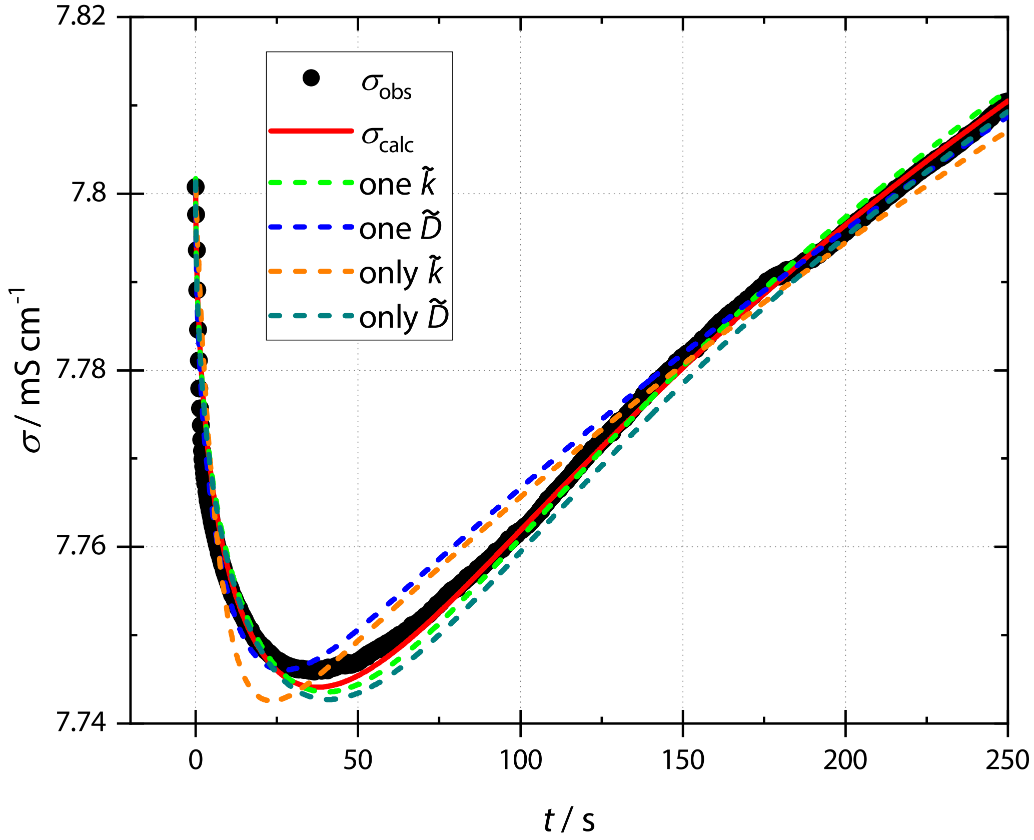
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic supplementary information (ESI)



S1 Sketch of the driving forces and concentration definitions for the simplified surface-reaction-limited case. Left: Time-dependent oxygen vacancy concentration upon hydration (red). The difference between the targeted concentration (blue) and red curve is the driving force at each time *t* (grey). The targeted concentration is always the equilibrium concentration in the simplified model with forward-reactions upon hydration only. Right: Time-dependent hydrogen concentration (red) and targeted hydrogen concentration (blue) that is also time-dependent. The driving force (grey) for the surface reaction is the difference between blue curve and red curve at each time *t*. The red curve shows a two-fold concentration relaxation for fast hydrogen and slow oxygen kinetics.



S2 Experimental ECR curve (black) and corresponding fit (red) shown in Fig. 2 in the article (first 250 s). A fit with the same model (see Appendix A) but with constraint $\tilde{k}_H^{eff} = \tilde{k}_O^{eff}$ (green) and $\tilde{D}_H^{eff} = \tilde{D}_O^{eff}$ (blue). The model giving respect to $\tilde{k}$ only (orange) shows a strong deviation and the position of the minimum cannot be fitted. The minimum of the model shown in blue (one $\tilde{D}$, two $\tilde{k}$) is also at a shorter time. The three other models use two diffusion coefficients to describe the curve. This is in agreement with Fig. 3 in the article: the fast hydrogen kinetics are at the verge to the diffusion controlled regime and $\tilde{k}_H^{eff}$ has thus not a large impact on the fit. However, best agreement with the curve (position of minimum and lowest residual) is achieved using the model with two surface reaction constants and two diffusion coefficients (red). The parameters obtained for the diffusion-limited case are $\tilde{D}_O^{eff} = 1 \times 10^{-5}$ cm^2 s^{-1} and $\tilde{D}_H^{eff} = 3 \times 10^{-4}$ cm^2 s^{-1} and for the surface-reaction-limited case $\tilde{k}_O^{eff} = 2 \times 10^{-4}$ cm s^{-1} and $\tilde{k}_H^{eff} = 2 \times 10^{-2}$ cm s^{-1}.