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Supporting Information

from "Transport properties and oxidation and hydration kinetics of Mo doped Nd_{5.5}WO_{11.25-δ}" by M. Ruf, C. Solís, S. Escolástico, R. Dittmeyer and J. M. Serra*

Supporting Figure S1: Thermogravimetric analysis under N_2 (black line) and air (red line) flow of Nd_{5.5}WO_{11.25- δ} shows no mass loss up to 1000 °C.



Supporting Figure S2: (a) Comparison of *k* and (b) *D* coefficients of $V_0^{\bullet\bullet}$ obtained upon oxidation and reduction (O₂-Air) with those obtained from hydration and dehydration (O₂-O₂+H₂O) as a function of inverse temperature.



Supporting Figure S3: (a) *k* and (b) *D* coefficients of both $V_0^{"}$ and protons upon hydration and dehydration, at 700 °C when changing from oxygen saturated at different $p(H_2O)$

The data used for pH_2O is the average pH_2O value in each relaxation step. In this case the increments and the overall pH_2O range are very small, especially when compared with the large range considered in the pO_2 study. In the whole studied pH_2O range, diffusion of protons, $D_{H,hyd}/D_{H,dehyd}$, is always faster than for oxygen ions, $D_{Vo,hyd}/D_{Vo,dehyd}$.¹

The parameters related to O^{-2} charge carrier ($k_{Vo,hyd}$, $k_{Vo,dehyd}$, $D_{Vo,hyd}$ and $D_{Vo,dehyd}$) exhibit a slight upward trend with increasing pH_2O . For the exchange reaction rate constant this trend can be a logical consequence of the higher H₂O surface coverage, which is proportional to pH_2O .

 $D_{Vo,hyd}$ and $D_{Vo,dehyd}$ are independent of p(H₂O) because of the obviously greater influence of $p(O_2)$ that was kept nearly constant with a changing p(H₂O) and mainly determines the oxygen vacancy concentration, as in reported perovskites^{2, 3} For hydrogen diffusion an increase is expected with increasing $p(H_2O)$.² In contrast, $D_{H,hyd}/D_{H,dehyd}$ for NWM do not show any correlation with $p(H_2O)$, but this can be explained by the narrow window of $p(H_2O)$ applied, as was observed for some perovkites in similar ranges of $p(H_2O)$.^{1,4}



Supporting Figure S4: Image of the impedance spectra of the bar sample in dry air (black symbols) and in moist oxygen (red symbols) at 700 °C.



Impedance spectra correspond to a pure resistive material with some capacitance and inductance components due to the experimental set up at high frequencies (> 10 kHz). Blue arrows and lines indicate the chosen measuring conditions at 100 Hz where $\phi=0^{\circ}$ and no capacitance contributions are taken into account.

References

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