Electronic Supplementary Information

Proton Conductivity in Mixed-Conducting BSFZ Perovskite from Thermogravimetric Relaxation

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(1) Impedance spectrum of a BSFZ pellet

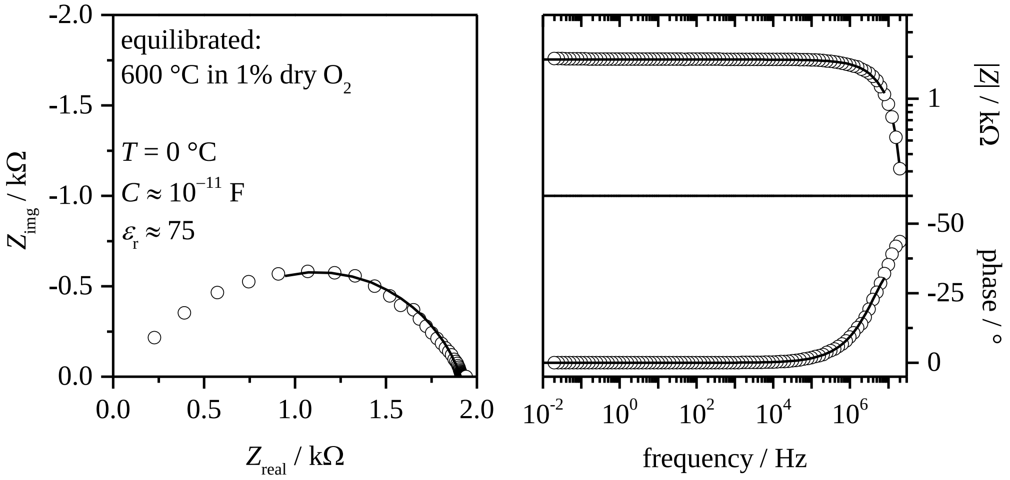

Fig. S1: Impedance spectrum of a BSFZ pellet measured at 0 °C temperature. The pellet was equilibrated at 600 °C in 1% O_2 and cooled to room temperature in 1% O_2 within ≈ 10 min. The line represents the fit with the equivalent circuit described in the text.

While a BSFZ pellet (thickness 0.1 cm, area 0.16 cm^2, Ag paste electrodes fired at 600 °C) annealed in air at 600 °C and cooled to 25 °C within a few minutes shows an electronic conductivity which is in good agreement with literature,[1] the bulk semicircle largely appears at frequencies higher than the measurement range (frequency of the highest point: $\omega = (RC)^{-1}$). Therefore, the pellet was annealed in 1% O_2 at 600 °C (to decrease the p-type electronic conductivity) and measured at 0 °C (decreasing the thermally activated electronic conductivity [1] by decreasing T). Fig. S1 shows the impedance spectrum measured with a Novocontrol Alpha A impedance analyzer. The spectrum shows a single semicircle, the capacitance of which corresponds to a dielectric constant of $\varepsilon_r \approx 75$ which is in the range of typical bulk ε_r values for perovskites. The semicircle was fitted with one resistance R and one constant phase element Q in parallel (shape parameter $p = 0.8$; note that the O stoichiometry within the pellet is slightly inhomogeneous owing to the cooling procedure) and a series connected $L = 3 \cdot 10^{-6}$ H to account for the inductive effects of cables/wiring. The capacitance was calculated from $C = (R^{1-p}Q)^{1/p}$.[2] The absence of a low-frequency semicircle with high capacitance (typical grain boundary capacitances are > 1000 C_{bulk}) proves that the grain boundaries are not blocking for holes. In cases where perovskites such as slightly Fe-doped $SrTiO_3$ exhibit blocking grain boundaries, this was found to be due to depletion of positive defects in space charge zones.[3-5] Thus, when no significant hole depletion is found for BSFZ, this indicates that also other positive defects such as $\mathrm{OH}_\mathrm{O}^{\bullet}$ and $\mathrm{V}_\mathrm{O}^{\bullet\bullet}$ should not be blocked at the grain boundaries.

(2) Error bars

The resolution of the Netzsch STA 449C thermobalance is 1 microgram. The baseline stability at elevated T and flowing gas (e.g. from the initial segment in fig. 2) is ±2 µg over 8 h. Reproducibility of weights is ±2 µg for several repetitions, and accuracy of absolute weights is better than $7 \cdot 10^{-5}$ relative to a calibrated lab balance. Thus, measured weight changes after $p\mathrm{H_2O}$, $p\mathrm{O_2}$ steps are rounded to microgram (rounding to tens of microgram potentially induces artificial inaccuracy).

Error bars are given for all extracted quantities. They correspond to three times the standard deviation of the respective individual measurements (iodometric titration for absolute δ, Δm from individual $p\mathrm{H_2O}$, $p\mathrm{O_2}$ changes for K_ox and K_hydrat, diffusion coefficients from four individual $p\mathrm{H_2O}$ jumps per temperature, error propagation from K_ox and K_hydrat to defect concentrations, and from D and concentrations to proton conductivity). These error bars are larger than the error which corresponds to rounding Δm values to 1 µg.

(3) Numerical calculation of defect concentrations

As mentioned in the main paper, K_hydrat and thus $[\mathrm{OH_O^\bullet}]$ at given $p\mathrm{H_2O}$, $p\mathrm{O_2}$ and T can be determined from the weight changes under the reasonable assumption that the activity coefficients implicitly used in extracting K_ox from isobars in dry $p\mathrm{O_2}$ do not change upon water incorporation. To analyze the thermodynamics the equilibrated states before and after $p\mathrm{H_2O}$ change (e.g. state 1 and 2 in Fig. 1 of the main paper) are considered. For the sake of simplicity the following definitions are used:

$$[\mathrm{OH_O^\bullet}] = c; \quad [\mathrm{V_O^{\bullet\bullet}}] = \delta; \quad [\mathrm{h^\bullet}] = p \tag{S1}$$

The concentration of the regular oxygen atoms can be calculated by

$$[\mathrm{O_O^\times}] = 3 - \delta - c \tag{S2}$$

The concentration of holes (formally corresponding to $\mathrm{Fe^{4+}}$ oxidation state) can be calculated from the electroneutrality condition:

$$\begin{gathered}[\mathrm{Ba'_A}] + [\mathrm{Sr'_A}] + [\mathrm{Zn'_{Fe}}] = 2\delta + c + p \\ p = 1.2 - 2\delta - c\end{gathered} \tag{S3}$$

K_ox can be calculated from the δ values obtained by isobaric measurements in dry $p\mathrm{O_2}$ (c = 0).

$$K_\mathrm{ox} = \frac{(3-\delta)(1.2-2\delta)^2}{p_{\mathrm{O_2}}^{1/2}\,\delta} \tag{S4}$$

Then, K_ox and K_hydrat are written for the two thermodynamically equilibrated states of the sample with the corresponding concentrations at state 1 (index 1) and 2 (index 2).

$$\begin{aligned} K_\mathrm{hydrat} &= \frac{c_1^2}{p_{\mathrm{H_2O},1}(3-\delta_1-c_1)\delta_1} \\ K_\mathrm{ox} &= \frac{(3-\delta_1-c_1)(1.2-2\delta_1-c_1)^2}{p_{\mathrm{O_2}}^{1/2}\,\delta_1} \\ K_\mathrm{hydrat} &= \frac{c_2^2}{p_{\mathrm{H_2O},2}(3-\delta_2-c_2)\delta_2} \\ K_\mathrm{ox} &= \frac{(3-\delta_2-c_2)(1.2-2\delta_2-c_2)^2}{p_{\mathrm{O_2}}^{1/2}\,\delta_2} \end{aligned} \tag{S5}$$

All unknowns are colored in red. As we have five unknowns but only four equations a fifth condition is necessary. This equation comes from the final mass change after changing $p\mathrm{H_2O}$ or $p\mathrm{D_2O}$ which is

$$\Delta m_{\infty 1,2} = n_{\mathrm{BSFZ}}[(c_2 - c_1)M_{\mathrm{H\ or\ D}} + (\delta_1 - \delta_2)M_{\mathrm{O}}] \qquad \text{(S6)}$$

with n_{BSFZ} mol of BSFZ and M molar weight of H, D and O. This means that the absolute proton concentration is obtained from the fit under the supposition that the increase of $[\mathrm{OH}_\mathrm{O}^\bullet]$ follows the $p\mathrm{H_2O}$-dependence as given by the defect model based on K_{ox} and K_{hydrat} (assuming that changes in the activity coefficients are negligible). The resulting set of five equations with five unknowns can be solved numerically using MatLab (fsolve function):

```
function F = Kccdd(x,k)
MHD = 1; %Set either to 1 (H) or 2 (D)
aO2 = k(1)/1000;
aH2O1 = k(2)/1000;
aH2O2 = k(3)/1000;
Kox = k(4);
nBSFZ = k(5); %mmol
dm = k(6); %mg
c1 = x(1);
c2 = x(2);
d1 = x(3);
d2 = x(4);
Khydrat = x(5);
F = [(c1^2)/(aH2O1*d1*(3-d1-c1))-Khydrat;
     (c2^2)/(aH2O2*d2*(3-d2-c2))-Khydrat;
     ((3-d1-c1)*(1.2-2*d1-c1)^2)/(sqrt(aO2)*d1)-Kox;
     ((3-d2-c2)*(1.2-2*d2-c2)^2)/(sqrt(aO2)*d2)-Kox;
     (nBSFZ*((c2-c1)*MHD+(d1-d2)*16))-dm];
end
```

The first jump at 400 °C in Fig. 1 of the main paper is given as an example:

$$\Delta m_{\infty 1,2} = 0.206\ \mathrm{mg};\ \ p_{\mathrm{H_2O},1} = 5.70\ \mathrm{mbar};\ \ p_{\mathrm{H_2O},2} = 9.83\ \mathrm{mbar};$$

$$K_{\mathrm{ox}} = 2.71;\ \ n_{\mathrm{BSFZ}} = 17.9\ \mathrm{mmol}$$

The set of equations is solved with

```
fsolve(@(x)Kccdd(x,[10;5.70;9.83;2.71;17.9;0.206]),
            [0.005;0.01;0.5;0.498;0.1]);
```

resulting in

$$c_1 = 0.00443;\ c_2 = 0.00581;\ \delta_1 = 0.48358;\ \delta_2 = 0.48295;\ K_{\mathrm{hydrat}} = 0.00283.$$

Although this is not the only solution (note that the set of eq. (S5) is nonlinear), other solutions obtained by changing the start parameters are meaningless as they are either outside physically reasonable values (δ much higher than in dry atmosphere, c much higher than obtained values from Karl-Fischer titration, negative values) or the condition $\delta_1 \geq \delta_2$ is not fulfilled. Hence, the solution above is the only reasonable one.

An example of error propagation for the fraction of protons incorporated by redox reaction is given here: c_1, c_2, δ_1, δ_2, K_{hydrat} and redox fraction z = $(c_2\text{-}c_1)\text{-}2(\delta_1\text{-}\delta_2)$ are calculated for

Δm = 206 µg and K_{ox}=2.71 as above, and compared with results for Δm larger or smaller by 5 µg (realistic estimate) or 10 µg (pessimistic estimate):

Δm/µg	c_1	c_2	δ_1	δ_2	K_{hydrat}	z
206	0.00443	0.00581	0.48358	0.48295	0.00283	0.00012
201	0.00432	0.00557	0.48363	0.48302	0.00269	0.00011
211	0.00453	0.00595	0.48353	0.48289	0.00297	0.00012
196	0.00421	0.00552	0.48368	0.48308	0.00256	0.00011
216	0.00464	0.00609	0.48348	0.48282	0.00311	0.00012

While c_1, c_2, δ_1, δ_2 values vary in the fourth digit after decimal point, the redox fraction which is the difference of (c_2-c_1) and 2(δ_1-δ_2) varies only in the fifth digit. This example shows that the finding of a small but nonzero redox fraction is robust against the realistically estimated uncertainty of 5 microgram and even a pessimistic estimate of 10 microgram in the input weight change (cf. also hole concentration change in fig. 6 which - including its error range - always remains in the negative).

(4) Effects of proton trapping

The attractive interaction of protonic carriers with other defects can (formally) be described by a trapping reaction with trap T according to

$$\mathrm{OH}_{\mathrm{O}}^{\bullet} + \mathrm{T} \rightleftharpoons (\mathrm{OH}_{\mathrm{O}}^{\bullet}\mathrm{T}) \quad \text{with} \quad K_T = \frac{[(\mathrm{OH}_{\mathrm{O}}^{\bullet}\mathrm{T})]}{[\mathrm{OH}_{\mathrm{O}}^{\bullet}][\mathrm{T}]} \tag{S7}$$

(the driving force for this reaction can be any defect interaction, e.g. electrostatic (in case of a negatively charged trap such as an acceptor dopant) but also of other origin (cf. ref. [6]) - thus it is not necessarily a charged trap). This trapping reaction will affect the hydrogen uptake reactions (eq. (1) and (3)) as well as the chemical diffusion coefficients $D^{\delta}_{\mathrm{H_2O}}$ and D^{δ}_{H}. In a recent publication, significant proton trapping was observed in the proton-conducting perovskite $\mathrm{BaZr_{0.8}Y_{0.2}O_{3-\delta}}$ over an extended temperature range from the combination of thermogravimetry, ac impedance and nuclear magnetic resonance, and an association enthalpy of -29 kJ/mol determined.[7] Thus, some association between protons and other defects may well appear also in the present BSFZ samples.

(4a) Effect on water / hydrogen uptake, exemplified for reaction (1)

For simplicity let us assume that water uptake occurs exclusively by reaction (1) (this assumption is realistic for BSFZ under the conditions applied here as Fig. 5 shows - the amount of hydrogen uptake at expense of holes according to reaction (3) is much smaller than by hydration of $[\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}]$). Let us further assume that the concentration of free traps is constant (i.e. the total proton concentration small compared to the trap concentration, again supported by the low proton content of BSFZ) and also the concentration changes of regular oxide ions and $\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$ are negligible relative to the proton concentration changes (while this is fulfilled for $p\mathrm{H_2O}$ changes at a given temperature, a temperature change will lead to moderate variations (cf. fig. 2) which in the full defect model is accounted for by reaction (2)). Please note that the key conclusions remain valid also without these assumptions, but the mathematical expressions become more involved. Then we can write with redefined mass action constants

$$K'_{\mathrm{hydrat}} = \frac{[\mathrm{OH}_\mathrm{O}^\bullet]^2}{p_{\mathrm{H_2O}}} \tag{S8}$$

$$K'_{\mathrm{T}} = \frac{[(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]}{[\mathrm{OH}_\mathrm{O}^\bullet]} \tag{S9}$$

with $[(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]$ denoting the concentration of trapped protons. The total proton concentration $[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge$ (conservative ensemble) as measured from TG amounts to

$$[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge = [\mathrm{OH}_\mathrm{O}^\bullet] + [(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})] = (1+K'_\mathrm{T})\sqrt{K'_{\mathrm{hydrat}}\,p\mathrm{H_2O}} \tag{S10}$$

Plotting an effective hydration mass action constant K''_{hydrat}

$$K''_{\mathrm{hydrat}} = \frac{[\mathrm{OH}_\mathrm{O}^\bullet]^{\blacklozenge 2}}{p\mathrm{H_2O}} = (1+K'_\mathrm{T})^2 K'_{\mathrm{hydrat}} \tag{S11}$$

calculated from measured $[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge$ versus reciprocal temperature will result in a slope determined by $\Delta H^0 = \Delta_{\mathrm{hydrat}}H^0$ for the case of small trapping ($K''_{\mathrm{hydrat}} \approx K'_{\mathrm{hydrat}}$), and a steeper slope determined by $\Delta H^0 = \Delta_{\mathrm{hydrat}}H^0 + 2\,\Delta_{\mathrm{trap}}H^0$ for the case of strong trapping ($K''_{\mathrm{hydrat}} \approx (1+K'_\mathrm{T})^2 K'_{\mathrm{hydrat}}$). The decrease of the slope for the hydration mass action constant in Fig. 3 at the highest temperatures (where the relative importance of the trapping reaction decreases) may be caused by this effect.

(4b) Effect on the chemical diffusion coefficient, exemplified for $D^\delta_{\mathrm{H_2O}}$:

In the presence of the trapping reaction (S7), instead of eq. (4) the chemical diffusion coefficient for water has to read (cf. refs. [8-10])

$$D^\delta_{\mathrm{H_2O}} = \frac{V_\mathrm{m}}{4F^2}\,\frac{\sigma^\blacklozenge_{\mathrm{OH}_\mathrm{O}^\bullet}\,\sigma_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}}{\sigma^\blacklozenge_{\mathrm{OH}_\mathrm{O}^\bullet} + \sigma_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}}\,\frac{\partial\mu_{\mathrm{H_2O}}}{\partial c_{\mathrm{H_2O}}} \tag{S12}$$

where $\sigma^\blacklozenge_{\mathrm{OH}_\mathrm{O}^\bullet} = \sigma_{\mathrm{OH}_\mathrm{O}^\bullet} + \sigma_{(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})}$ is the sum of the conductivity contributions from free and trapped protons, $\partial c_{\mathrm{H_2O}} = -\partial c_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}} = 0.5(\partial c_{\mathrm{OH}_\mathrm{O}^\bullet} + \partial c_{(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})}) = 0.5\partial c^\blacklozenge_{\mathrm{OH}_\mathrm{O}^\bullet}$ with $c^\blacklozenge_{\mathrm{OH}_\mathrm{O}^\bullet}$ denoting the sum of free and trapped protons, and $\partial\mu_{\mathrm{H_2O}} = 2\partial\mu_{\mathrm{OH}_\mathrm{O}^\bullet} - \partial\mu_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}$. Thus

$$\frac{\partial\mu_{\mathrm{H_2O}}}{\partial c_{\mathrm{H_2O}}} = 4\frac{\partial\mu_{\mathrm{OH}_\mathrm{O}^\bullet}}{\partial[\mathrm{OH}_\mathrm{O}^\bullet]}\,\frac{\delta[\mathrm{OH}_\mathrm{O}^\bullet]}{\delta[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge} + \frac{\partial\mu_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}}{\partial c_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}} = \frac{4RT}{[\mathrm{OH}_\mathrm{O}^\bullet]}\,\frac{\delta[\mathrm{OH}_\mathrm{O}^\bullet]}{\delta[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge} + \frac{RT}{[\mathrm{V}_\mathrm{O}^{\bullet\bullet}]} \tag{S13}$$

where an additional differential defect fraction $\chi_{\mathrm{OH}_\mathrm{O}^\bullet} \equiv \delta[\mathrm{OH}_\mathrm{O}^\bullet]/\delta[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge$ appears (eq. (S13) assumes absence of trapping for $\mathrm{V}_\mathrm{O}^{\bullet\bullet}$). For obtaining the variation of free proton concentration with total proton concentration, the trapping mass action constant K_T (eq. (S7), with $[\mathrm{T}]_{tot} = [(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]+[\mathrm{T}]$) has to be inserted, yielding

$$\begin{aligned}\chi_{\mathrm{OH}_\mathrm{O}^\bullet}{}^{-1} &= \left(\frac{\delta[\mathrm{OH}_\mathrm{O}^\bullet]}{\delta[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge}\right)^{-1} = 1+\frac{\delta[(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]}{\delta[\mathrm{OH}_\mathrm{O}^\bullet]} = 1+\frac{K_\mathrm{T}[\mathrm{T}]_{tot}}{(1+K_\mathrm{T}[\mathrm{OH}_\mathrm{O}^\bullet])^2} \\ &= \frac{[\mathrm{T}]_{tot}+K_\mathrm{T}([\mathrm{T}]_{tot}-[(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})])^2}{[\mathrm{T}]_{tot}}\end{aligned} \tag{S14}$$

For $[\mathrm{T}]_{tot} \approx [\mathrm{T}]$ (i.e. trap concentration >> proton concentration) it follows that

$$\frac{\partial \mu_{\mathrm{H_2O}}}{\partial c_{\mathrm{H_2O}}} = \frac{1}{1+K_\mathrm{T}[\mathrm{T}]_{tot}}\frac{4RT}{[\mathrm{OH}_\mathrm{O}^\bullet]}+\frac{RT}{[\mathrm{V}_\mathrm{O}^{\bullet\bullet}]} \tag{S15}$$

and thus

$$D_{\mathrm{H_2O}}^{\delta} = \frac{RTV_\mathrm{m}}{4F^2}\frac{\sigma_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}\sigma_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}}{\sigma_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}+\sigma_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}}\left(\frac{1}{1+K_\mathrm{T}[\mathrm{T}]_{tot}}\frac{4}{[\mathrm{OH}_\mathrm{O}^\bullet]}+\frac{1}{[\mathrm{V}_\mathrm{O}^{\bullet\bullet}]}\right) \tag{S16}$$

Assuming strong trapping (typically at low temperatures) $K_\mathrm{T}[\mathrm{T}]_{tot} >> 1$ and inserting $K_\mathrm{T}[\mathrm{T}]_{tot}[\mathrm{OH}_\mathrm{O}^\bullet] = [(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]$ this results in

$$D_{\mathrm{H_2O}}^{\delta} = \frac{RTV_\mathrm{m}}{4F^2}\frac{\sigma_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}\sigma_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}}{\sigma_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}+\sigma_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}}\left(\frac{4}{[(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]}+\frac{1}{[\mathrm{V}_\mathrm{O}^{\bullet\bullet}]}\right) \tag{S17}$$

The quantity $\sigma_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}$ contains contributions from the diffusivity of the trapped species itself which we can ignore (the trap is most probably an immobile acceptor dopant), hence $\sigma_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge} = \sigma_{\mathrm{OH}_\mathrm{O}^\bullet} = \dfrac{F^2 D_{\mathrm{OH}_\mathrm{O}^\bullet}[\mathrm{OH}_\mathrm{O}^\bullet]}{RTV_\mathrm{m}}$. Nonetheless it is convenient to relate $\sigma_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}$ to an effective proton diffusivity $D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}$. For strong trapping $[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge \approx [(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]$, hence it formally follows that

$$\sigma_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge} = \frac{F^2 D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge}{RTV_\mathrm{m}} \approx \frac{F^2 D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}[(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]}{RTV_\mathrm{m}} \tag{S18}$$

Note that because of $D_{\mathrm{OH}_\mathrm{O}^\bullet}[\mathrm{OH}_\mathrm{O}^\bullet] = D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge$ it follows that $D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge} = D_{\mathrm{OH}_\mathrm{O}^\bullet}[\mathrm{OH}_\mathrm{O}^\bullet]/[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge \approx D_{\mathrm{OH}_\mathrm{O}^\bullet}[\mathrm{OH}_\mathrm{O}^\bullet]/[(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})] << D_{\mathrm{OH}_\mathrm{O}^\bullet}$. Inserting (S18) together with $X = \dfrac{[\mathrm{OH}_\mathrm{O}^\bullet]^\blacklozenge}{2[\mathrm{V}_\mathrm{O}^{\bullet\bullet}]_{(p_{\mathrm{H_2O}}=0)}} \approx \dfrac{[(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]}{2[\mathrm{V}_\mathrm{O}^{\bullet\bullet}]_{(p_{\mathrm{H_2O}}=0)}}$ and $[\mathrm{V}_\mathrm{O}^{\bullet\bullet}] = (1-X)[\mathrm{V}_\mathrm{O}^{\bullet\bullet}]_{(p_{\mathrm{H_2O}}=0)}$ into (S17) yields

$$D_{\mathrm{H_2O}}^{\delta} = \frac{(2-X)D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}D_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}}{XD_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}+2(1-X)D_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}} \tag{S19}$$

which is isomorphic to eq. (4), with the proton diffusivity being now replaced by an effective diffusivity $D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}$. $D_{\mathrm{H_2O}}^{\delta}$ lies between the diffusion coefficient of the oxygen vacancy $D_{\mathrm{V}_\mathrm{O}^{\bullet\bullet}}$ and the effective proton diffusivity $D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}$, depending on the degree of hydration. Yet, note that $D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge} = D_{\mathrm{OH}_\mathrm{O}^\bullet}[\mathrm{OH}_\mathrm{O}^\bullet]/[(\mathrm{OH}_\mathrm{O}^\bullet\mathrm{T})]$. Thus in case of strong trapping, the activation energy of $D_{\mathrm{OH}_\mathrm{O}^\bullet}^{\blacklozenge}$ will be higher than the migration energy of the free protons. At high temperatures the effect of trapping decreases, and eq. (4) becomes relevant which contains only $D_{\mathrm{OH}_\mathrm{O}^\bullet}$ (activation energy = free proton migration energy). This can be one reason for the decreasing slope in Fig. 9 with increasing temperature.

(4c) Effect on proton conductivity as calculated from eq. (6):

Inserting the effective proton diffusivity $D^{\blacklozenge}_{\mathrm{OH_O^\bullet}}$ (with $D^{\blacklozenge}_{\mathrm{OH_O^\bullet}} \approx D^{\delta}_{\mathrm{H_2O}}$ for low degrees of hydration) and the total proton concentration $[\mathrm{OH_O^\bullet}]^*$ into the Nernst-Einstein equation (cf. eq. (S18)) results in an effective proton conductivity $\sigma^{\blacklozenge}_{\mathrm{OH_O^\bullet}}$, which would be directly measured (if not covered by the higher electronic conductivity). This is valid irrespective of the trapping effect. The conductivity always originates from the free protons (the acceptors acting as traps are immobile). For strong trapping the fraction of free protons is determined by the trapping equilibrium eq. (S9) leading to an increased activation energy.

For higher degrees of hydration the protonic conductivity would be underestimated in the present analysis as the measured $D^{\delta}_{\mathrm{H_2O}}$ is lower than the effective proton diffusion coefficient $D^{\blacklozenge}_{\mathrm{OH_O^\bullet}}$. Nevertheless, when we argue whether this conductivity is high enough to enable the bulk path for the oxygen reduction reaction, we are on the safe side with eq. (S21) as we never overestimate the protonic conductivity. This is one reason for the “greater-than-or-equal-to” sign in eq. (S21) and (6) in the main paper.

$$\sigma^{\blacklozenge}_{\mathrm{OH_O^\bullet}} \geq \frac{F^2 D^{\delta}_{\mathrm{H_2O}}[\mathrm{OH_O^\bullet}]^{\blacklozenge}}{RTV_{\mathrm{m}}} \tag{S21}$$

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