Enhanced proton uptake in triple-conducting $Ba_ySr_{1-y}(Fe_{0.75}Mo_{0.25})_{1-2x}Zr_xZn_xO_{3-\delta}$ perovskites

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Table S1. Sintering conditions for all $Ba_ySr_{1-y}(Fe_{0.75}Mo_{0.25})_{1-2x}Zr_xZn_xO_{3-\delta}$ compositions. The samples marked with italics were prepared according to a different methodology: The precursors were mixed in a vibrating mill and then subjected to a 3-stage calcination in a powder form, with a final temperature of 1150 °C. to be isostatically pelletized at a pressure of 200 t.

		Ba content				
		0	**0.25**	**0.5**	**0.75**	**1**
Zn and Zr content	**0**	1200 °C air	1200 °C air	1150 °C air	1150 °C air	1200 °C air
	0.05	1200 °C air		*1200 °C* *N_2*		1200 °C air
	0.1	1200 °C air	1200 °C air	1200 °C air	1200 °C N_2	1200 °C N_2
	0.15	1200 °C air		*1200 °C* *air*		1250 °C N_2
	0.2	1200 °C air	1200 °C air	*1200 °C* *air*	*1150 °C* *N_2*	*1150 °C* *N_2*

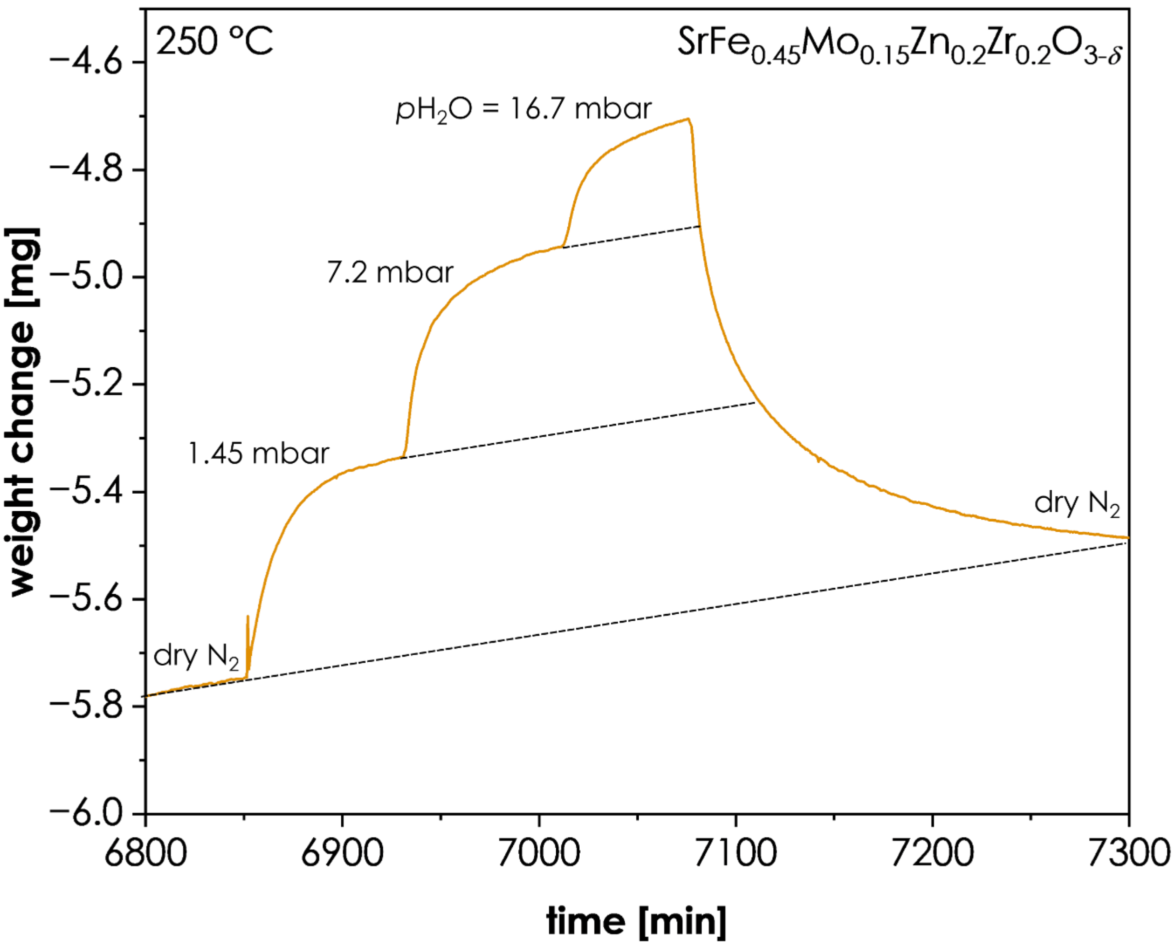

Fig. S1. Weight changes of $SrFe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$ at 250 °C in dry conditions and in three different pH_2O: 1.45, 7.2 and 16.7 mbar.

The samples were quenched from 700 °C in N_2 (with a residual O_2 content of approximately 100 ppm in the TG setup). As a result, at lower temperatures the oxygen stoichiometry is not at equilibrium and there remains a thermodynamic driving force for oxygen incorporation into the lattice. However, due to the combined effect of low temperature and low pO_2, the kinetics of this oxidation process are slow. Although not negligible, this results in an approximately linear increase in sample mass over time. A similar slope is observed across plateaus at different pH_2O values, as now indicated by dashed lines in Fig. S1. Water uptake upon changes in pH_2O is therefore evaluated relative to this baseline.

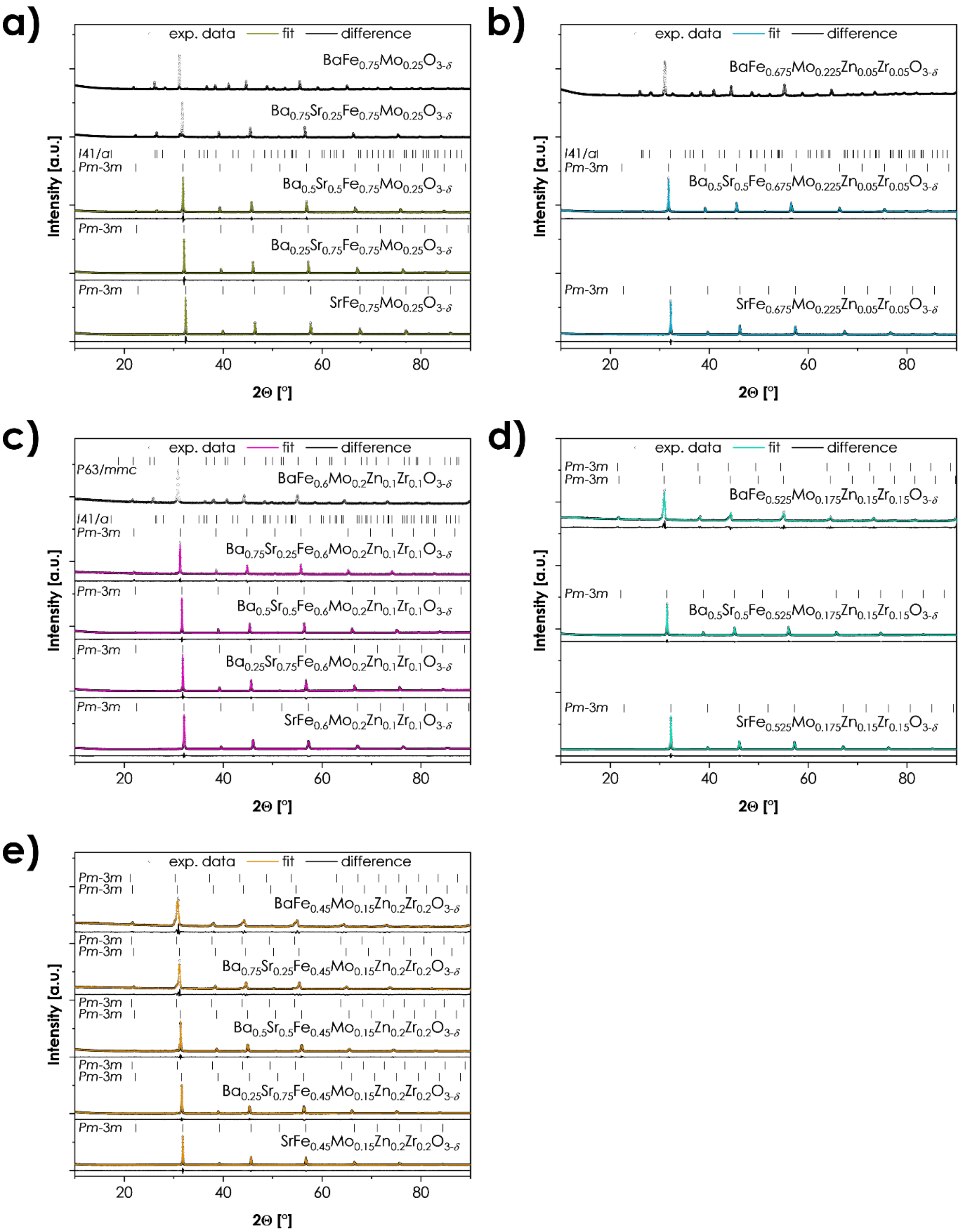

Fig. S2. X-ray diffractograms for $Ba_ySr_{1-y}(Fe_{0.75}Mo_{0.25})_{1-2x}Zr_xZn_xO_{3-\delta}$ compositions measured before TG measurements.

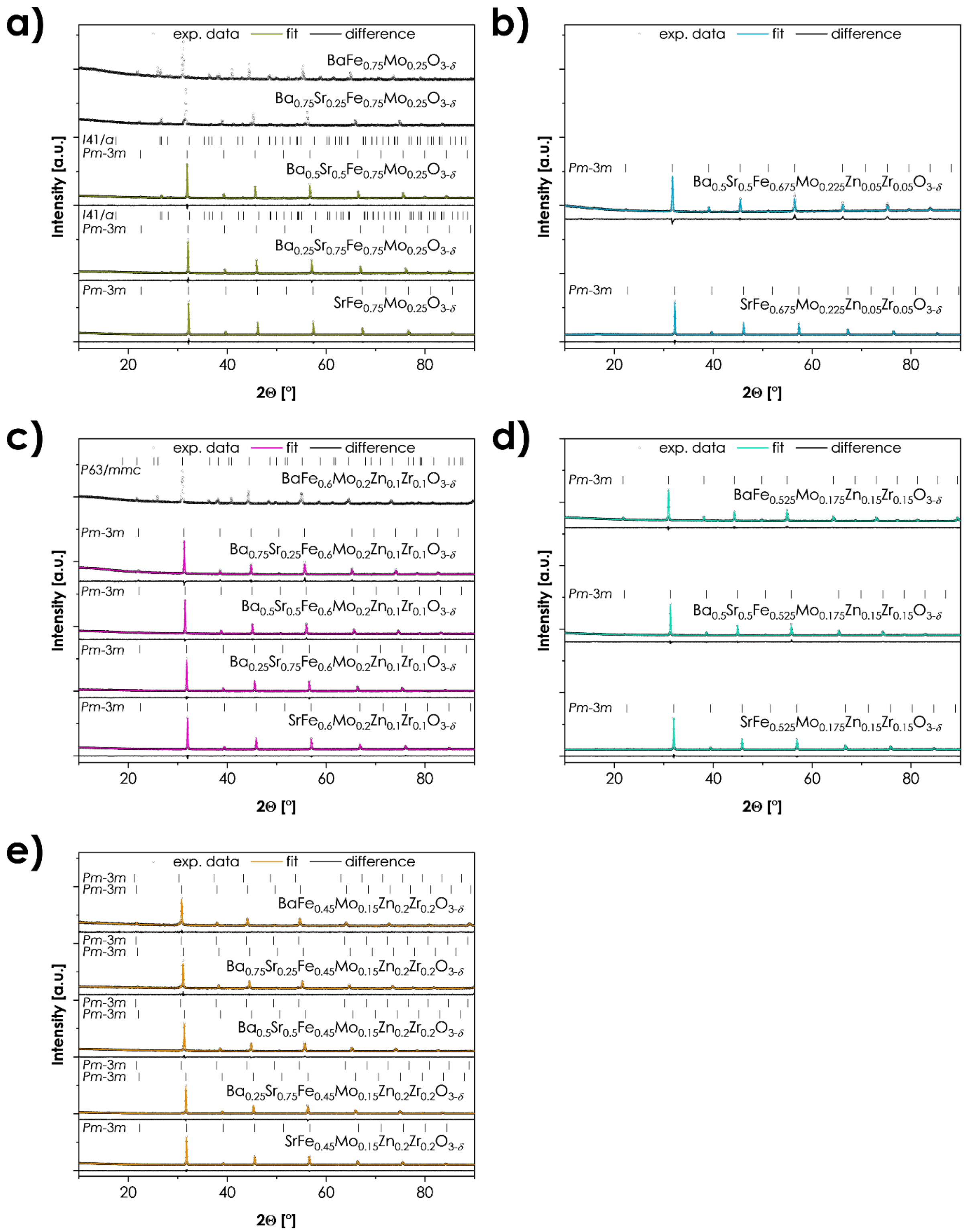

Fig. S3. X-ray diffractograms for $Ba_ySr_{1-y}(Fe_{0.75}Mo_{0.25})_{1-2x}Zr_xZn_xO_{3-\delta}$ compositions measured after TG measurements.

Table S2. The results of Rietveld refinement for $Ba_ySr_{1-y}(Fe_{0.75}Mo_{0.25})_{1-2x}Zn_xZr_xO_{3-\delta}$ ($x \leq 0.2$; $y \leq 1$) samples (before TG measurements).

Composition	Space group	Content [wt. %]	*a* [Å]	*c* [Å]	GoF [-]	Rwp [%]
$SrFe_{0.75}Mo_{0.25}O_{3-\delta}$	*Pm*-3*m*	100	3.9188(1)		1.29	3.34
$Ba_{0.25}Sr_{0.75}Fe_{0.75}Mo_{0.25}O_{3-\delta}$	*Pm*-3*m*	100	3.9425(1)		1.86	3.29
$Ba_{0.5}Sr_{0.5}Fe_{0.75}Mo_{0.25}O_{3-\delta}$	*Pm*-3*m* *I*41/*a*	95.6 4.4	3.9620(1) 5.5521(11)	12.8321(23)	2.10	4.24
$Ba_{0.75}Sr_{0.25}Fe_{0.75}Mo_{0.25}O_{3-\delta}$	-	-	-		-	-
$BaFe_{0.75}Mo_{0.25}O_{3-\delta}$	-	-	-		-	-
$SrFe_{0.675}Mo_{0.225}Zn_{0.05}Zr_{0.05}O_{3-\delta}$	*Pm*-3*m*	100	3.9292(1)		1.72	2.21
$Ba_{0.5}Sr_{0.5}Fe_{0.675}Mo_{0.225}Zn_{0.05}Zr_{0.05}O_{3-\delta}$	*Pm*-3*m* *I*41/*a*	98.8 1.2	3.9819(1) 5.5605(19)	12.8056(42)	1.78	2.70
$BaFe_{0.675}Mo_{0.225}Zn_{0.05}Zr_{0.05}O_{3-\delta}$	-	-	-		-	-
$SrFe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	*Pm*-3*m*	100	3.9393(1)		2.45	2.75
$Ba_{0.25}Sr_{0.75}Fe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	*Pm*-3*m*	100	3.9693(1)		1.84	3.35
$Ba_{0.5}Sr_{0.5}Fe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	*Pm*-3*m*	100	3.9969(1)		1.60	3.19
$Ba_{0.75}Sr_{0.25}Fe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	*Pm*-3*m* *I*41/*a*	98.3 1.7	4.0396(1) 5.5779(89)	12.7913(185)	1.28	6.68
$BaFe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	-	-	-		-	-
$SrFe_{0.525}Mo_{0.175}Zn_{0.15}Zr_{0.15}O_{3-\delta}$	*Pm*-3*m*	100	3.9564(1)		2.15	2.92
$Ba_{0.5}Sr_{0.5}Fe_{0.525}Mo_{0.175}Zn_{0.15}Zr_{0.15}O_{3-\delta}$	*Pm*-3*m*	100	4.0164(1)		1.82	2.80
$BaFe_{0.525}Mo_{0.175}Zn_{0.15}Zr_{0.15}O_{3-\delta}$	*Pm*-3*m* *Pm*-3*m*	81.0 19.0	4.0818(3) 4.1185(6)		3.12	6.20
$SrFe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	*Pm*-3*m*	100	3.9712(1)		2.08	3.04
$Ba_{0.25}Sr_{0.75}Fe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	*Pm*-3*m* *Pm*-3*m*	97.6 2.4	3.9984(1) 4.1149(6)		1.47	2.82
$Ba_{0.5}Sr_{0.5}Fe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	*Pm*-3*m* *Pm*-3*m*	95.7 4.3	4.0276(1) 4.1225(6)		1.80	3.71
$Ba_{0.75}Sr_{0.25}Fe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	*Pm*-3*m* *Pm*-3*m*	89.7 10.3	4.0646(3) 4.1271(7)		2.52	5.43
$BaFe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	*Pm*-3*m* *Pm*-3*m*	86.1 13.9	4.1003(5) 4.1707(12)		2.44	5.82

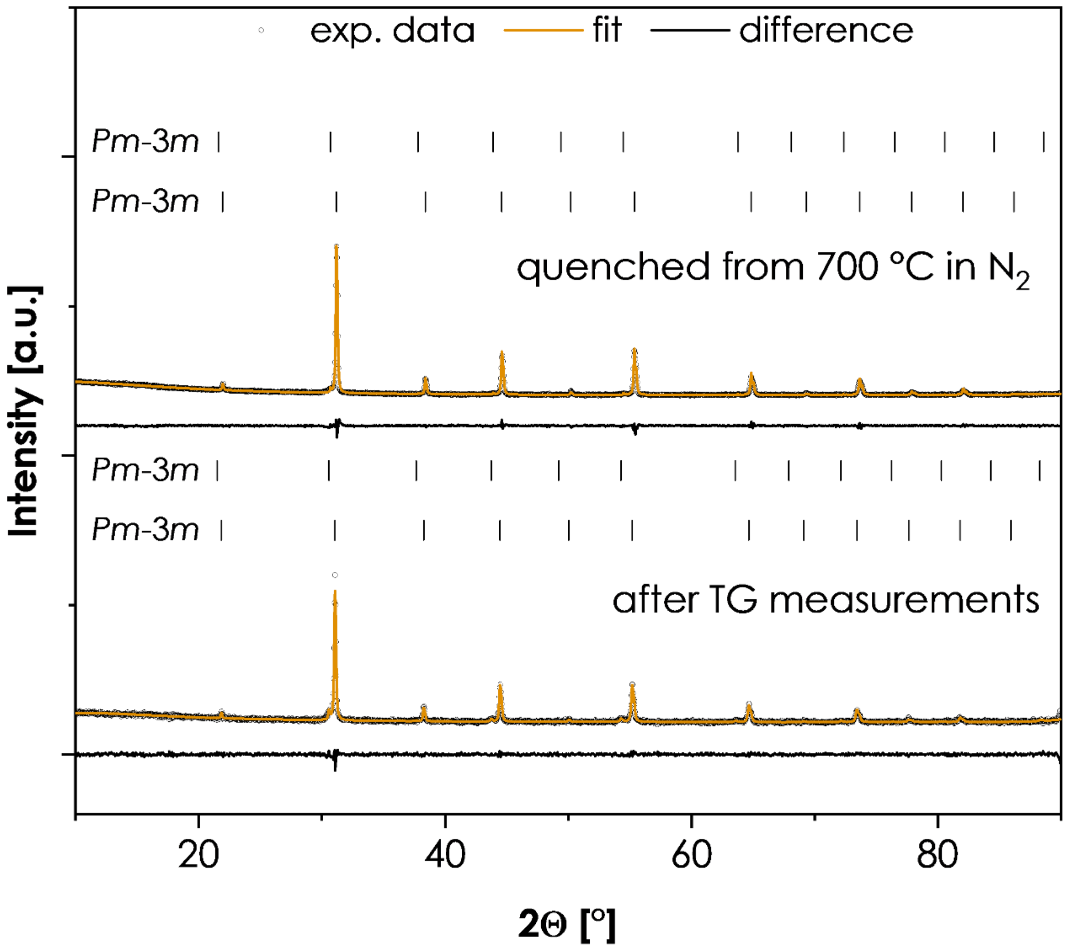

Fig. 4. Comparison of X-ray diffractograms measured for sample $Ba_{0.75}Sr_{0.25}Fe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$ after TG measurement (in N_2 with different pH_2O) and for sample quenched from 700 °C in N_2.

Table 3. The results of Rietveld refinement for sample $Ba_{0.75}Sr_{0.25}Fe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$ after TG measurement (in N_2 with different pH_2O) and for sample quenched from 700 °C in N_2.

Conditions	**Space group**	**Content [wt.%]**	***a* [Å]**	***c* [Å]**	**GoF [-]**	**Rwp [%]**
after TG measurements	*Pm*-3*m* *Pm*-3*m*	94.8 5.2	4.0776(2) 4.1409(11)		1.02	6.70
quenched from 700 °C in N_2	*Pm*-3*m* *Pm*-3*m*	98.8 1.2	4.0692(1) 4.1320(7)		1.44	3.10

Table S4. Full data of proton concentrations of $Ba_{y}Sr_{1-y}(Fe_{0.75}Mo_{0.25})_{1-2x}Zn_{x}Zr_{x}O_{3-\delta}$ series.

Composition	700 °C	600 °C	500 °C	450 °C	400 °C	350 °C	300 °C	250 °C	200 °C	175 °C	150 °C
$SrFe_{0.75}Mo_{0.25}O_{3-\delta}$	0.02402	0.00801	0.04003	0.02402	0.04483	0.03042	0.04003	0.04964	0.05444	0.06885	0.09447
$Ba_{0.25}Sr_{0.75}Fe_{0.75}Mo_{0.25}O_{3-\delta}$	0.02551	0.02892	0.03402	0.01361	0.03572	0.03742	0.03232	0.05613	0.08165	0.12077	0.16840
$Ba_{0.5}Sr_{0.5}Fe_{0.75}Mo_{0.25}O_{3-\delta}$	0.01094	0.05471	0.07221	0.08096	0.10722	0.12910	0.19694	0.28447	0.48140	0.70022	0.95187
$Ba_{0.75}Sr_{0.25}Fe_{0.75}Mo_{0.25}O_{3-\delta}$	0.11998	0.20373	0.27164	0.33955	0.47538	0.70175	1.12053	1.70909	2.79567	3.81433	5.14991
$BaFe_{0.75}Mo_{0.25}O_{3-\delta}$	0.38111	0.61373	0.96514	1.32398	1.81892	2.31387	3.10578	4.44213	4.68960	4.31839	2.31387
$SrFe_{0.675}Mo_{0.225}Zn_{0.05}Zr_{0.05}O_{3-\delta}$	0.06217	0.05751	0.06373	0.06839	0.09170	0.10725	0.10103	0.15854	0.27822	0.32485	0.44297
$Ba_{0.5}Sr_{0.5}Fe_{0.675}Mo_{0.225}Zn_{0.05}Zr_{0.05}O_{3-\delta}$	0.09260	0.22636	0.42185	0.51445	0.79225	1.26554	1.88287	2.97350	4.53742	5.71036	6.73925
$BaFe_{0.675}Mo_{0.225}Zn_{0.05}Zr_{0.05}O_{3-\delta}$	0.28439	0.48915	0.89867	1.30818	1.55845	1.78596	1.78596	1.53569	0.78491		0.28439
$SrFe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	0.05963	0.07252	0.10314	0.09186	0.12892	0.18049	0.23368	0.45929	0.82995	1.00722	1.50681
$Ba_{0.25}Sr_{0.75}Fe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	0.12282	0.10703	0.13685	0.19475	0.25265	0.34564	0.46495	0.74567	1.28958	1.55276	2.14930
$Ba_{0.5}Sr_{0.5}Fe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	0.11401	0.12889	0.20159	0.31230	0.42136	0.61303	0.91707	1.44584	2.15636	2.93298	3.77570
$Ba_{0.75}Sr_{0.25}Fe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	0.12441	0.20735	0.27647	0.42853	0.64971	0.94000	1.46530	2.25324	3.16559	3.82912	4.13324
$BaFe_{0.6}Mo_{0.2}Zn_{0.1}Zr_{0.1}O_{3-\delta}$	0.26285	0.47140	0.66691	1.05142	1.27517	1.66185	2.33527	2.24838	1.77046	1.31427	0.81463
$SrFe_{0.525}Mo_{0.175}Zn_{0.15}Zr_{0.15}O_{3-\delta}$	0.12104	0.09346	0.13177	0.17467	0.23595	0.41215	0.57915	0.94993	1.60110	1.95349	2.44378
$Ba_{0.5}Sr_{0.5}Fe_{0.525}Mo_{0.175}Zn_{0.15}Zr_{0.15}O_{3-\delta}$	0.13749	0.26353	0.45831	0.61872	0.83641	1.38638	2.02801	2.80714	3.33419	2.78422	2.41757
$BaFe_{0.525}Mo_{0.175}Zn_{0.15}Zr_{0.15}O_{3-\delta}$	0.37853	0.54677	0.85520	1.27580	1.80855	2.76189	4.02367	5.11721	6.51918	5.67800	6.65938
$SrFe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	0.12875	0.13795	0.24830	0.35314	0.47454	0.68974	1.07599	1.51742	1.86689	1.97724	2.25314
$Ba_{0.25}Sr_{0.75}Fe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	0.09260	0.22636	0.42185	0.51445	0.79225	1.26554	1.88287	2.97350	4.53742	5.71036	6.73925
$Ba_{0.5}Sr_{0.5}Fe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	0.26651	0.40951	0.71502	1.24586	1.52753	1.98254	3.08757	4.21426	4.12759	3.62925	3.30424
$Ba_{0.75}Sr_{0.25}Fe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	0.33458	0.68677	1.14461	1.35593	1.98987	3.01122	4.17344	5.68785	7.83621	9.35062	11.35810
$BaFe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$	0.38015	0.72028	1.34052	2.02078	3.02117	4.34168	6.50252	8.98348	12.70492	14.70570	16.30632

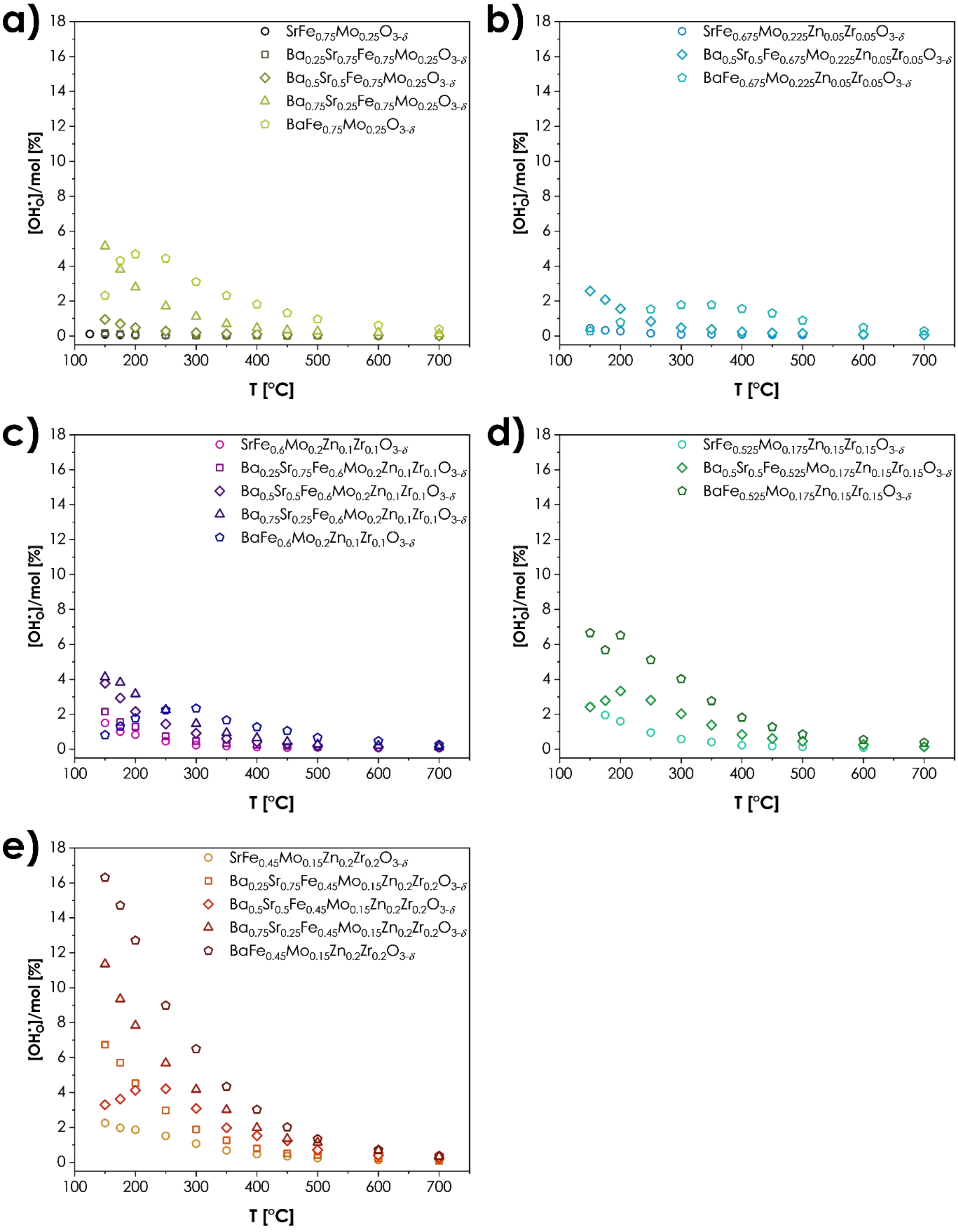

Fig. S5. Protonic defects concentration of $Ba_ySr_{1-y}(Fe_{0.75}Mo_{0.25})_{1-2x}Zn_xZr_xO_{3-\delta}$ series as a function of temperature.

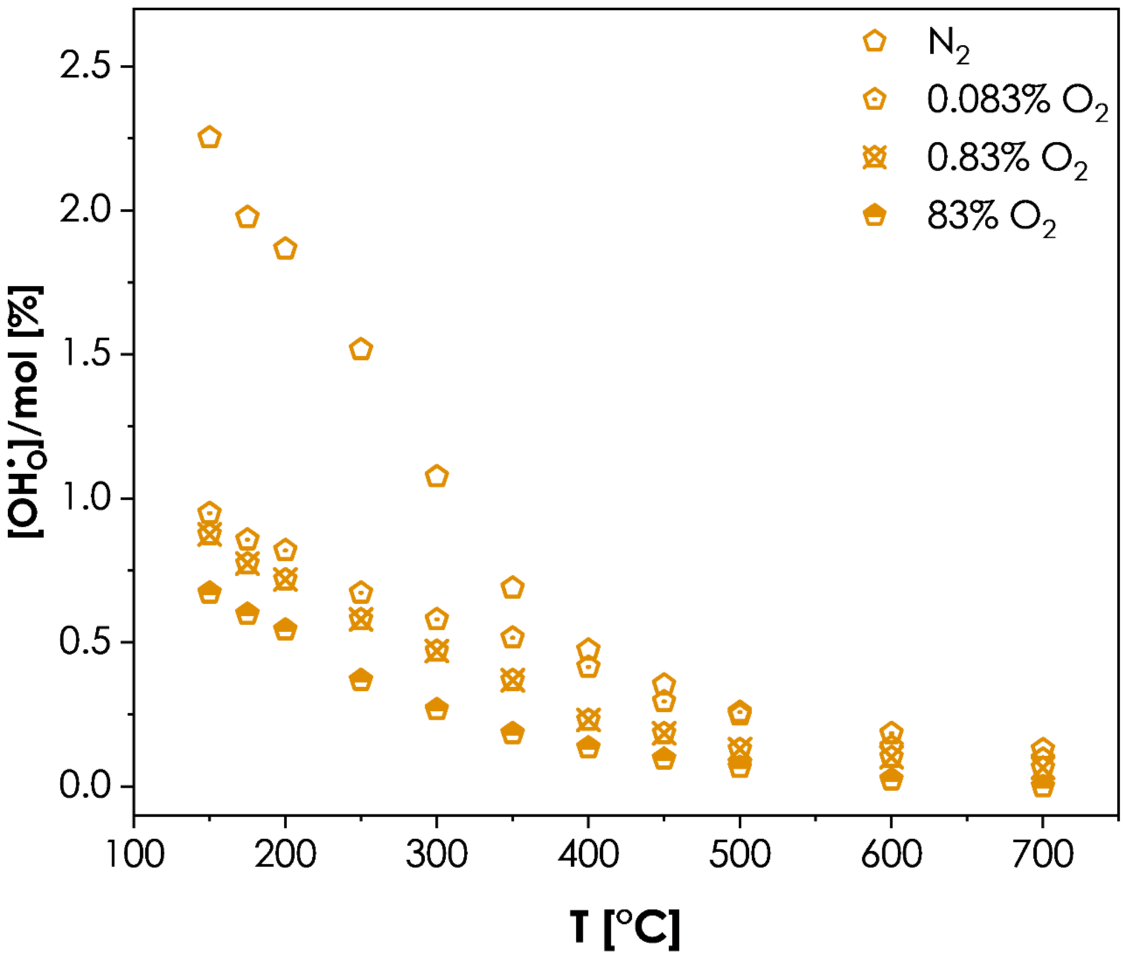

Fig. S6. Equilibrated proton concentration as a function of temperature under different values of pO_2 for $SrFe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$ composition.

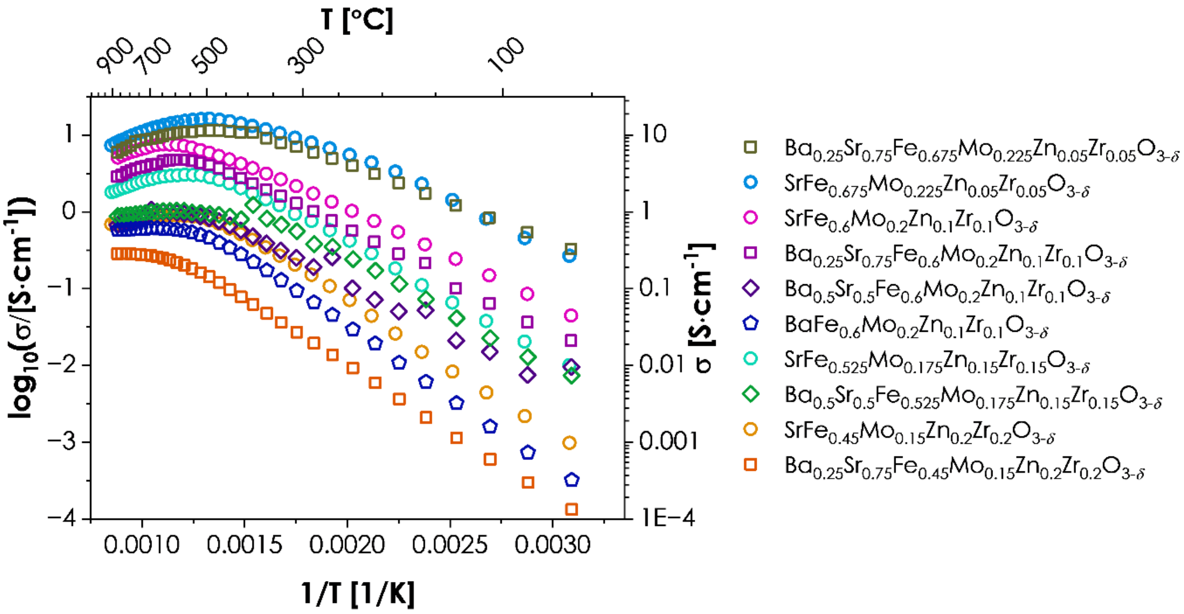

Fig. S7. Total electrical conductivity values in dry air for selected, single-phase compositions, as a function of temperature. Presented in Arrhenius coordinates.

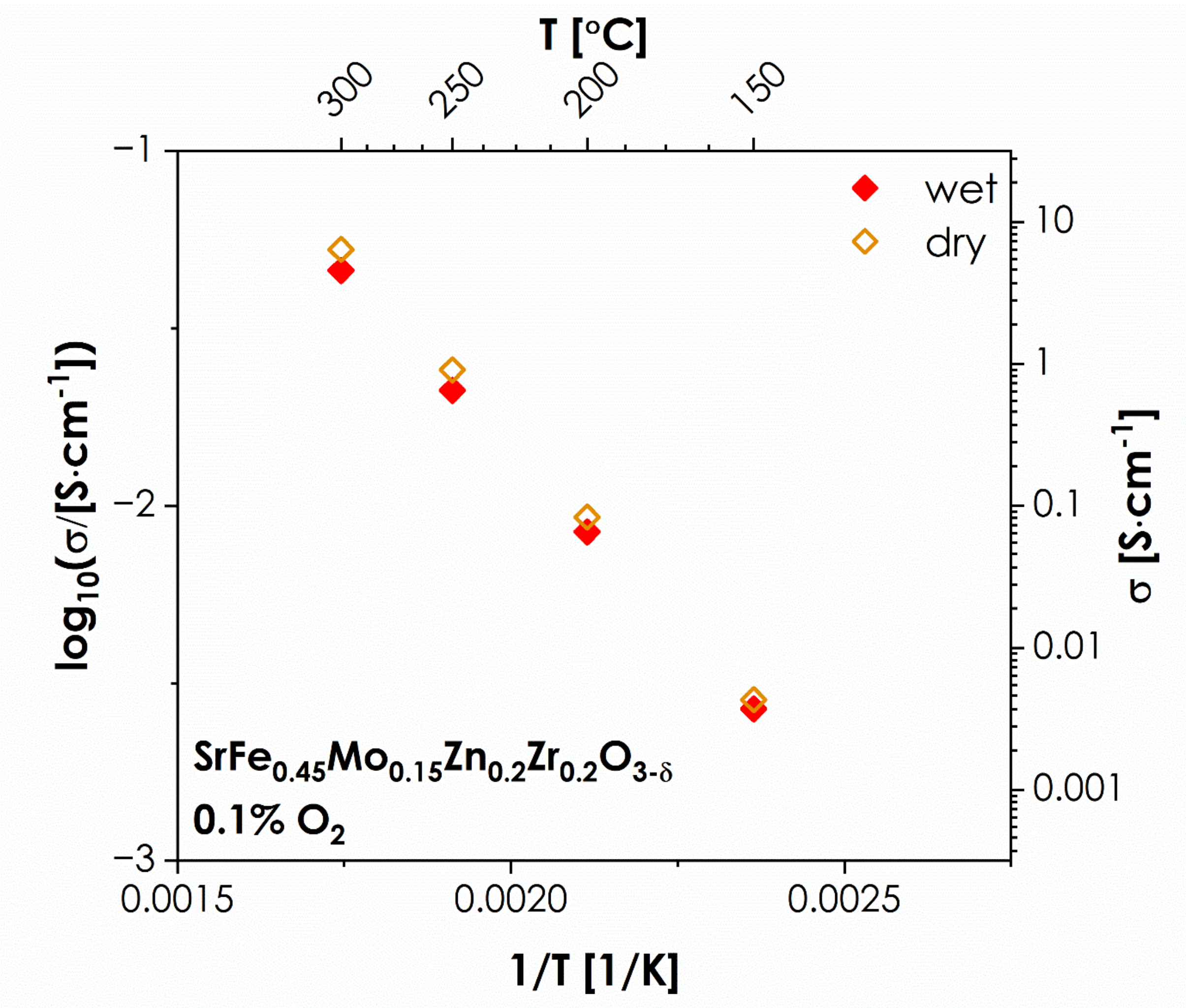

Fig. S8. Total electrical conductivity for $SrFe_{0.45}Mo_{0.15}Zn_{0.2}Zr_{0.2}O_{3-\delta}$ composition under dry and humid (pH$_2$O of 20 mbar) conditions.

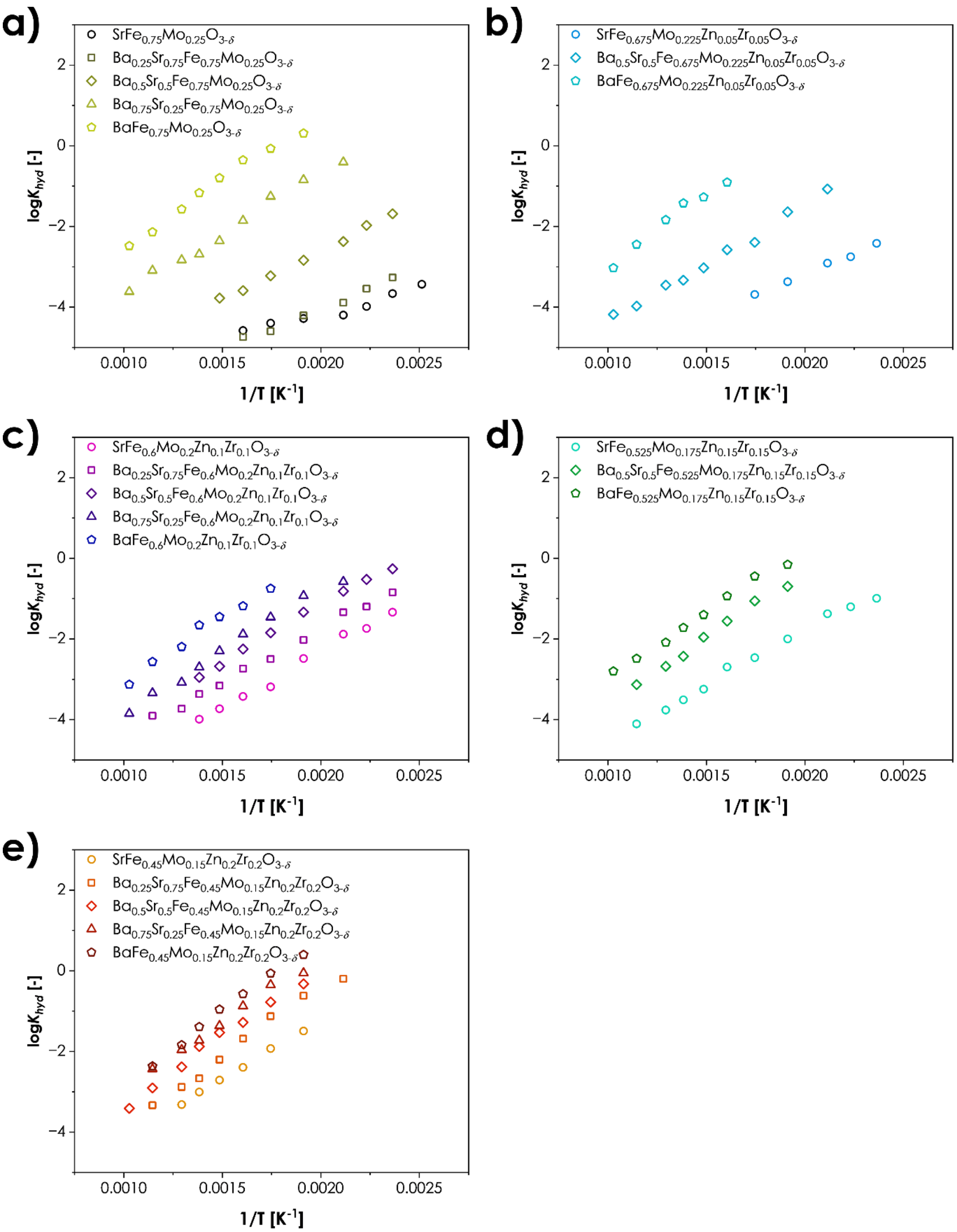

Fig. S9. Van't Hoff plots of K_{hyd} according to the hydration reaction. The different linear ranges were selected because of low data quality at high temperatures (due to the noise) and interactions between defects at low temperatures.