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


# Supplementary Information

# Oxygen deficiency in $Sr_2FeO_{4-x}$: Electrochemical control and impact on magnetic properties

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**Table S1** Partial pressures of oxygen in the system Ar-$H_2$-$H_2O$ (in bar)

| $H_2/H_2O$ | 500 °C | 600 °C | 700 °C | 800 °C | 900 °C | 1000 °C |
|---|---|---|---|---|---|---|
| 100 | $1.7\cdot10^{-32}$ | $1.2\cdot10^{-28}$ | $1.4\cdot10^{-25}$ | $4.5\cdot10^{-23}$ | $5.2\cdot10^{-21}$ | $2.9\cdot10^{-19}$ |
| 10 | $1.7\cdot10^{-30}$ | $1.2\cdot10^{-26}$ | $1.4\cdot10^{-23}$ | $4.5\cdot10^{-21}$ | $5.2\cdot10^{-19}$ | $2.9\cdot10^{-17}$ |
| 1 | $1.7\cdot10^{-28}$ | $1.2\cdot10^{-24}$ | $1.4\cdot10^{-21}$ | $4.5\cdot10^{-19}$ | $5.2\cdot10^{-17}$ | $2.9\cdot10^{-15}$ |
| 0.1 | $1.7\cdot10^{-26}$ | $1.2\cdot10^{-22}$ | $1.4\cdot10^{-19}$ | $4.5\cdot10^{-17}$ | $5.2\cdot10^{-15}$ | $2.9\cdot10^{-13}$ |
| 0.01 | $1.7\cdot10^{-24}$ | $1.2\cdot10^{-20}$ | $1.4\cdot10^{-17}$ | $4.5\cdot10^{-15}$ | $5.2\cdot10^{-13}$ | $2.9\cdot10^{-11}$ |
| 0.001 | $1.7\cdot10^{-22}$ | $1.2\cdot10^{-18}$ | $1.4\cdot10^{-15}$ | $4.5\cdot10^{-13}$ | $5.2\cdot10^{-11}$ | $2.9\cdot10^{-9}$ |

**Table S2** Refinement results for $Sr_2FeO_4$ powder. The data were refined with the program WinCSD (Ref. 46 of the main paper).

| $Sr_2FeO_4$ | $a$ [Å] | $c$ [Å] | $V$ [Å$^3$] | | | |
|---|---|---|---|---|---|---|
| | 3.86283(2) | 12.39327(8) | 184.926(3) | | | |
| *I*4/*mmm* | Wyckoff-Position | $x$ | $y$ | $z$ | $U_{iso/eq}$ | |
| Sr | 4*e* | 0 | 0 | 0.35682(4) | 0.0098(2) | |
| Fe | 2*a* | 0 | 0 | 0 | 0.0146(5) | |
| O1 | 4*e* | 0 | 0 | 0.1568(2) | 0.0056(9) | |
| O2 | 4*c* | 0 | 1/2 | 0 | 0.0044(8) | |
| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
| Sr | 0.0070(2) | 0.0070(2) | 0.0152(4) | 0 | 0 | 0 |
| Fe | 0.0118(7) | 0.0118(7) | 0.020(1) | 0 | 0 | 0 |

$R_p = 0.0872$, $R_I = 0.0254$ ($R_I = \sum||I_{obs}| - |I_{calc}||/\sum|I_{obs}$)

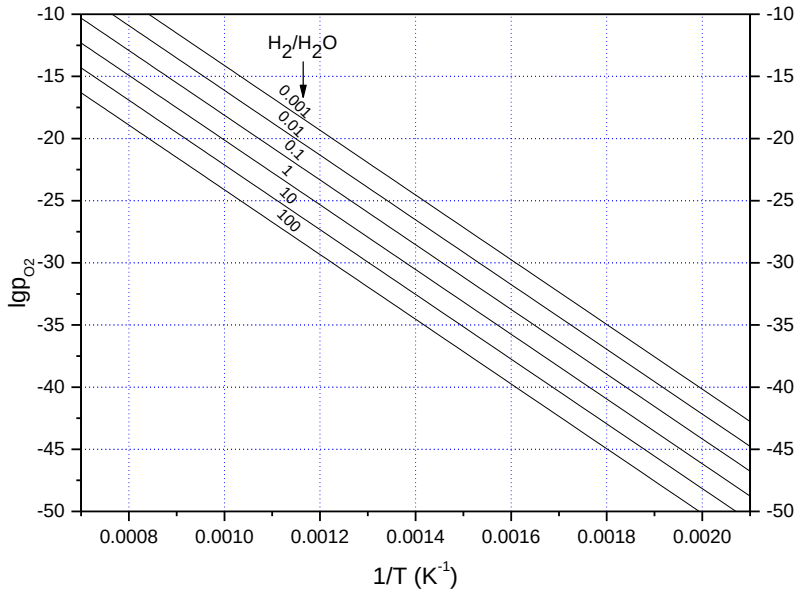


**Fig. S1** Solid state electrolyte coulometry. Plot of log $p_{O2}$ vs. $1/T$ representing the equilibrium 2 $H_2O \leftrightarrow 2\ H_2 + O_2$, for a set of given $H_2/H_2O$ ratios.

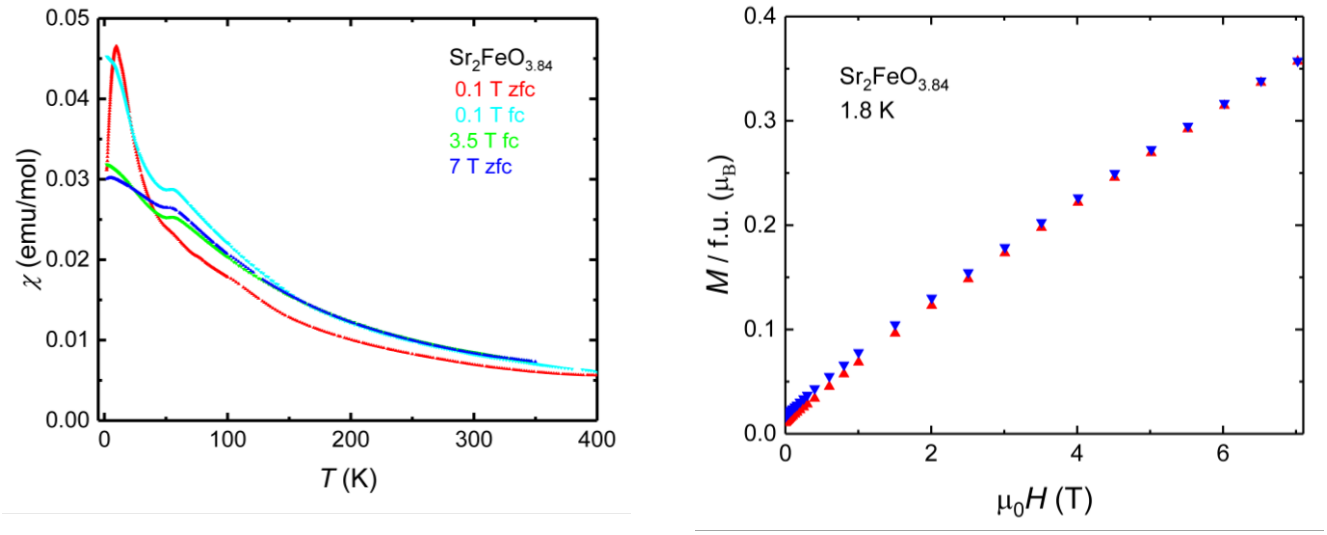


**Fig. S2** Magnetic properties of a $Sr_2FeO_{3.84}$ sample which was part of the batch used for PND studies. Left: Temperature dependence of the magnetic susceptibility. Right: Magnetization curve at 1.8 K.

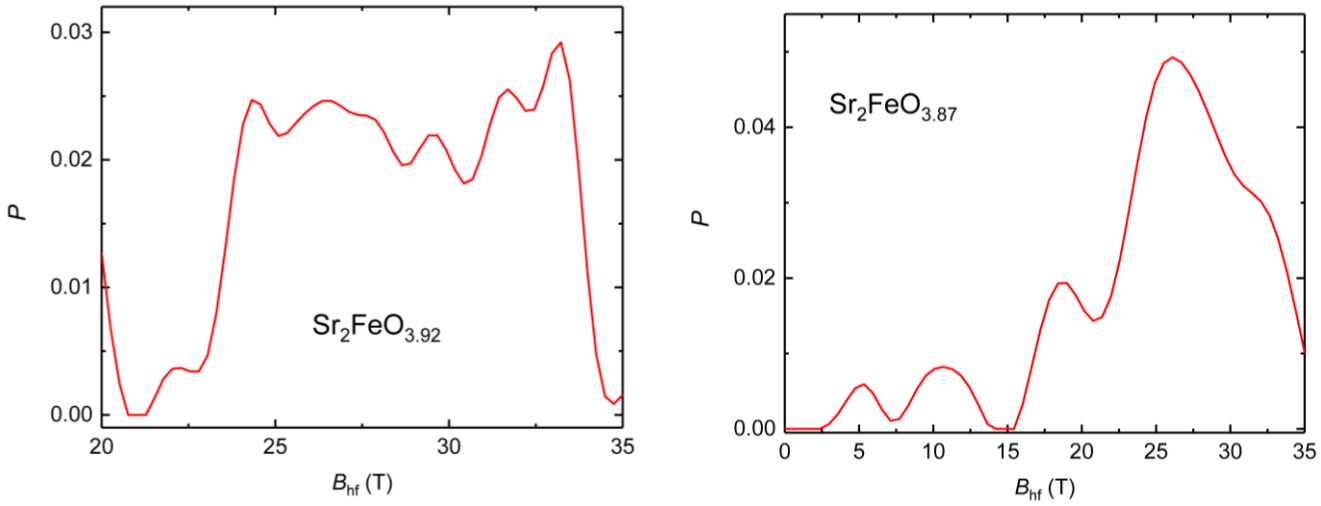


**Fig. S3** Hyperfine field distributions $P(B_{hf})$ of the $Fe^{4+}$ component for $Sr_2FeO_{3.92}$ and $Sr_2FeO_{3.87}$ as obtained from the fits displayed in Fig. 9(b) of the main paper.

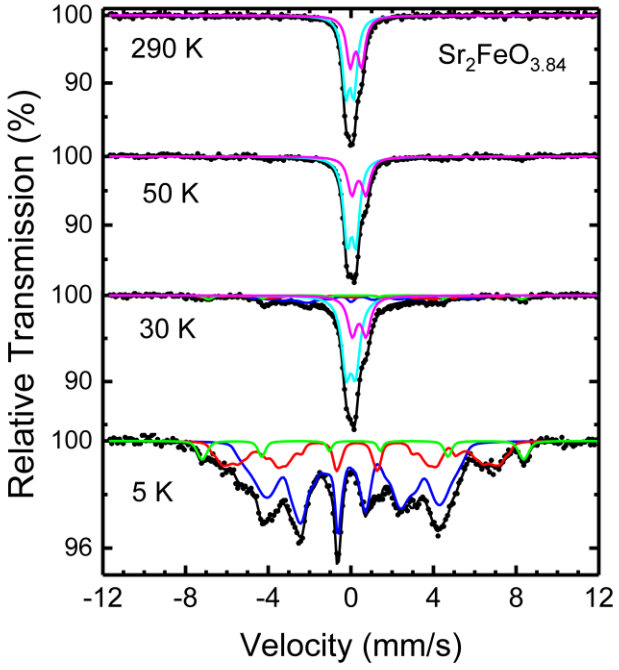


**Fig. S4** Mössbauer spectra of a sample of oxygen-deficient $Sr_2FeO_{3.84}$ measured at the indicated temperatures. The sample was part of the batch measured by PND. Dots correspond to the experimental data, solid lines to the best fits. The subspectra are shown as colored lines (blue and cyan correspond to magnetically ordered and paramagnetic $Fe^{4+}$, red and green to magnetically ordered $Fe^{3+}$, and pink to paramagnetic $Fe^{3+}$ sites, respectively).

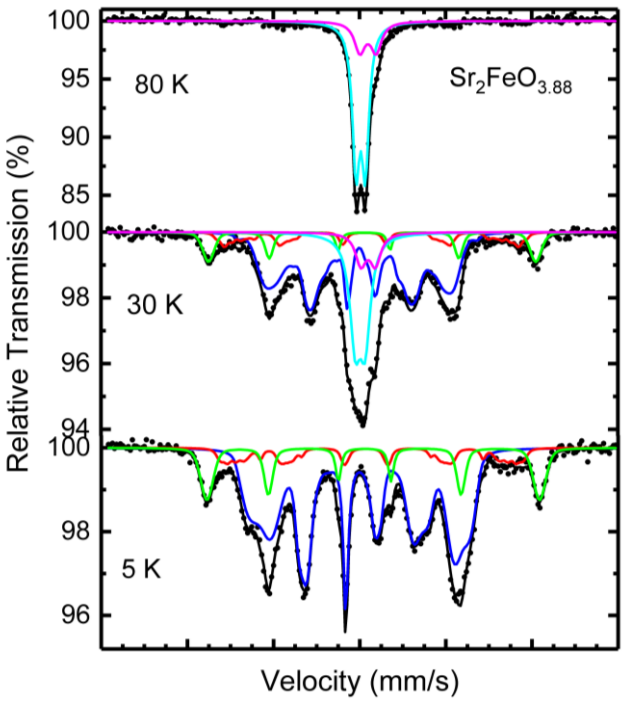


**Fig. S5** Mössbauer spectra of a sample of oxygen-deficient $Sr_2FeO_{3.88}$ measured at the indicated temperatures. Dots correspond to the experimental data, solid lines to the best fits. The subspectra are shown as colored lines (blue and cyan correspond to magnetically ordered and paramagnetic $Fe^{4+}$, red and green to magnetically ordered $Fe^{3+}$, and pink to paramagnetic $Fe^{3+}$ sites, respectively). Note the different ratio between the two $Fe^{3+}$ components and the increased fraction of the magnetic component at 30 K compared to the spectra of a sample of $Sr_2FeO_{3.87}$ displayed in Fig. 9(b).