Experimental report

17/09/2021

Proposal:	**5-23-763**	**Council:**	10/2020
Title:	In situ monitoring of the oxygen content of dual phase oxygen transport membranes by thermogravimetry and neutron diffraction		
Research area:	Materials		

This proposal is a new proposal

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Samples: $Ce_{0.8}Pr_{0.2}O_2$ - $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_3$
$Ce_{0.8}Nd_{0.2}O_2$ - $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_3$
$Ce_{0.8}Pr_{0.2}O_{2-x}$
$La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-x}$

Instrument	Requested days	Allocated days	From	To
D1B	4	2	22/06/2021	24/06/2021

Abstract:

Combined in situ neutron diffraction and thermogravimetry at D1B will beused to track the change of the oxygen content in the dual-phase oxygen transport membrane material $Ce_{0.8}Pr_{0.2}O_{2-x}$/$La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_3$. The sample shows deviating thermal behavior in comparision to $CeREO_{2-x}$ (RE = La, Nd, Sm, Gd) having together with Gd containig the highest oxygen permeation flux, but they differ totally in there thermal behavior. Neutron diffraction is needed to monitor the individual changes in the oxygen content in fluorite and perovskite phase.

In situ monitoring of the oxygen content of dual phase oxygen transport membranes by thermogravimetry and neutron diffraction (5-23-763)

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Two dual phase membrane materials have been synthesized by a combination of EDTA-citric acid soft chemistry and mechanochemistry. Within the series of dual-phase membrane materials, the mixture of 60 wt% $Ce_{0.8}Pr_{0.2}O_{2-d}$ (CPO) and 40 wt% $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-x}$ (LSFCO) showed peculiar behavior in thermochemical studies (TGA) and the resulting oxygen transport performance as well. Combined studies by X-ray photoemission and Raman spectroscopy together with refinements of the XRD pattern revealed that a transition from Pr^{4+} to Pr^{3+} state plays a major role.[1] The aim of this study was to analyze the oxygen release and uptake in dual phase membranes 60 wt% $Ce_{0.8}RE_{0.2}O_{2-d}$ (RE = La, Pr, Nd, Sm, Gd) and 40 wt% $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-x}$ (LSFCO) in more details. Due to time constrains it was possible to measure only one additional sample. In this regard, $Ce_{0.8}La_{0.2}O_{2-d}$ (CLO) was selected as a reference showing not only a larger size difference in ionic radius to Pr as compared to Nd, but also a negligible neutron absorption in comparison to Sm and Gd. Both samples have been measured in air from 300 K to 1173 K with a heating rate of 1–2 $K \cdot min^{-1}$, while carrying out long measurements of 1 h at distinct temperatures of 300 K, 600 K, and 1173 K. The samples have been studied on D1B diffractometer using an incident wavelength of 1.28 Å. In parallel the mass changes are recorded by the D1B thermobalance.

During heating, a negative mass change was observed for both samples, which is in good agreement with the TGA results previously reported [1]. It should be mentioned that more pronounced mass changes were observed for CPO-LSFCO ($\Delta m = -0.93$ %) compared to CLO-LSFCO ($\Delta m = -0.5$ %) pointing to an oxygen release from the samples. During isothermal treatment at 1173 K the mass remains almost constant, while during cooling an oxygen uptake down to about 573 K was observed. Based on the recorded mass changes the oxygen exchange reactions were found to be reversible by about 85 % and 69 %, respectively, under the given rather fast cooling regime. Higher degrees of reversibility are expected when a lower cooling rate is applied.

A first preliminary set of Rietveld refinements using the cubic subcell of LFSCO allowed the study of temperature-dependent evolution of the unit cell parameters (s. Fig. 1) and hence the linear isotropic thermal expansion coefficients α. The determined values agreed well with literature values (s. Tab. 1). Refinement studies with updated strategies are planned by considering the correct space group of LSFCO and the rather short exposure times of 5 min for more detailed results on e.g. the evolution of the oxygen contents of the respective phases.

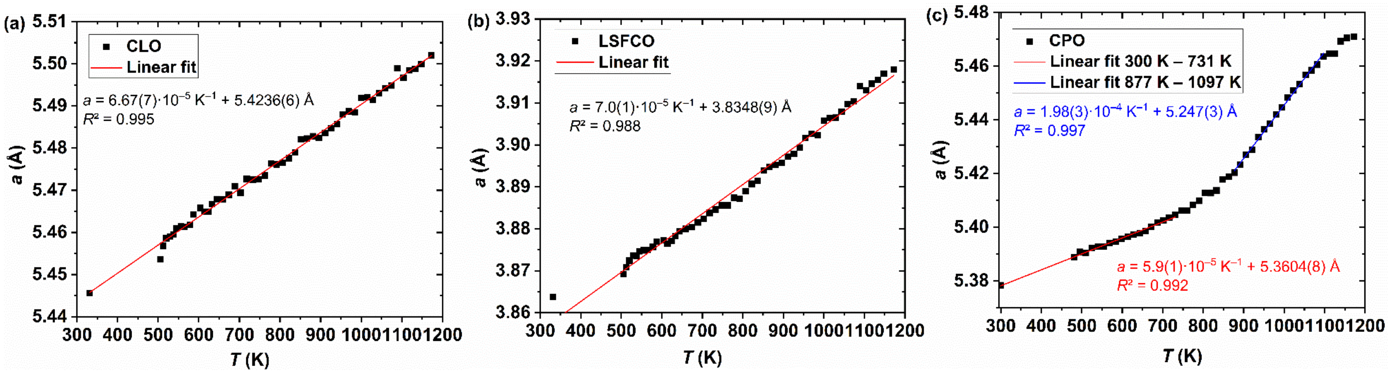

Fig. 1. Temperature dependent unit cell parameters of (a) CLO, (b) LSFCO, and (c) CPO together with the linear fits used to determine α.

Tab. 1. Linear isotropic thermal expansion coefficients of CMO and LSFCO based on Rietveld refinements of neutron diffraction data.

Sample	***T* (K)**	**α (K^{-1})**	**Reference**
M = La	298–1273	11.9×10^{-6}	[2]
M = La	302–1173	$12.3(1)\times10^{-6}$	This work
M = Ce	298–1273	11.8×10^{-6}	[2]
M = Pr	373–673	11.7×10^{-6}	[3]
M = Pr	923–973	41×10^{-6}	[2]
M = Pr	300–731	$11.0(2)\times10^{-6}$	This work
M = Pr	877–1097	$37.7(6)\times10^{-6}$	This work
M = Nd	298–1273	11.9×10^{-6}	[2]
M = Sm	298–1273	12.2×10^{-6}	[2]
M = Gd	298–1273	12.1×10^{-6}	[2]
LSFCO	298–1173	17.7×10^{-6}	[4]
LSFCO	302–1173	$18.3(3)\times10^{-6}$	This work

References

[1] G. Chen et al., *J. Membr. Sci*. **2021**, *639*, 119783.
[2] S. Sameshima et al., *J. Ceram. Soc. Jpn.* **2002**, *110*, 597–600.
[3] M. Heidenreich et al., *Solid State Ionics* **2015**, *283*, 56–67.
[4] J. Lu, *Electrochem. Commun*. **2015**, *61*, 18–22