



Strength and elastic modulus of lanthanum strontium cobalt ferrite membrane materials

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Abstract

Mixed ionic electronic ceramic transport membranes have a large potential for industrial oxygen supply and carbon emission reduced fossil power plant concepts. Although permeation and phase stability are main development aspects, mechanical robustness is of concern especially for the long term performance and reliability under application relevant thermo-mechanical loads. Lanthanum strontium cobalt ferrite materials appear to be advantageous, especially with respect to CO₂ stability. However, the effect of the A-site stoichiometry on the mechanical properties needs to be assessed. Furthermore, advanced design concepts rely on thin layers supported by a porous substrate and therefore also the porosity is an important factor. Hence, these aspects were investigated for dense and porous La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} and dense La_{0.38}Sr_{0.62}Co_{0.2}Fe_{0.8}O_{3-δ}. The specimens were investigated using a ring-on-ring bending set-up. The work summarizes the effect of the stoichiometry and porosity on the mechanical properties and compares the temperature dependencies of elastic moduli and fracture stresses.

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1. Introduction

Mixed ionic electronic conducting (MIEC) ceramic membranes are an interesting option for oxygen supply in industrial processes and to implement carbon capture concepts in fossil power plants [1,2]. Especially in the OXYFUEL process, the use of membranes promises the lowest losses in power plant efficiency compared to the conventional methods. With the aid of dilution of the permeated oxygen by recirculated flue gas at the membrane further savings in energy consumption can be made, compared to high pressure or vacuum operation modes [3,4]. Currently perovskite materials reach the highest permeation rates, where advanced concepts use thin membrane layers that are supported by porous substrates [2,5]. In order to reduce expansion mismatch induced stresses, membrane layer and substrate are often composed of identical materials.

The most promising materials with respect to permeation rates are the mixed ionic electronic conducting perovskites. Whereas the material with the highest reported flux [6] Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} suffers from phase instabilities at elevated temperatures [7–10] and is not stable under CO₂ [11,12], the lanthanum strontium cobalt ferrite membrane materials, i.e. La_xSr_{1-x}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCFX), appear to be more stable. Annealing experiments at operation temperature indicated that LSCF58 and LSCF38 are stable under CO₂ (99.995%) and also when exposed to a model flue gas (95% CO₂, 5% O₂ and 400 ppm SO₂) [13].

However, also a careful consideration of the mechanical stability is required to warrant long term performance and reliability under application relevant thermo-mechanical loads. With respect to mechanical aspects, elastic, fracture and creep behavior of dense LSCF58 have been the focus of recent studies [14–16]. Intermediate temperature mechanical anomalies have been reported that were associated with a ferroelastic behavior [17,18]. A rhombohedral to cubic phase change close to operation relevant temperatures affected the mechanical

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properties [17,19] and furthermore, the material showed rather large creep rates at operation relevant temperatures [20,21]. Contrary to this, the effect of materials' stoichiometry and porosity on the mechanical properties has not been discussed in detail; i.e. data on the mechanical behavior of porous LSCF substrates are limited [22] and there are also no reports for dense LSCF38. With respect to the application, it is important to assess elastic modulus and fracture stress, since the former links applied strains to induced stresses, whereas the latter gives the tolerable stress levels and associated failure probabilities. In particular the effect of substrate porosity on resulting mechanical properties needs to be assessed and

elevated temperature elastic and fracture properties are a prerequisite for understanding and modeling of stresses under application relevant conditions. The current study summarizes these data for LSCF with different stoichiometries (LSCF58 and LSCF38) and addresses the effect of porosity for LSCF58 as obtained using ring-on-ring fracture tests along with complementary microstructural analyses.

2. Experimental

Investigated was rather dense (6% porosity) and porous (46% porosity) LSCF60 (LSCF60_6% and LSCF60_46%) and

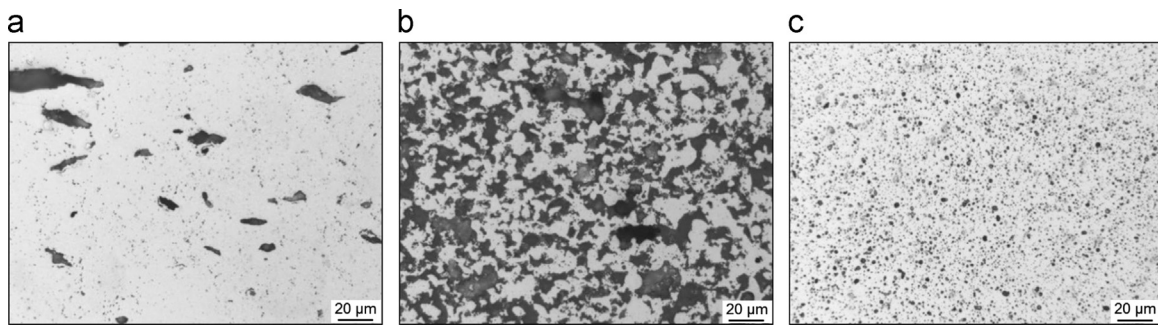


Fig. 1. LM images of the microstructure observed on the polished cross-sections of dense LSCF60 (a), porous LSCF60 (b) and dense LSCF38 (c).

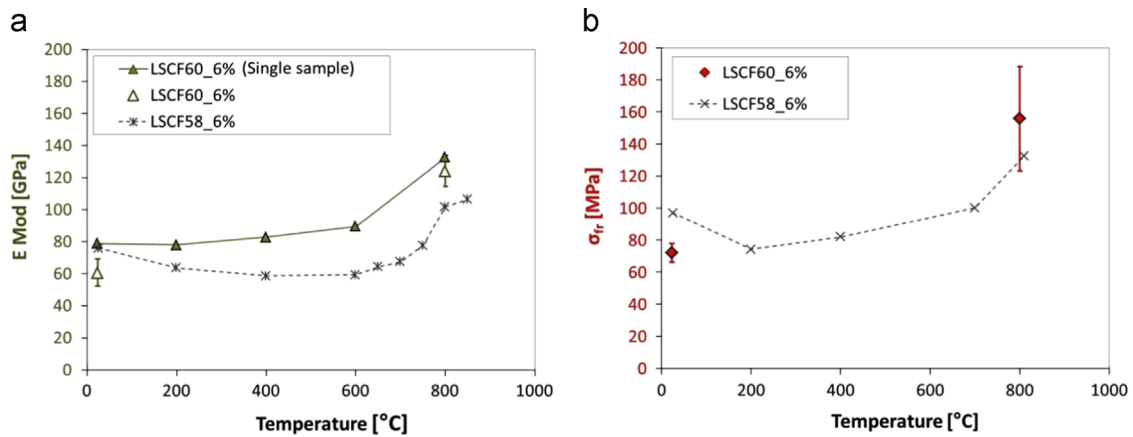


Fig. 2. Elastic modulus (a) and average fracture stress (b) of rather dense LSCF60_6% as a function of temperature.

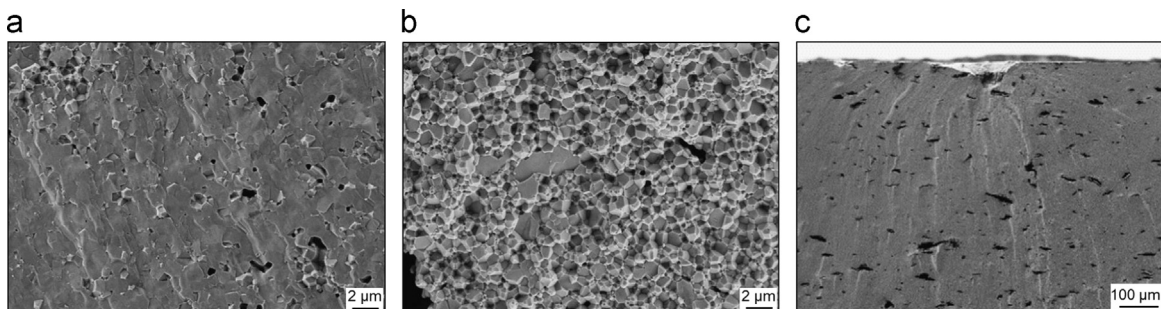


Fig. 3. SEM images of the fracture surfaces of LSCF60_6% samples. Transgranular and intergranular fracture surfaces of the samples tested in ring-on-ring test at RT (a) and 800 °C (b). Example of the structural defect (large porous localized just beneath the sample surface in the top, central part of the image) identified as typical failure origin (c). A typical fracture mirror appearance can be observed in (c) with numerous hackles (bowed lines with brighter appearance) converging at the fracture origin.

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