

Electron microscopy study of surface-functionalized $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes for oxygen separation

P Müller^{1,4}, B Albrecht¹, H Störmer¹, D Fuchs², C Niedrig³, S F Wagner³,
E Ivers-Tiffée^{3,4} and D Gerthsen^{1,4}

1. Laboratorium für Elektronenmikroskopie (LEM), Karlsruhe Institute of Technology (KIT),
76131 Karlsruhe/Germany
2. Institut für Festkörperphysik (IFP), Karlsruhe Institute of Technology (KIT),
76344 Eggenstein-Leopoldshafen/Germany
3. Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruhe Institute of Technology (KIT),
76131 Karlsruhe/Germany
4. DFG Center for Functional Nanostructures, Karlsruhe Institute of Technology (KIT),
76131 Karlsruhe/Germany

philipp.mueller@kit.edu

Keywords: BSCF; TEM; oxygen separation membrane

Among several perovskite materials cubic $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582) was reported to be a high performance mixed ionic-electronic conductor [1]. Beside a potential application as cathode material in solid oxide fuel cells, the mixed conduction is essential for use in highly selective oxygen separation membranes. These ceramic devices enable an environmentally friendly way to pure oxygen production.

The main aims of current efforts in this field are to decrease the operation temperature without performance penalty and to improve phase stability. Oxygen flux is controlled by both the membrane thickness and the surface exchange rate of oxygen. As mechanical stability limits minimum thickness of such a device, this study focuses on surface conditioning to enhance the surface oxygen exchange coefficient.

Recent electron microscopical studies on the degradation behaviour of the BSCF5582 perovskite [2,3] revealed the formation of both a hexagonal phase and plate-like polytypes within the application relevant temperature range (650-1000 °C). Therefore, conditioning the surface must ensure high oxygen exchange rates as well as phase stability. In the present study nanoporous $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC64) was chosen as surface conditioner because of its promising properties as SOFC cathode material [4].

Thin BSCF5582 films were deposited on NdGaO_3 (NGO) single crystal substrates employing pulsed laser deposition and electron-beam deposition. Subsequently, a nanoporous layer of LSC64 was deposited by a sol-gel process. The resulting structure was characterised by scanning electron microscopy and different transmission electron microscopy (TEM) techniques with regard to microstructure, phase composition and interdiffusion processes. Conductivity relaxation measurements were conducted to determine the influence of the surface coating on membrane performance.

Figure 1a shows a scheme of the described layer sequence. A high-angular annular dark-field scanning TEM (HAADF STEM) image of a corresponding sample region is shown in Figure 1b. Both cubic (1) and hexagonal (2) BSCF phases were found and analysed by energy dispersive X-ray spectroscopy. The hexagonal phase is cobalt enriched, consistent with findings reported for BSCF5582 bulk samples [2]. The crystal structure of the nanoporous LSC64 layer was analysed by Debye electron diffraction (Figure 2a). A background subtracted radial line-scan (Figure 2b) was extracted from the diffraction pattern (thin curve) and peaks were fitted (broad curve) using the method described in [5]. Simulations on the basis of the rhombohedral perovskite structure of LSC64 [6,7,8] match perfectly with the observed Bragg reflections indicated in Figure 2b.

Detailed electron energy loss spectroscopy investigations are currently in progress to evaluate the cobalt valence states of BSCF5582 before and after degradation. These studies are motivated by the strong influence of the cobalt valence state on the performance and phase stability.

References

- [1] Z Shao and SM Haile, *Nature* **431** (2004) p. 170.
 [2] P Müller *et al*, *SSI* **206** (2012) p. 57.
 [3] K Efimov, Q Xu and A Feldhoff, *Chem. Mater.* **22** (2010) p. 5866.
 [4] L Dieterle *et al*, *Adv. Energy Mater.* **1** (2011) p. 249.
 [5] C Gammer *et al*, *Scripta Materialia* **63** (2010) p. 312.
 [6] P Stadelmann, JEMS software package.
 [7] VG Sathe *et al*, *J. Phys.: Condens. Matter* **8** (1996) p. 3889.
 [8] R Sonntag *et al*, *Physica B* **241** (1998) p. 393.
 [9] This work has been performed within the project F2 of the DFG Research Center for Functional Nanostructures (CFN). It has been further supported by a grant from the Ministry of Science, Research and the Arts of Baden-Württemberg (Az: 7713.14-300).

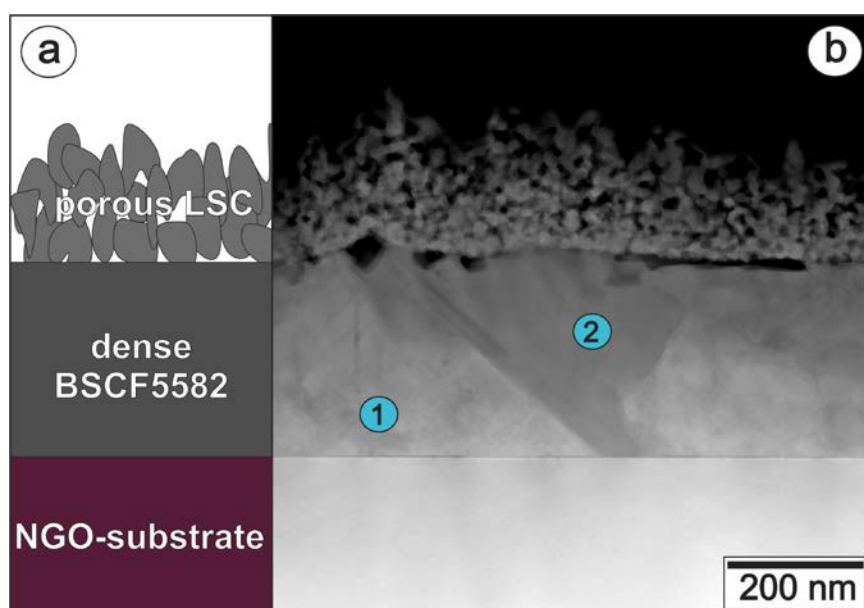


Figure 1. (a) Layer sequence of membrane samples. (b) HAADF STEM image of a corresponding sample area showing the cubic BSCF5582 phase (1) and a region containing the hexagonal phase (2).

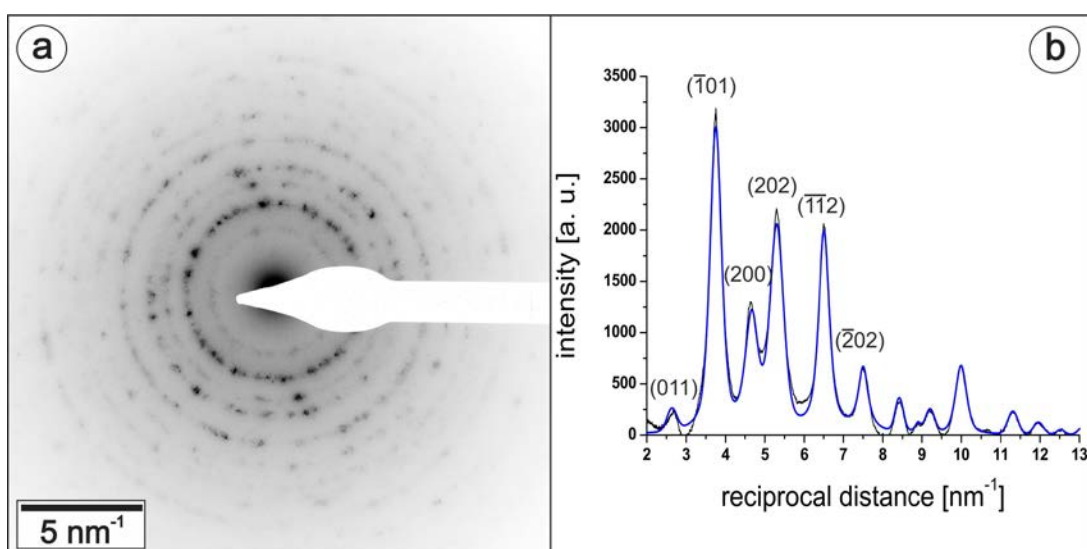


Figure 2. (a) Electron diffraction pattern of the porous LSC64 layer. (b) Background subtracted radial line-scan (black line) and simulated Debye diffraction pattern on the basis of the rhombohedral LSC structure (blue line).