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Investigation of carbonates in oxygen-transporting membrane ceramics by analytical transmission electron microscopy

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Mixed oxygen-ionic and electronic conductors (MIECs) can be used as oxygen-transporting membranes in gas separation, which is needed in concepts for energy conversion technologies as solid oxide fuel cells and “clean-coal” oxy-fuel combustion with less environmental pollution as compared to alternative approaches. These applications require chemical stability of the membrane material against carbon dioxide in the gas atmosphere. Already tiny carbonate scales on membrane surfaces, which are then impermeable for oxygen, must be avoided by proper choice of the material. Out-performing membrane ceramics with respect to total oxygen flux are based on perovskite-type oxides containing the alkaline-earth elements barium and strontium [1]. These constituents, however, form carbonates during membrane operation under CO₂-containing atmosphere [2, 3]. An example is given in Figure 1 with the out-performing cobalt-free Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-δ} perovskite, which was operated for two hours at 1023 K while sweeping with carbon dioxide on the oxygen-release side. A reaction zone with severe damage to the perovskite structure is noticed. Alternative materials, which avoid barium and strontium offer better chemical stability on the cost of lower oxygen flux [4].

A reliable analytical tool to identify tiniest carbonate scales on membrane surfaces is given by electron energy-loss spectroscopy (EELS) in the energy-filtering transmission electron microscope (EFTEM). The carbon-K and the oxygen-K ionization edges of carbonate and perovskite-type oxide phases show characteristic spectral signatures to distinguish them on the nanometer scale in properly prepared membrane cross-sections like shown in Figure 2. Here we study if partial cationic substitution of alkaline-earth elements can conserve high oxygen flux and give sufficient chemical stabilization. The TEM-based analytical method is applied to MIEC membranes after long-term operation (i.e. > 100 hours) of oxide ceramic membranes under technologically relevant conditions in presence of carbon dioxide. In the prominent perovskite SrCo_{0.8}FeO_{3-δ} (SCF) strontium was partially substituted by lanthanum to yield La_{1-x}Sr_xCo_{0.8}FeO_{3-δ} (LSCF) with x down to 0.4, and oxygen permeation experiments were correlated to the microstructure analysis. The later shows different amounts of carbonates at the CO₂-exposed sweep side of the membrane. Effects on total oxygen flux and chemical stability towards CO₂ as seen by oxygen permeation experiments are also discussed.

1. T. Klande, O. Ravkina, A. Feldhoff, *J. Eur. Ceram. Soc.* 33 (2013) 1129.
2. M. Arnold, H. Wang, A. Feldhoff, *J. Membr. Sci.* 293 (2007) 44.
3. J. Martynczuk, K. Efimov, L. Robben, A. Feldhoff, *J. Membr. Sci.* 344 (2009) 62.
4. Y. Wei, O. Ravkina, T. Klande, H. Wang, A. Feldhoff, *J. Membr. Sci.* 429 (2013) 147.

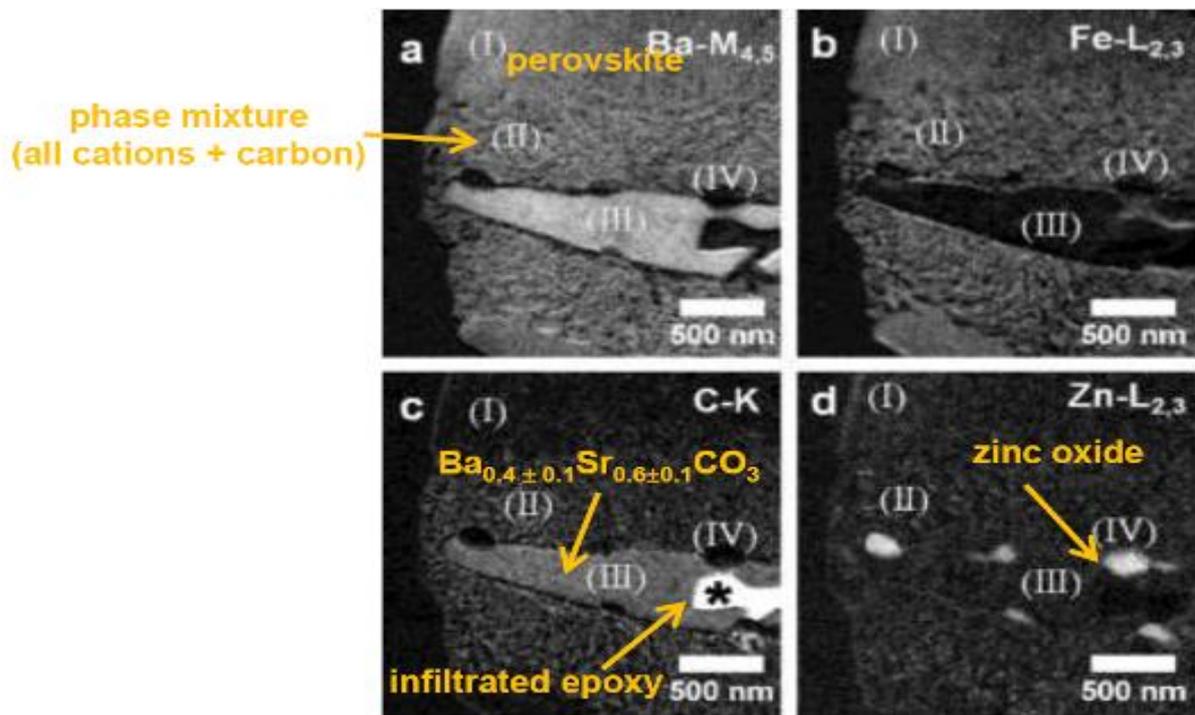


Figure 1. Elemental distributions by energy-filtered transmission electron micrographs of the reaction zone at the permeate side of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ perovskite after treatment with CO_2 for 2 h at 1023 K. High elemental concentration is shown by bright contrast: (a) barium, (b) iron, (c) carbon and (d) zinc. The asterisk (*) in (c) refers to a pore filled by epoxy due to TEM specimen preparation.

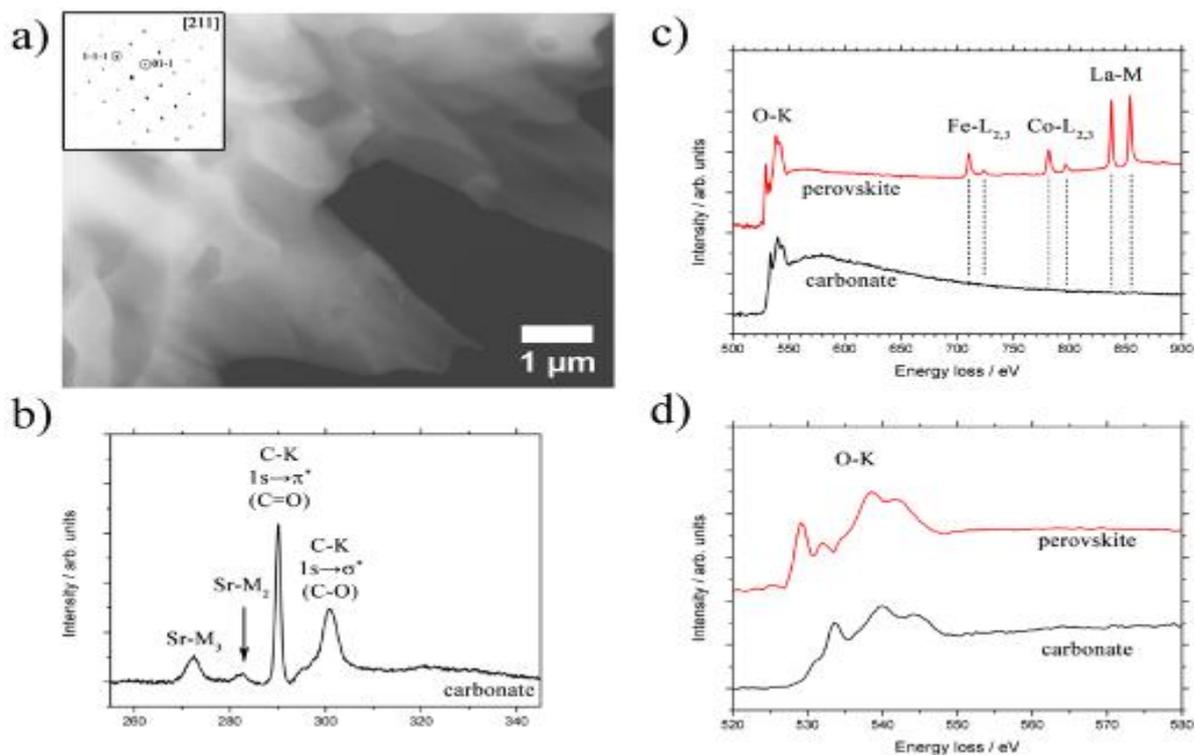


Figure 2. Transmission electron microscope analysis of sweep-side near region in $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membrane after 200 hours of operation at 1173 K while sweeping with 100% CO_2 : (a) High-angular dark field micrograph and selected area electron diffraction pattern, (b-d) electron energy-loss spectra of different locations showing signals from original perovskite and carbonate. Note different energy-loss scales.