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In-situ X-ray diffraction study of carbonate formation and decomposition in perovskite-type BCFZ

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ABSTRACT

The effect of CO_2 on the two phase perovskite with average composition of $BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$ is investigated by *in-situ* X-ray diffraction (XRD) as well as transmission electron microscopy (TEM). Partial decomposition of the BCFZ into high-temperature rhombohedral $BaCO_3$ polymorph was observed during annealing in an atmosphere, which contained 50 vol% CO_2/50 vol% N_2 at 1173 K. This carbonate structure is not quenchable and cannot be detected by *ex-situ* methods. Additionally, the reversible phase transition of $BaCO_3$ from orthorhombic to rhombohedral to cubic at different temperatures accompanied by formation of CoO was shown by *in-situ* XRD and TEM. Furthermore, complete regeneration of perovskite phase was obtained after high-temperature treatment under CO_2-free conditions.

1. Introduction

Doped perovskites (ABO_3) with multivalent cations as mixed ionic and electronic conductors are a hot topic in materials science today, e.g. as membrane materials for the separation of oxygen from oxygen containing gases like air with unrivaled selectivities [1] or as cathode material in solid-oxide fuel cells [2]. In the last decade, these membranes have attracted great academic and industrial interest, since they have also large potential applications in chemical processes in which a constant supply or removal of oxygen is required [3]. For prospective industrial applications as membrane reactors for oxidative activation reactions of light hydrocarbons [4] or as oxygen separators in zero emission plants in which oxygen permeable membranes are flushed with CO_2-containing exhaust gases [5], a sufficient stability especially in reducing gas atmospheres or atmospheres containing CO_2 is essential.

The poisoning effect of CO_2 arises from alkaline earth metal cations in the perovskite structure, which tend to form carbonates. Carolan et al. [6] reported that the oxygen permeation flux of $La_{0.8}Ba_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta}$ decreased significantly when 430 ppm CO_2 was introduced into the operation gas. It was further discovered that $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ is converted to the carbonate at 1123–1273 K under pure CO_2 atmosphere and the perovskite structure is disrupted [7].

Arnold et al. [8] investigated the influence of CO_2 on the oxygen permeation performance and the microstructure of perovskite-type $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes. It was found that when having air on the feed side, using pure CO_2 as sweep gas at 1148 K caused an immediate stop of the oxygen permeation flux, which could be recovered by sweeping with pure helium. A detailed surface analysis of a BSCF cathode after operation in 1% CO_2/O_2 at 723 K for 24 h revealed that its surface was destroyed and mixed barium–strontium carbonate was formed as a top layer [9].

Systems using dense perovskite hollow fiber membranes of the composition $BaCo_xFe_yZr_zO_{3-\delta}$ $(x+y+z=1)$, which is a novel oxygen permeable membrane material with high O_2 permeation fluxes and excellent thermal and mechanical stability [10], have been presented by our group, e.g. for the direct decomposition of nitrous oxide to nitrogen by *in-situ* oxygen removal [11], the simultaneous production of hydrogen and synthesis gas by combining water splitting with partial oxidation of methane [12] as well as the multi-step oxidative dehydrogenation of ethane [4] and propane (ODP) [13]. Furthermore, the oxidative coupling of methane to C_2 products could be successfully demonstrated in a $BaCo_xFe_yZr_zO_{3-\delta}$ hollow fiber membrane reactor [14].

Summarizing, the effect of CO_2 on the membrane permeation performance plays an important role and thus was examined recently [15]. Under exposure of 50 vol% CO_2 in He, the perovskite structure is impaired up to a depth of ca. 15 μm after 5 h and approximately 30 μm after 10 h, respectively. Furthermore, it was found that both microstructure as well as oxygen permeation are recovered in a CO_2-free atmosphere.

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In order to get a deeper understanding of the processes occurring during application in CO_2 containing atmospheres, we carried out an *in-situ* X-ray diffraction (XRD) as well as transmission electron microscopy (TEM) study on the powder with the composition of $BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$, which is similar to that of $BaCo_xFe_yZr_zO_{3-\delta}$ hollow fiber, and can be considered as a model system.

2. Experimental

Powder with average composition of $BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$ (denoted as BCFZ) was obtained from the Fraunhofer-Institute for Ceramic Technologies and Systems (IKTS, Hermsdorf) from the hydrolysis of corresponding metal nitrates by an ammonium hydroxide solution followed by calcination. $BaCo_xFe_yZr_zO_{3-\delta}$ $(x+y+z=1)$ hollow fiber membranes were manufactured by phase inversion spinning followed by sintering as described elsewhere [1]. The O_2 permeation experiments of the $BaCo_xFe_yZr_zO_{3-\delta}$ hollow fiber membrane, were carried out on a high-temperature permeation reactor which is described in detail elsewhere [1]. *In-situ* powder XRD was conducted on the Bruker D8 Advance diffractometer in Bragg-Brentano geometry using Cu-*K*α radiation with interval of 0.02 and count times of 0.3 s per step. The diffractometer was equipped with an Anton Paar 1200 N high-temperature chamber and superfast 1D Lynxeye detector. XRD data were analyzed using TOPAS 4.0 software (Bruker AXS). Quantitative analyses of XRD collected at isothermal conditions were carried out by Rietveld method. During the *in-situ* experiments at rising and falling temperatures, phases with unknown structures were observed. These phases were included in the refinement by Pawley fits. Then, the phase contents were estimated from the integrated scattered intensities of corresponding phases. The reliability of the both methods was controlled by XRD experiments on BCFZ powder at room temperature in ambient air using of known amount of $BaCO_3$ as internal standard. Structural data for the known phases were taken from ICSD database (FIZ Karlsruhe) with file numbers: $BaCoO_{2.23}$ [28865], $BaZrO_3$ [27048], $BaCO_3$ (orthorhombic) [15196], $BaCO_3$ (rhombohedral) [158389], $BaCO_3$ (cubic) [27449], CoO [28505], and FeO [24635]. Scanning TEM (STEM) was conducted at 200 kV on a JEOL JEM-2100 F-UHR field-emission instrument. A light-element energy dispersive X-ray (EDX) spectrometer, Oxford Instruments INCA-200 TEM, was used for elemental analysis. In order to obtain a TEM sample, the powder was glued between two alumina bodies, polished, and finally Ar^+ sputtered to electron transparency.

3. Results and discussion

The effect of CO_2 on the oxygen permeation performance of the $BaCo_xFe_yZr_zO_{3-\delta}$ hollow fiber at 1173 K is shown in Fig. 1. Insertion of 10 vol% CO_2 on the sweep side of a membrane leads to the diminution of oxygen permeation flux after only few minutes. Then, the oxygen flux through perovskite hollow fiber is almost stopped after dwell time of 30 min. However, the fast recovery of the oxygen permeation can be observed, if the sweep gas is changed to pure He. The value of oxygen flux reaches two-thirds of the initial performance after 5 min. The complete regeneration occurs after testing for 30 min.

According to Czuprat et al. [15], the decline of oxygen permeation flux in presence of CO_2 is due to formation of $BaCO_3$, which was observed by XRD and scanning electron microscopy (SEM) on the surface of quenched $BaCo_xFe_yZr_zO_{3-\delta}$ perovskite hollow fiber. The full recovery of the flux points out to the decomposition of poisoning $BaCO_3$ and the regeneration of the initial structure of hollow fiber.

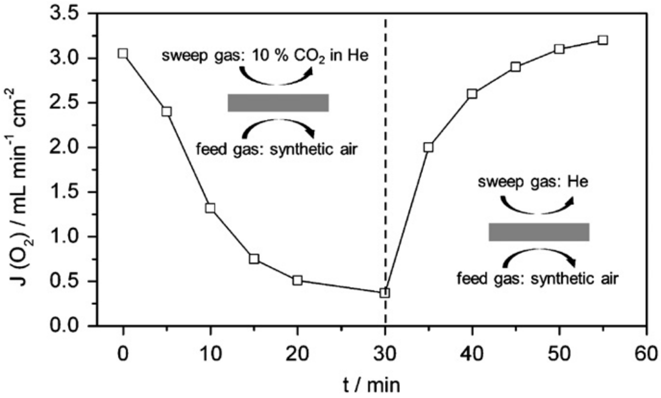

Fig. 1. Decline of O_2 permeation through a $BaCo_xFe_yZr_zO_{3-\delta}$ hollow fiber membrane with effective thickness of 140 μm under CO_2 exposure on the sweep side (sweep side: $F_{total}=50$ mL min^{-1} 10 vol% CO_2 in He; feed side: 150 mL min^{-1} synthetic air (80 vol% N_2, 20 vol% O_2,) and recovery as a function of time while sweeping with pure He at 1173 K (sweep side: 50 mL min^{-1} He; feed site: 150 mL min^{-1} synthetic air (80 vol% N_2, 20 vol% O_2,)).

To prove this hypothesis, the high-temperature *in-situ* XRD in CO_2 containing atmosphere was carried out on the BCFZ powder. Fig. 2 shows *in-situ* XRD-patterns of BCFZ collected at (a) room temperature, (b) at 1173 K in flowing synthetic air consisting 80 vol% N_2 and 20 vol% O_2, and (c) at 1173 K in an atmosphere containing 50 vol% CO_2 and 50 vol% N_2. As can be seen in the room temperature XRD (Fig. 2a), the original BCFZ powder consists of two perovskite systems as reported by Caro et al. [16] previously. The Rietveld analysis of XRD data combined with the EDXS investigation of the initial BCFZ powder exhibit, that the main compound is a $BaCo_{0.5-\gamma}Fe_{0.5-\gamma}Zr_{2\gamma}O_{3-\delta}$ ($\gamma=0.015$–0.025) with cubic structure (space group $Pm\overline{3}m$, $a=4.072$ Å). Furthermore, the powder contains approximately 16 wt% of cubic $BaZrO_3$ perovskite (space group $Pm\overline{3}m$, $a=4.18$ Å). Note, the co-existence of two cubic perovskite phases after doping of 5–10% Zr was also reported for similar perovskite systems like $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2-x}Zr_xO_{3-\delta}$ and $SrCo_{0.4}Fe_{0.6-x}Zr_xO_{3-\delta}$ [17,18]. The high-temperature XRD pattern taken from the BCFZ powder annealed at 1173 K for 30 min in the flowing synthetic air evidences no structural changes. Only slight shift of Bragg-reflection positions to smaller angles can be recognized here due to thermal lattice expansion. The annealing of the BCFZ powder at 1173 K for 90 min under 50 vol% CO_2/50 vol% N_2 leads to the partial decomposition of perovskite structure. $BaCO_3$ can be detected in the *in-situ* XRD pattern (Fig. 2c) alongside of BCFZ. The pattern of $BaCO_3$ relates to the high-temperature rhombohedral polymorph (space group $R3m$), which is stable in the temperature range from approximately 1073 K to 1233 K as reported by Antao et al. [19]. The structure of this phase is not quenchable and cannot be detected by *ex-situ* methods. Quantitative Rietveld analysis was applied to estimate the $BaCO_3$ content in the sample to be about 29 wt%. Additionally, the presence of a fourth phase is obvious by weak intensities at 36.3° and 42.1° 2Θ. This phase can be understood as CoO with help of TEM experiments (see Fig. 5) on the sample quenched in CO_2-containing atmosphere. Change-over of the gas atmosphere to the CO_2-free synthetic air or pure N_2 leads to the complete decomposition of $BaCO_3$ and regeneration of both perovskite phases.

In order to elucidate the kinetics of the carbonate formation and decomposition, series of *in-situ* XRD experiments accompanied by quantitative analysis were carried out determining the content of $BaCO_3$ in the BCFZ powder as function of time. Fig. 3 summarizes the results of quantitative analysis of diffraction patterns collected at 1173 K in time intervals of 15 min at different gas atmospheres. In presence of 50 vol% CO_2 in N_2, the content of $BaCO_3$ amounts to approximately 15 wt% after the first 15 min. After half an hour, the content of $BaCO_3$ reaches about 24 wt%. Then, the amount of carbonate increases slowly and reaches the value of approximately 29 wt% during 90 min. The sluggish kinetic of carbonate formation after the dwell time of 30 min may be explained by the development of the dense