ARTICLE

Influence of CO_2 on Oxygen Surface Exchange Kinetics of Mixed-Conducting $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Oxide

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The poisoning effect of CO_2 on the oxygen surface exchange kinetics of BSCF ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$) is investigated with a novel pulse isotopic exchange technique. The surface exchange rate of BSCF severely decreases after *in situ* exposure to CO_2, which is ascribed to carbonate formation on the material surface. The detrimental effect of CO_2 starts at a low temperature of 375 °C and concentration as low as 1%, and becomes more pronounced at higher temperatures. Degradation of the surface exchange kinetics is associated with a rapid loss of oxygen permeation performance of BSCF in CO_2.

Key words: Surfaces, Solid oxide fuel cells, Oxygen separation, Functional, Perovskite

I. INTRODUCTION

Mixed ionic and electronic conducting (MIEC) perovskite oxides have attracted considerable attention during the last decades for their potential application as cathode materials for solid oxide fuel cells, and as membrane for oxygen separation [1, 2]. One of the most widely studied model materials is $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) due to its excellent mixed-conducting performance [3−6]. Nevertheless, MIEC oxides, particularly BSCF, have been found to be susceptible to the poisoning gas, such as CO_2 [5−9]. Formation of carbonates as well as decomposition of perovskite structure on the surface have been reported in concurrence with degradation of their electrochemical performance.

As degradation of the perovskite bulk is relatively sluggish, the fast reduction of the performance of BSCF is most likely a result of quick degradation in the oxygen surface exchange kinetics [8, 9]. Nevertheless, direct evidence of this correlation, which is very important for understanding the materials properties, is still lacking. In present work, the oxygen surface exchange kinetics of BSCF subjected to CO_2 exposure is studied with the pulse ^{18}O-^{16}O isotope exchange (PIE) technique [10, 11], and discussed in combination with results of stability tests and oxygen permeation flux measurements.

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II. EXPERIMENTS

BSCF powders were prepared by thermal decomposition of a solution of metal nitrates using ethylenediaminetetraacetic acid as the complexing agent. Next, the powders were calcined at 950 °C for 5 h. Disk-shaped membrane was obtained by sintering the pressed powders at 1100 °C for 10 h.

The C1s binding energy of samples was measured using a Quantera SXM scanning XPS. Phase composition was characterized by X-ray diffraction (XRD, Philips PANalytical PW1830). Microstructure examination was performed with scanning electron microscopy (SEM). Temperature-programmed desorption (TPD) was performed as follows. Firstly, BSCF powders, loaded in a quartz micro-reactor, were annealed in a 20%CO_2/21%O_2/He gas stream at a certain temperature for 1 h, and then the temperature was adjusted to 450 °C. After being flushed for 2 h with a CO_2-free stream (21%O_2/He), the sample was cooled to room temperature. The flow rate of both gas streams was 50 mL/min. The reactor was then heated to 850 °C, and the mass spectrometer response of m/z=44 for CO_2 at the exit of the reactor was monitored. Oxygen permeation flux through a BSCF membrane was measured using an apparatus as described in Ref.[12], wherein synthetic air was fed to one (feed) side of the membrane and He or CO_2 to the other (sweep) side. The concentrations of oxygen and nitrogen in the effluent of the sweep side were monitored with an online GC to determine the oxygen permeation flux.

Pulse ^{18}O-^{16}O PIE measurements were performed at a constant Po_2 of 0.21 atm, using a continuous flow packed-bed micro-reactor. Detailed principle

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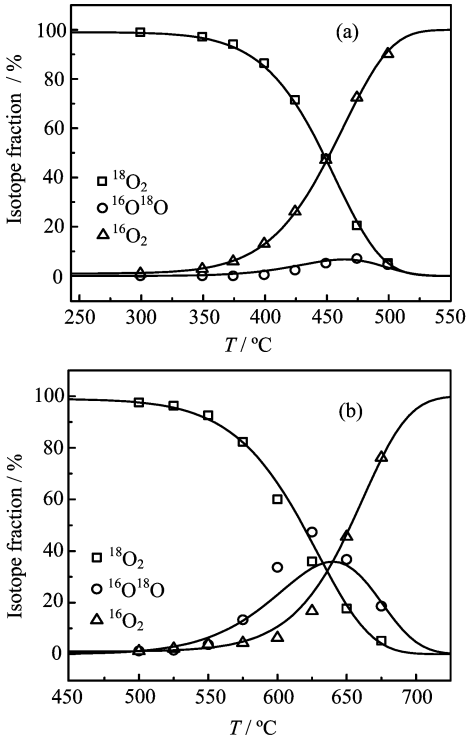

FIG. 1 Isotope fractions of $^{18}O_2$, $^{16}O^{18}O$, and $^{16}O_2$ measured with PIE for BSCF powders pre-equilibrated *in situ* in different carrier gas. (a) CO_2-free and (b) 20% CO_2 at 700 °C for 1 h.

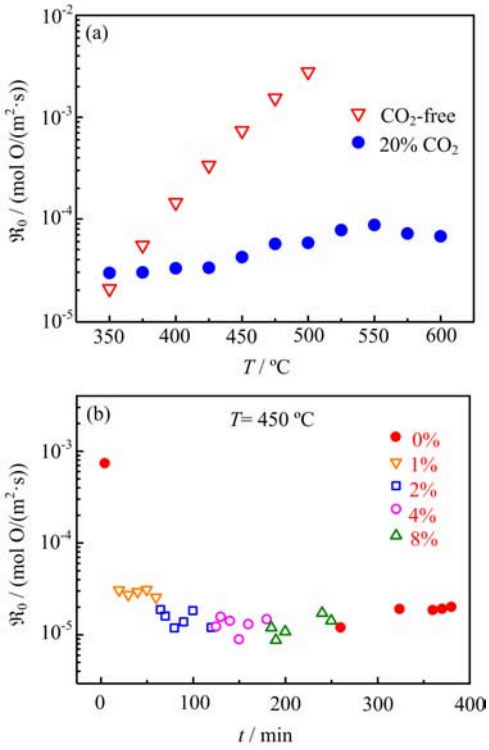

FIG. 2 $\Re_0$ of BSCF at different (a) temperatures and (b) CO_2 concentrations.

and method for the PIE measurements have been described in Ref.[10]. Briefly, BSCF packed bed was pre-equilibrated *in situ* in a 50 mL/min CO_2-free or CO_2-containing (ranged from 1%−20%) $^{16}O_2$/He carrier gas. After injection of 0.5 mL $^{18}O_2/N_2$ gas pulse, oxygen isotopomers ($^{18}O_2$, $^{16}O^{18}O$, and $^{16}O_2$) in the exhaust were analyzed by on-line mass spectrometry (Omni Star™ GSD 301, Pfeiffer-Vacuum). Next, the surface exchange rate ($\Re_0$) was calculated.

III. RESULTS AND DISCUSSION

Figure 1 shows two representative profiles of isotopic exchange fractions during the PIE measurements. Apparently, significant ^{18}O uptake by the sample, indicating onset of oxygen surface exchange, occurs at a temperature starting as low as ∼350 °C for pristine BSCF. In great contrast, after *in situ* exposure of the samples to 20% CO_2 at 700 °C, the onset temperature shifts to ∼525 °C. This results suggest a detrimental blocking effect of CO_2 on $\Re_0$.

Figure 2(a) shows clearly that in a CO_2-free carrier gas, the overall oxygen $\Re_0$ for BSCF, increases significantly with temperature and reaches as high as 2.8 mmol O/(m^2·s) at 500 °C. As 20% CO_2 is introduced into the carrier gas, however, distinct decrease in $\Re_0$ can be observed at 375 °C. The detrimental effect of CO_2 on $\Re_0$ becomes more pronounced at higher temperatures, leading to a 17-fold and 50-fold reduction of $\Re_0$ at 450 and 500 °C, respectively. Figure 2(b) shows the effect of CO_2 concentration on $\Re_0$ of BSCF in another test. It can be seen that upon *in situ* exposure of the sample to 1% CO_2 at 450 °C, $\Re_0$ rapidly drops by 25 times within 20 min. Further increase of the CO_2 concentration only slightly aggravates the $\Re_0$ decline. After removal of CO_2 from the carrier gas, $\Re_0$ basically remains at the reduced value and does not recover. With increase of the post-annealing temperature to 850 °C (Fig.S1 in supplementary material), $\Re_0$ (measured at 450 °C) is restored to 82% of the original value. Furthermore, it is also found that for a higher temperature of CO_2 exposure, the extent of recovery of $\Re_0$ decreases, suggesting more pronounced irreversible damage of CO_2 to the material.

Figure 3(a) shows the C1s binding energy spectra for BSCF samples that have been exposed to 20% CO_2 for 1 h at 450 and 700 °C, both of which exhibit two peaks. The peak at ∼289 eV is associated with the presence of CO_3^{2-} groups, while the one at ∼285 eV is attributed to surface contamination [13]. The more intense peak at ∼289 eV, which is observed after annealed at 700 °C, suggests more significant carbonate formation on the sample surface at higher temperatures. Carbonate formation on BSCF is confirmed by XRD (Fig.S2 in supplementary material), and has been elaborated previously [9]. Figure 3(b) shows the TPD profiles for BSCF powders pre-treated in 20% CO_2. Within

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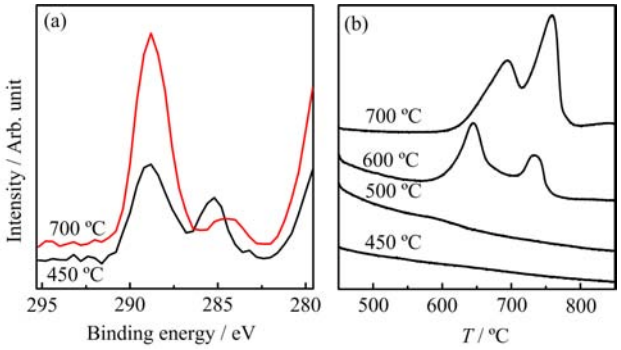

FIG. 3 (a) C1s binding energy spectra and (b) TPD profiles for BSCF samples pre-treated in 20% CO_2 for 1 h at different temperatures.

the detection limit of the mass spectrometric analysis used, no significant desorption of CO_2 is observed for the pre-treatment temperature at 450 and 500 °C. In contrast, two CO_2 desorption peaks are evident in the temperature range of 600−800 °C in the profiles for the pre-treatment temperature at 600 and 700 °C. The presence of two (instead of one) CO_2 desorption peaks could be due to that different carbonate phases are formed during the carbonation reaction of BSCF. The TPD results are principally consistent with the PIE and XPS measurements, indicating that the reaction between BSCF and CO_2 becomes more pronounced at higher temperatures, leading to slower oxygen surface exchange kinetics.

The influence of CO_2 on the performance of BSCF is also studied by measuring the oxygen permeation flux through a 0.5 mm-thick dense BSCF membrane at 900 °C (Fig.S3 in supplementary material). Upon exposure of the sweep side of the membrane to CO_2, the oxygen permeation flux decreased instantly and drastically from a very high value, 2.7 mL/min/cm^2 to almost zero within 60 min. Consistently, significant formation of an impurity layer, which can be ascribed to carbonate [9], can be clearly observed on the surface of a membrane exposed to CO_2 (Fig.S3 in supplementary material). The above-presented results reveal that exposure of BSCF to CO_2 leads to significant degradation of the surface exchange kinetics, due to blocking of the membrane surface by the formed carbonate. The carbonate gives rise to marked decrease or even complete loss of the oxygen permeation performance.

IV. CONCLUSION

It has been demonstrated that PIE is a versatile technique to investigate the kinetics of surface oxygen exchange of oxides. The measurements show that the oxygen surface exchange kinetics of BSCF severely degrades due to blocking of the materials surface by the formed carbonate. The detrimental effect of CO_2 is observed to start from a low temperature of 375 °C and concentration as low as 1%, and becomes more pronounced at higher temperatures. Partial recovery of $\Re_0$ can be achieved by annealing at 850 °C in a CO_2-free atmosphere. Severe degradation of the surface exchange kinetics yields loss of oxygen permeation performance of BSCF in CO_2.

Supplementary material: Influence of the pre-treatment temperature on the recovery of the surface exchange rate by post-annealing BSCF, X-ray powder diffraction patterns of BSCF before and after exposure to CO_2, and oxygen permeation flux of BSCF measured in CO_2 sweep gas are given.

V. ACKNOWLEDGMENTS

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