Influence of CO2 on Oxygen Surface Exchange Kinetics of Mixed-Conducting Ba0.5Sr0.5Co0.8Fe0.2O3-δ Oxide

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The poisoning effect of CO2 on the oxygen surface exchange kinetics of BSCF (Ba0.5Sr0.5Co0.8Fe0.2O3-δ) is investigated with a novel pulse isotopic exchange technique. The surface exchange rate of BSCF severely decreases after in situ exposure to CO2, which is ascribed to carbonate formation on the material surface. The detrimental effect of CO2 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 CO2.

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 Ba0.5Sr0.5Co0.8Fe0.2O3-δ (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 CO2 [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 CO2 exposure is studied with the pulse 18O16O isotope exchange (PIE) technique [10, 11], and discussed in combination with results of stability tests and oxygen permeation flux measurements.

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%CO2/21%O2/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 CO2-free stream (21%O2/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 CO2 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 CO2 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 18O16O PIE measurements were performed at a constant PO2 of 0.21 atm, using a continuous flow packed-bed micro-reactor. Detailed principle...
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.

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 $\mathcal{R}_0$.

Figure 2(a) shows clearly that in a CO$_2$-free carrier gas, the overall oxygen $\mathcal{R}_0$ 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 $\mathcal{R}_0$ can be observed at 375 °C. The detrimental effect of CO$_2$ on $\mathcal{R}_0$ becomes more pronounced at higher temperatures, leading to a 17-fold and 50-fold reduction of $\mathcal{R}_0$ at 450 and 500 °C, respectively. Figure 2(b) shows the effect of CO$_2$ concentration on $\mathcal{R}_0$ of BSCF in another test. It can be seen that upon in situ exposure of the sample to 1% CO$_2$ at 450 °C, $\mathcal{R}_0$ rapidly drops by 25 times within 20 min. Further increase of the CO$_2$ concentration only slightly aggravates the $\mathcal{R}_0$ decline. After removal of CO$_2$ from the carrier gas, $\mathcal{R}_0$ 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), $\mathcal{R}_0$ (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 $\mathcal{R}_0$ decreases, suggesting more pronounced irreversible damage of CO$_2$ to the material.

FIG. 2 $\mathcal{R}_0$ of BSCF at different (a) temperatures and (b) CO$_2$ concentrations.

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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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 \(^\circ\)C and concentration as low as 1\%, and becomes more pronounced at higher temperatures. Partial recovery of \(\mathcal{R}_0\) can be achieved by annealing at 850 \(^\circ\)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.

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