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Oxygen sorption and desorption properties of Sr–Co–Fe oxide

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Abstract

$SrCoFeO_x$ has been investigated as a new sorbent for air separation and oxygen removal at high temperatures. X-ray diffraction analysis of a $SrCoFeO_x$ sample prepared by liquid citrate method reveals that the sample contains an intergrowth ($Sr_4Fe_{6-x}Co_xO_{13\pm\delta}$), perovskite ($SrFe_{1-x}Co_xO_{3-\delta}$), and spinel ($Co_{3-x}Fe_xO_4$) phase. Both oxygen vacancies ($V_{\ddot{O}}$) and interstitial oxygen ions (O_i'') are involved in the oxygen adsorption and desorption process for $SrCoFeO_x$. Compared with the perovskite-type oxide $La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$, $SrCoFeO_x$ has stronger structure stability in a reducing environment and it also exhibits a larger oxygen sorption capacity at temperatures higher than 800 °C. Meanwhile, unlike $La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$ which shows a fast adsorption rate and a slow desorption rate at 900 °C, $SrCoFeO_x$ shows a fast desorption rate and slow adsorption rate at the same temperature. X-ray diffraction data reveals that $SrCoFeO_x$ samples sintered at 1140 °C have a higher amount of the intergrowth phase than samples sintered at 950 °C due to slow formation kinetics. X-ray diffraction and thermogravimetric analysis of $SrCoFeO_x$ samples prepared by the citrate and solid state method show that the synthesis method strongly influences the amount of the three phases in a sample.

Keywords: Air separation; Mixed-conducting oxides; Defect chemistry; Adsorption

1. Introduction

Air separation or oxygen removal from oxygen containing streams at high temperatures is highly desirable for several processes. For example, oxycombustion is a carbon capture technology where the fuel is burned in an oxygen or oxygen enriched carbon dioxide stream rather than air, resulting in a highly pure carbon dioxide exhaust that requires little separation. Barriers for oxycombustion include the high cost associated with oxygen production through cryogenic air separation and energy loss due to large quantities of CO_2 exhaust recycle to control combustion temperatures (Klara and Srivastava, 2002; Rodewald et al., 2005). If air can be separated at high temperatures, warm oxygen can be directly used for the oxycombustion providing substantial energy saving for air separation.

Recently, Lin and co-workers reported an air separation process with a perovskite-type metal oxide sorbent (Lin et al., 2000; Yang et al., 2002). This process not only separates air at high temperatures but offers extremely high selectivity for oxygen. The new sorption separation process takes advantage of the unique properties of these perovskite-type oxides that can adsorb large quantities of oxygen, but not other gases, into the oxygen vacancy sites at high temperatures. The sorption and desorption mechanism is based on the reversible defect reaction involving the gas phase molecular oxygen, oxygen vacancy, lattice oxygen, and electronic hole (Mizusaki et al., 1984, 1989). Infinitely high selectivity for oxygen over nitrogen and high oxygen adsorption amounts are the major characteristics of this group of materials.

A series of fundamental studies on perovskite-type oxides as sorbents were performed in our laboratory including: selection and syntheses of materials (Yang et al., 2002; Yang and Lin, 2002), oxygen sorption equilibrium, (Yang et al., 2002; Yang and Lin, 2002, 2003a), oxygen sorption thermal effects, (Yang and Lin, 2005), and oxygen sorption and desorption kinetics as well as fixed-bed process performance (Yang and Lin, 2003b). To be a promising sorbent material for air separation, the perovskite-type oxide must have a high oxygen sorption capacity as well as a fast sorption/desorption

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rate. It has been reported that the perovskite-type oxide, $La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$ (LSCF1991), can adsorb oxygen up to 0.6 mmol/g with no sorption for nitrogen. The process has a fast oxygen sorption rate but a rather slow oxygen desorption rate. The desorption rate needs to be increased in order to achieve a high O_2—product purity and to improve sorbent regeneration efficiency.

Our group has recently reported several approaches to increase the oxygen desorption rate of LSCF1991 for air separation. One approach is to decrease the crystalline size of the sorbent by decreasing the powder sintering temperature (Yin et al., 2006). We also found that both the oxygen sorption capacity and desorption rate can be improved by taking advantage of the oxygen vacancy order–disorder phase transition for some lanthanum cobaltites (Yin and Lin, 2007). For some perovskite-type ceramics below the phase transition temperature, decreasing the oxygen partial pressure (oxygen desorption) is accompanied with a phase transition from the oxygen vacancy disordered to ordered structure. Such a phase transition significantly enhances the oxygen desorption rate and the reverse oxygen adsorption step yields much higher oxygen sorption capacity as compared to the process without the order–disorder phase transition. The third approach to improve the properties of perovskite-type metal oxides is to dope Ag^+/Ni^+ ions in the perovskite-type structure (Yin and Lin, 2006). Doping Ag^+/Ni^+ into the LSCF1991 lattice structure increases the tendency of order–disorder phase transition and enhances the surface catalytic properties for oxygen sorption and desorption. These efforts can improve the oxygen sorption properties of perovskite-type oxide LSCF1991 in the temperature range of 600–800 °C.

The approaches listed above are based on modifying or taking advantage of the unique properties of the existing perovskite-type metal oxides. As a result, there are limitations in the above approaches with respect to improving the sorption and desorption properties for this group of metal oxide sorbents. For example, enhancement in the desorption rate by the disorder to order phase transition will only take place below the phase transition temperature (typically below 800 °C). Therefore, the logical step to identify sorbents with improved properties is to explore metal oxides of different structure or composition. Ma et al. (1996a, b) reported that $SrFeCo_{0.5}O_x$ membranes exhibit high oxygen ion conductivity with a stable oxygen permeation flux of 10^{-6} mol cm^{-2} s^{-1} at 900 °C. This material consists of an intergrowth phase ($Sr_4Fe_{6-x}Co_xO_{13\pm\delta}$), a perovskite phase ($SrFe_{1-x}Co_xO_{3-\delta}$), and a spinel phase ($Co_{3-x}Fe_xO_4$) (Ma et al., 1998; Guggilla and Manthiram, 1997; Fjellvag et al., 1997). This paper reports a study on the oxygen adsorption and desorption of this group of materials with a focus on a new non-perovskite-type material $SrCoFeO_x$ (SCF111) that exhibits much improved properties as a sorbent for air separation at temperatures higher than 800 °C.

2. Experimental

$SrCo_zFe_yO_x$ (SCF) with different values of z and y were prepared by the liquid citrate method. Stoichiometric amounts of the corresponding metal nitrates $Sr(NO_3)_2$, $Fe(NO_3)_2$ and $Co(NO_3)_2$ were first dissolved by de-ionized water in a beaker and then citric acid (50% excess for the reaction) was added. The resulting solutions were under heating and stirring conditions during the polymerization and condensation reactions, which were carried out at 100–105 and 105–110 °C, respectively. At the end of the condensation reaction, viscous gels were obtained. Self-ignition was performed at approximately 400 °C in air to burn out the organics from the resulting gels after they had been dried at 110 °C for 20 h. Finally, the powders were sintered at 1140 °C (or 950 °C for studying the sintering temperature effect) for 20 h with a ramping rate of 60 °C h^{-1}. For comparison, perovskite-type oxide LSCF1991 was prepared by the same citrate method by the procedure detailed in a previous publication (Yin and Lin, 2007). SCF oxides were also prepared by the solid state reaction (SSR) method. In this method, stoichiometric amounts of $SrCO_3$, Fe_2O_3, and $Co(NO_3)_2$ were dissolved into ethanol and ball-milled for 20 h. The obtained mixtures were calcined in air at 950 °C for 16 h. Finally, the resulting calcined powder was ball-milled again for 8 h. The morphologies and particle sizes of the resulting samples were studied by using SEM (Hitachi, S-4000). X-ray diffraction (XRD) (Simens, D50, CuKα1) was utilized to characterize the crystal structure of the samples.

Oxygen sorption and desorption on the samples were measured by a simultaneous DSC/TGA instrument (TA Instruments, SDT 600). The oxygen sorption/desorption process starts when the sample experiences a sudden increase/decrease in the oxygen activity of the gas stream passing through the sample compartment at a given temperature. For a typical experimental measurement, about 50 mg of a powder sample was placed in the alumina sample holder. Then the sample compartment was heated to 110 °C to remove the water in the sample. The weight of the sample was monitored until a stable value was achieved. The dry sample was then heated to the desired temperature (e.g., 900 °C) in a He atmosphere ($P_{O_2} = 0.0001$ atm, determined by the impurity of helium) and kept isothermally until a stable weight was observed from the thermogravimetric analysis (TGA) kinetic curves. The feed gas was subsequently quickly switched from He ($Po_2 = 0.0001$ atm) to dry air ($Po_2 = 0.21$ atm) to initiate the oxygen sorption process. The corresponding weight change and the heat effect were automatically recorded by TGA/DSC instrument.

The oxygen sorption capacity of the metal oxide was determined from the following equation by TGA measurements:

$$q = \frac{1}{2M_O}\left[\frac{w(\mathrm{air}) - w(\mathrm{He})}{w(0)}\right], \tag{1}$$

where $w(\mathrm{air})$ and $w(\mathrm{He})$ are the equilibrated sample weight at a particular temperature in air and He, respectively. $w(0)$ is the initial oxygen nonstoichiometry and weight of the sample under reference conditions (room temperature and 1 atm air). $M_o(=16)$ is atomic weight of oxygen. In addition, the kinetics and heat effect during the desorption process were also measured for the same sample subjected to a change of the surrounding gas from air to He.