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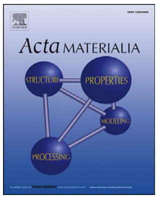

Full length article

Panoscopic alloying of cobalt in CeO_2–ZrO_2 solid solutions for superior oxygen-storage capacity

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ABSTRACT

Oxygen processes (reduction and evolution) play a central role in a variety of physical and chemical applications to meet the growing demands for energy and environmental protection. However, the discovery and optimization of such functional materials are great challenges because they are still hampered by material inherencies and thermodynamic limits. Here, we demonstrate the fabrication of a novel material structure via atomistic doping and nanoscale compositing, a panoscopic alloying powder (PAP) of cobalt in a CeO_2–ZrO_2 solid solution. This novel structure possesses superior oxygen-storage capacity (OSC) and improved structural stability because it retains the best features of both transition-metal oxides and ceria-based ceramics. According to the thermogravimetry and dilatometry measurements of a 10 mol% PAP sample, $(Ce_{0.65}Co_{0.10})Zr_{0.25}O_{2-\delta}$, at 800 °C under cyclic reduction–oxidation, an OSC of 2312 μmol-O g^{-1} was successfully obtained with negligible structural change and a linear strain of 1%.

1. Introduction

In the current era of heightened energy and climate concerns, solid-state materials that serve as reversible oxygen carriers have drawn interests for a variety of applications, including gas-phase treatments (automotive three-way catalysts [1–3] and air separation [4]), electrochemical devices (sensor [5], batteries [6], and fuel cells [7,8]), and fuel processing (chemical looping combustion and syngas generation) [9–11]. In particular, any oxygen-carrier material that can feasibly store and release oxygen reversibly and spontaneously on a large scale [3,12,13], denoted as a material with oxygen-storage capacity (OSC) [14–16], is considered as one of the most important tool for achieving a novel and superior energy and environmental device (or facility). To understand the OSC phenomenon and to search for a high-performance OSC material, various theoretical, computational, and experimental studies have been extensively performed in the last three decades [3,16–20].

Ceria (CeO_2)-based oxides are one of the most commonly used and studied OSC materials [1,21,22]. Depending on the surrounding atmosphere [18,23], this fluorite-structured material (space group: No. 225, $Fm\bar{3}m$) undergoes a considerable reversible reduction–oxidation (redox) reaction [$CeO_2 \leftrightarrow CeO_{2-\delta} + (\delta/2)O_2$ for $\delta = 0$ to 0.5]. After the first report on the OSC of CeO_2 in the mid-1980s [19], researchers have extensively investigated ways to improve its OSC performance and durability by employing the cation substitution, doping, and structural meso- and nano-architecture [24,25]. Among such approaches, the well-established ceria–zirconia (CeO_2–ZrO_2, $Ce_{1-x}Zr_xO_2$, or CZ) solid solutions offer improved OSC performance and notable structural stability. Substituting isovalent and small-sized Zr^{4+} ions for Ce^{4+} ions in the lattice stabilizes the $CeO_{2-\delta}$ structure during the severe redox cycle, and it was recently shown that notable OSC values of 730 [26] and 1116 [27] micromoles of oxygen per gram of the sample (μmol-O g^{-1}) were obtained at 500 and 700 °C. The use of some trivalent rare-earth ions (La, Pr, Sm, Tb, and Y) [1,13,16,20] and aliovalent transition elements (Cr, Mn, Cu, Ru, and Pb) [28,29] at Ce^{4+} sites have also been reported at varying ranges of composition, atmosphere (e.g. oxygen partial pressure, P_{O_2}), and temperature (T). Despite the remaining ambiguities regarding the oxygen-

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storage mechanism, many researchers have made great strides in the improvement and application of OSC materials.

In addition to CeO_2-based oxides, many other metal oxides and non-stoichiometric oxide materials can be good candidates for next-generation OSC materials. Despite their multiple oxidation states and capability of oxygen incorporation and evolution, they are not classified as OSC materials because of their limitations in three essential aspects of OSC—reversibility, scale, and speed [11,28,30]. Cobalt and its oxide are also negatively affected by similar redox features because of their multiple oxidation states over an extensive temperature range (at $P_{O_2} = 0.21$, $T_{CoO_x \rightarrow Co_3O_4} \approx 325$ °C and $T_{Co_3O_4 \rightarrow CoO} \approx 890$ °C) [31], and this results in the slow kinetics of their redox behaviour. In addition, metallic Co has been observed to show severe volume shrinkage in a highly reducing atmosphere (i.e. sintering) and inhibit the reversibility of OSC performance during the redox cycle. However, other interesting inherencies (e.g. high catalytic and alloying activities) [32] of Co-based oxides still render them one of the most attractive group of next-generation OSC materials. So far, attempts to employ metal oxides as superior OSC materials have not been successful because of the above-mentioned inadequate redox properties and limitations of structural configurations [28,30–32].

In the study reported here, we synthesized a novel panoscopic alloying powder (PAP), $(Ce_{0.65}Co_{0.10})Zr_{0.25}O_{2-\delta}$ or CCo10Z for short, which consisted of a heterogeneous multiscale structure of Co and CZ formed from an integration of multiscale processes ranging from atomic alloying to nanoscale compositing. The powder improved the OSC performance of Co and CZ, surpassing the well-known material limits of CZ and suppressing structural changes in the high-temperature redox cycle. Using the comprehensive thermophysical analysis and spectroscopy techniques, we quantified its exact OSC performance as a function of temperature and investigated the origins of anomalies in the PAP of Co and CZ.

2. Experimental

2.1. Sample preparation

All the powders were prepared by a single-step glycine–nitrate process (GNP). Cerium (III) nitrate hexahydrate (Kanto chemicals), zirconyl nitrate solution (35 wt% in diluted nitric acid, Sigma Aldrich), cobalt (II) nitrate hexahydrate (Junsei Chemical) were used as the sources of Ce, Zr, and Co respectively. Glycine (Junsei Chemicals) was used as a combustion fuel for GNP. In a typical GNP, stoichiometric amounts of $Ce(NO_3)_3 \cdot 6H_2O$, $ZrO(NO_3)_2$, and $Co(NO_3)_3 \cdot 6H_2O$ were used to obtain samples of $(Ce_{0.70}Co_{0.05})Zr_{0.25}O_2$, $(Ce_{0.65}Co_{0.10})Zr_{0.25}O_2$, $(Ce_{0.55}Co_{0.20})Zr_{0.25}O_2$, and $Ce_{0.75}Zr_{0.25}O_2$, hereafter referred to as CCo5Z, CCo10Z, CCo20Z, and CCo25Z, respectively. These chemical compounds were dissolved in distilled water and 0.55 mol of glycine was added to each mole of nitrate. The mixture was stirred with a magnetic stirrer at 200 rpm for 3 h, followed by heating to evaporate water in the solution. Combustion was carried out in a large-volume beaker on a hot plate. The powder produced by spontaneous ignition was collected from the reaction chamber and then sieved to sort the powder into proper size (~150 μm). After that, the sorted powder was calcined at 600 °C for 3 h to remove the polymer. Finally, the powder was ball-milled for 48 h to obtain homogeneous particles. In addition, several composites of $Ce_{0.75}Zr_{0.25}O_2$ and Co_3O_4 (obtained via GNP) were prepared by mixing and grinding the two powders in agate mortar.

2.2. Sample characterization

The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) of each prepared powder was measured by N_2 adsorption using a fully automated surface analyser (TriStar II, Micromeritics). Before analysis, the samples were pretreated at 300 °C for 1 h under vacuum condition in a sample degassing system (VacPrep 061, Micromeritics). The crystalline phases of each prepared powder were analysed by using an X-ray diffractometer (XRD; D/Max 2500, Rigaku) with Cu K_α radiation. In order to determine the change in electrovalence of cobalt in the doped and composite samples in a reduction atmosphere, the samples were heated at 800 °C in a reduction atmosphere (4%H_2–Ar) for 3 h. A transmission electron microscope (TEM; Talos F200X, FEI) equipped with an energy-dispersive spectrometer was operated at 200 kV to analyse the distribution of various elements in the PAP and composite samples. Another TEM (Titan 80–300, FEI) equipped with an electron energy-loss spectrometer (EELS) was operated at 300 kV to determine the change in electrovalence of cobalt in the doped and composite samples in a reduction atmosphere. The samples were heated at 800 °C in 4%H_2–Ar for 3 h. The linear thermal expansion of each prepared powder was measured by using a horizontal pushed dilatometer (DIL 402C, Netzsch). The samples were heated to 1400 °C at a rate of 10 °C min^{-1} under atmospheric condition. The chemical expansion of each powder was obtained under isothermal and gas-changing conditions. To set up the oxidation and reduction environments, 18%O_2–Ar and 0.73%H_2–Ar were used repetitively for 3 h at 800 °C.

2.3. OSC measurements

Thermogravimetric analysis (TGA; SETSYS evolution, Setaram) was carried out. About 50 mg of each prepared sample was placed into a platinum crucible and heated to 500 or 800 °C. The redox atmosphere in the analyser was obtained by alternating between the auxiliary gas of O_2 and 4%H_2–Ar (40 sccm) every 3 h. An Ar balance (180 sccm) was used to prevent the impact of the gas inlet while the percentage weight loss was monitored. Temperature-programmed reduction (TPR; AutoChem II 2920, Micromeritics) spectra of the prepared powders were acquired by using 10% H_2–Ar at a flow rate of 100 sccm and the furnace temperature was increased to 900 °C at a linear ramp of 10 °C min^{-1}. The samples were pretreated at 300 °C for 1 h before analysis.

3. Results and discussion

3.1. Synthesis of a panoscopic alloying powder, cobalt in CeO_2-ZrO_2 solid solutions

The concept of panoscopic alloying is designed for the fabrication of a novel structure, and it includes multiscale approaches like atomistic doping and nanoscale compositing. As shown in Fig. 1a, we applied this concept to the system of cobalt in a CZ structure, and the product was expected to yield superior OSC performance from the best features of cobalt oxides (flexible oxidation states and remarkable oxygen uptake ability) [11,13,33] and CZ solid-solutions (fast oxygen mobility and excellent reversibility) [1–3]. Two key features of this PAP synthesis are (i) the cobalt solubility limit in CZ and (ii) the homogeneous dispersion of nanoscale cobalt oxides for nanostructured composites of Co_3O_4 and CZ. As mentioned in the Experimental section, we developed a novel process for synthesizing this PAP structure via a single-step GNP, offering homogeneous dispersion of cobalt dopants and heterogeneous structures of precipitated cobalt oxides in CZ because of the limited cobalt solubility. The structural properties of various PAP samples with different concentrations of cobalt (CCo5Z: CZ with 5 mol% Co; CCo10Z: CZ with 10 mol% Co; CCo20Z: CZ with 20 mol% Co) and a comparison group (CZ solid-solution and a conventional CZ–Co composite) were investigated by various experimental techniques,