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A Thermodynamic Study of Nonstoichiometric $Ce_{0.97}Zr_{0.03}O_{2-\delta}$ for Dissociation of H_2O

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The thermodynamic properties of 3%mol zirconia doped ceria nano-size powders prepared by sol–gel were studied by thermogravity analysis. The entropy and enthalpy extracted from the data of thermogravity experiment of 3%mol zirconia doped ceria compared with undoped ceria were analyzed. The data of Gibbs free energy calculated by the data of entropy and enthalpy of 3%mol zirconia doped ceria compared with undoped ceria and water were investigated. The temperature range and the heat energy required of dissociating water obtained from the data of Gibbs free energy of 3%mol zirconia doped ceria compared with undoped ceria were shown as the result of this study.
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1. Introduction

Ceria is widely studied for its thermodynamic property of nonstoichiometry.[1)] Recently, the thermodynamic property of ceria is developed to dissociate water to produce hydrogen in the field of clean energy.[2,3)] The redox reaction of Ceria is shown in eqs. (1) and (2). At the high temperature ceria is reduced and release the oxygen. While at the low temperature, the reduced ceria is oxidized again and absorb

$$\text{High temperature:}\quad CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2}O_2 \qquad (1)$$

$$\text{Low temperature:}\quad \delta H_2O + CeO_{2-\delta} \rightarrow \delta H_2 + CeO_2 \qquad (2)$$

the oxygen from water resulting in the releasing of hydrogen. Furthermore, in order to improve the efficiency of the hydrogen production researchers try to explore new materials to substitute for ceria. Ceria-zirconia solid solutions are the ideal candidate for dissociating water because they have been proved to provide more oxygen-storage capacitance in automotive three-way catalysts than ceria.[4–10)] But the doping level of zirconia is the key factor for the efficiency of hydrogen production. Pyrochlore phase which is proved to impede the efficiency of hydrogen production is found in 50%–75%mol zirconia doped ceria.[11)] 20%mol zirconia doped ceria is much easier to be reduced than undoped ceria but the very lower temperature of hydrogen production leads to the low kinetic of such process.[12)] In this study, the rather small amount 3%mol zirconia doped ceria (ZDC03) was studied to compare with the undoped ceria and it shows us some advantage thermodynamic properties for dissociating water.

2. Experimental

2.1 Thermogravity (TG) sample preparation

In order to prepare the nano-size powders for the thermogravity measurement sol–gel method was used to prepare ZDC03 powders. The sol–gel synthesis process is as following: Dissolve 3 mol% $ZrO(NO_3)_2{\cdot}2.3H_2O$ in the dilute HNO_3 and dissolve 97%mol $Ce(NO_3)_3{\cdot}6H_2O$ in water (~800 mL). Mix the two solutions with EDTA and citric acid then add about 100 mL (gradually) NH_4OH to achieve pH ~ 10. Stir while heating at 80°C until gelation. Put the beaker into combustion oven in the hood, set to max and dry till crispy. The top should be covered with aluminum foil with holes to allow gas going out. Move the powder from the beaker to a large alumina crucible (to avoid overflowing in the next step). Put the alumina crucible into the heating mantle and evolve at 300°C (~10 h). Stir and compact the gel a few times during this period. Move the crucible to Bistromath furnace and calcine at 950°C for 10 h.

The as-prepared ZDC03 powders must be sintered at 600°C for 2 h to make sure there are no oxygen vacancies at the beginning status before the TG measurement.

2.2 Microstructural characterization

The microstructure of ZDC03 powders Phase analysis was performed by X-ray diffraction using a Phillips X'Pert Pro powder diffractometer (Cu KR, 45 kV, 40 mA). Rietveld refinement was used to analyze the phase composition by the software of Highscore plus.

2.3 TG measurement

The as-prepared powders were put into the platinum crucible of the TG equipment (Netzsch 2000, Germany). The same weight (300 mg) powders were used in every test. The test gas combination, temperature and stabilizing time are shown in Tables 1 and 2. The actual oxygen partial pressure was checked by the oxygen sensor.

Table 1 Test gas combination and temperature scope at TGA.

Gas	Temperature scope
0.1%H_2 (wet)	600–1500°C
1%H_2 (wet)	
10%H_2 (wet)	
0.01%O_2	
1%O_2	

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Table 2 TGA temperature control scheme.

Temp	Stabilizing time	Temp	Stabilizing time
600°C	0.5 h	1100°C	1 h
700°C	0.5 h	1200°C	1 h
800°C	0.5 h	1300°C	2 h
900°C	0.5 h	1400°C	3 h
1000°C	1 h	1500°C	4 h

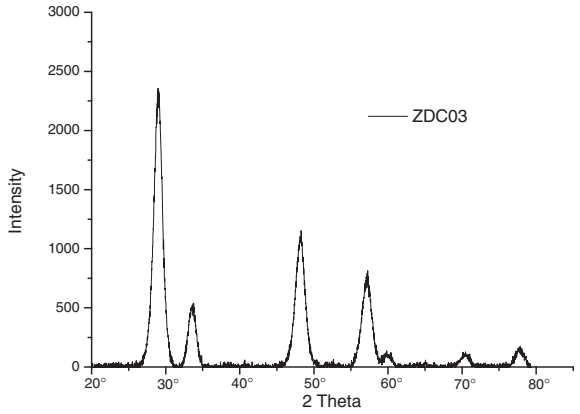

Fig. 1 XRD pattern of ZDC03 powder.

3. Results and Discussions

The crystal structure of ZDC03 is shown in Fig. 1. The XRD result shows that 3%mol zirconia doping doesn't change the original crystal structure of undoped ceria which is 100% cubic phase.

Nonstoichiometry value δ of ZDC03 could be calculated through the data of the weight loss of ZDC03 which is shown in eq. (3). Where Δm is the weight loss of

$$\frac{\Delta m}{m} = \frac{M_O \delta}{M_{ZDC}}. \tag{3}$$

ZDC03; m is the original weight of ZDC03; M_O is the atomic weight of oxygen atom; M_{ZDC} is the atomic weight of ZDC03. Different nonstoichiometry values of oxygen atom of ZDC03 at different temperature and different oxygen partial pressure are shown in Fig. 2. The δ of ZDC03 and undoped ceria are similar at the same temperature and the same oxygen partial pressure. With the increase of the oxygen partial pressure the δ of ZDC03 is slightly lower than that of undoped ceria. It means ZDC03 is more difficult to be reduced than undoped ceria in the higher oxygen partial pressure area. Additionally, as shown in Fig. 2, the distance between every two isothermal curves becomes shorter from the data of same material. It means the tendency of the changing of the values of δ goes slowly with the increase of the temperature. In other words the increasing tendency of the appearance of oxygen vacancies becomes slowly.

The thermodynamic parameter entropy (ΔS) and enthalpy (ΔH) at different temperature and different oxygen partial pressure could be obtained by the results of Fig. 2. According to eq. (4), the equilibrium constant for oxidation of ZDC03 is directly related to $P(O_2)$, since the activities of solid phases

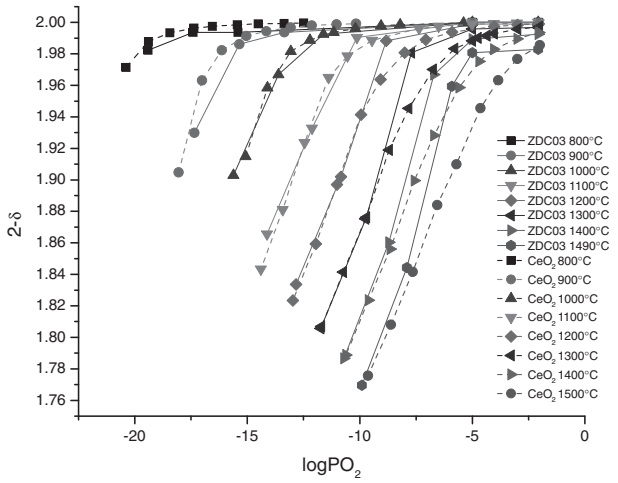

Fig. 2 TG measurement results of ZDC03 VS CeO_2.

are one we can get $K = P_{O_2}^{-1}$. Therefore, the measurement of $P(O_2)$ as a function of δ provides the equilibrium

$$\Delta G_T = -RT \ln K = \Delta H - T\Delta S \tag{4}$$

constant and the Gibbs free energy, ΔG, for reaction at that value of δ. So the thermodynamic parameter entropy (ΔS) and enthalpy (ΔH) at different temperature and different oxygen partial pressure could be fitted and calculated using eqs. (5) and (6). The data of ΔS and ΔH of ZDC03 compared to undoped ceria corresponding

$$\Delta H = -R \frac{\partial(\ln P_{O_2})}{\partial T^{-1}}\bigg|_{\delta} \tag{5}$$

$$\ln_{P_{O_2}} = \frac{\Delta H}{R} T^{-1} - \frac{\Delta S}{R} \tag{6}$$

to the different δ are shown in Fig. 3. Compared with undoped ceria, in the range of which the value of δ is from 0 to 0.067 ZDC03 possesses much lower ΔH. While in the range of which the value of δ is from 0.067 to 0.155, the value of ΔH of ZDC03 is slightly higher than that of undoped ceria. Shortly, at the beginning stage of reduction, the heat energy ΔH of undoped ceria is much higher than that of ZDC03 which means ZDC03 is much easier to be reduced than undoped ceria. While with the increase of the oxygen vacancies the values of ΔH of undoped ceria and ZDC03 become similar and ZDC03 even processes a little higher values of ΔH.

The data of Gibbs free energy, ΔG, could be easily obtained from eq. (4) using the data from Fig. 3. The data of Gibbs free energy of ZDC03 and undoped ceria compared to the gas water are shown in Fig. 4. As shown in Fig. 4, the two pink lines are the free energy of the beginning of reduction and the end of reduction of ZDC03 while the two dot black lines are those of undoped ceria. The single red line is the free energy of gas water at different temperature. According to the concept of Gibbs free energy, the oxygen of gas water could be taken by ZDC or ceria in the case of the ΔG of those two materials are lower than that of gas water. So the temperature range of ZDC03 to dissociate water is from 830 to 960°C while the temperature range is from 800 to 960°C which is very similar for undoped ceria. As a result, ZDC03 has the similar temperature range which is proved to be the ideal temperature range[2)] for dissociating water to

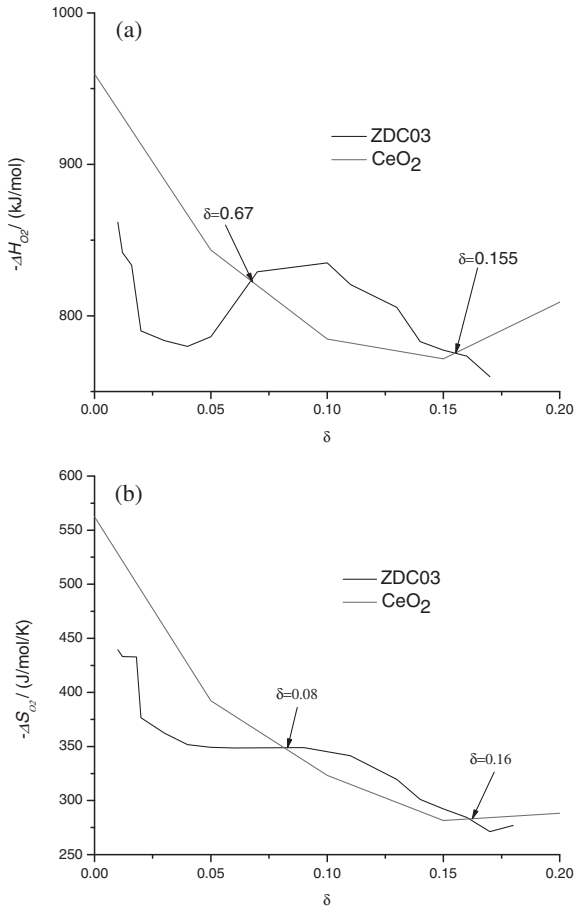

Fig. 3 Comparison of thermodynamic properties of ZDC03 and undoped CeO_2 (a) enthalpy (b) entropy.

undoped ceria. The efficiency and the productivity of the hydrogen comparison of ZDC03 and ceria will be studied in our future research.

4. Conclusions

ZDC03 has the same crystal structure with undoped ceria. ZDC03 is easier to be reduced than undoped ceria because it needs much less heat energy than undoped ceria especially in the range of small δ by analyzing the data of ΔH. ZDC03 doesn't suffer the problem of low kinetic for dissociating water because it processes the similar higher temperature range to undoped ceria.

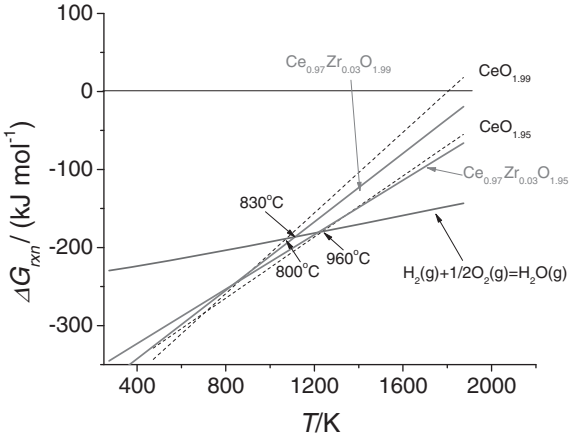

Fig. 4 Comparison of the Gibbs free energy of the gas-phase hydrogen oxidation reaction, of ZDC03, and undoped CeO_2 with different oxygen nonstoichiometry.

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