The electronic conductivity of samarium doped ceria

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Introduction

Samarium doped ceria ($Ce_{0.8}Sm_{0.2}O_{1.9}$, SDC) as a promising electrolyte material for solid oxide fuel cells (SOFCs) has been extensively researched for its higher ionic conductivity at intermediate temperature compared with standard yttria-stabilized zirconia [1]. However, SDC exhibits mixed electronic and ionic conduction, especially at low oxygen partial pressure, which results in an inner short-circuit and lower the open circuit voltage of SOFC [2].

In this work, the electronic conductivity of SDC was measured with the modified e.m.f. method which is an effective technique to determine the minor electronic contributions to the total conductivity of the mixed ionic and electronic conductors [3]. Besides, a novel concentration cell with a reference electrode was constructed to combine the e.m.f. method with three-electrode system to verify the effectiveness of the modified e.m.f. method.

Materials and Methods

$Ce_{0.8}Sm_{0.2}O_{1.9}$ was prepared with the oxalate co-precipitation method [4]. As-prepared SDC powders were uniaxially pressed under 250 MPa into a pellet with 13 mm in diameter and 1 mm in thickness, and then sintered at 1500 °C for 5 h in air to form a dense pellet with about 96% of the theoretical density. The sintered pellet was polished to a slice with 0.3 mm in thickness. The annular platinum electrodes with 11 mm in outer diameter and 4 mm in inner diameter and the platinum reference electrode with diameter of 2 mm were painted on the pellet. Then the painted pellet was calcined at 1273 K for 1 h to ensure high adherence.

The modified e.m.f. method combined with AC impedance spectroscopy and three-electrode system was used to measure the electronic conductivity and oxygen ionic transport number of SDC and verify the effectiveness of the modified e.m.f. method in the temperature range of 500-700 °C with the oxygen chemical gradient of 1/0.21 atm.

Results and Discussion

The electronic and ionic conductivities of SDC measured under our experimental condition are listed in Table 1. At lower temperatures, i.e., 500-600 °C, the ionic conductivity is approximately 2 orders of magnitude higher than the electronic conductivity, but as the temperature rises, the advantage for ionic conduction is gradually weakened. When the temperature is higher than 650 °C, the electronic conduction becomes more obvious, and at 700 °C the oxygen ionic transport number reduces to 0.956.

The open circuit voltages of the concentration cell predicted from the data measured with the e.m.f. method and three-electrode system are listed in Table 2 and are compared with the measured values, and the differences are less than 2 mV, which indicates that modified e.m.f. method is an effective method to measure the electronic conductivity of SDC.

Table 2 also gives the oxygen ionic transport numbers calculated with different methods, i.e., the classical e.m.f. method ($t_{\text{classical emf}}$) [5], the modified e.m.f. method ($t_{\text{modified emf}}$), and the method that Näfe recommended ($t_{\text{recommend}}$) [6]. As is shown in Table 2, the ionic transport numbers calculated with the traditional e.m.f. method are much lower than those with the modified e.m.f. method due to the non-negligible electrode polarization resistances, and the ionic transport numbers calculated with the modified e.m.f. method are highly accorded with the values calculated with the method recommended by Näfe.

Table 1. Electronic and oxygen ionic conductivities of SDC at different temperatures

T (°C)	$\sigma_e \times 10^5$ (S cm^{-1})	$\sigma_o \times 10^3$ (S cm^{-1})	t_o
500	0.916	3.56	0.997
550	2.18	4.85	0.996
600	7.21	10.2	0.993
650	28.6	16.8	0.984
700	116	24.9	0.956

Table 2. Comparison of the predicted and measured open circuit voltages and the oxygen ionic transport numbers calculated with different methods

T	open circuit voltage (mV)		oxygen ionic transport number		
(°C)	$U_{\text{predicted}}$	U_{measured}	$t_{\text{classical emf}}$	$t_{\text{modified emf}}$	$t_{\text{recommend}}$
500	14.5	13.2	0.505	0.997	0.997
550	16.5	15.0	0.541	0.996	0.995
600	19.0	19.5	0.663	0.993	0.994
650	21.1	21.1	0.677	0.983	0.983
700	22.9	24.6	0.751	0.955	0.965

Significance

The electronic conductivity of SDC was measured at 500-700 °C under the oxygen chemical gradient of 1/0.21 atm and the apparent activation energy of electronic and oxygen ionic conduction were calculated, i.e., 1.65 eV and 0.74 eV, respectively. The effectiveness of the modified e.m.f. method was verified.

References

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