

## ARTICLE

**Ionic Conduction and Fuel Cell Performance of  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  Ceramic**

Li-gan Qiu\*

Department of Chemistry, Yancheng Normal College, Yancheng 224002, China

(Dated: Received on July 25, 2005; Accepted on October 9, 2005)

The perovskite-type-oxide solid solution  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  was prepared by high temperature solid-state reaction and its single-phase character was confirmed by X-ray diffraction. The ionic conduction of the sample was investigated using electrical methods at elevated temperatures, and the performance of the hydrogen-air fuel cell using the sample as solid electrolyte was measured, which were compared with those of  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ . In wet hydrogen,  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  almost exhibits pure protonic conduction at 600-1000 °C, and its protonic transport number is 1 at 600-900 °C and 0.99 at 1000 °C. Similarly,  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  exhibits pure protonic conduction with the protonic transport number of 1 at 600-700 °C, but its protonic conduction is slightly lower than that of  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ , and the protonic transport number are 0.99-0.96 at 800-1000 °C. In wet air, the two samples both show low protonic and oxide ionic conduction. For  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ , the protonic and oxide ionic transport numbers are 0.01-0.11 and 0.30-0.31 respectively, and for  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ , 0.01-0.09 and 0.27-0.33 respectively. Ionic conductivities of  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  are higher than those of  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  under wet hydrogen and wet air. The performance of the fuel cell using  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  as solid electrolyte is better than that of  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ . At 1000 °C, its maximum short-circuit current density and power output density are 465 mA/cm<sup>2</sup> and 112 mW/cm<sup>2</sup>, respectively.

**Key words:**  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ , Protonic conduction, Conductivity, Gas concentration cell, Fuel cell

**I. INTRODUCTION**

Some trivalent cation doped perovskite-type ceramics based on  $\text{BaCeO}_3$ ,  $\text{Ba}_x\text{Ce}_{1-y}\text{M}_y\text{O}_{3-\alpha}$  ( $x > 1, = 1, < 1$ ), exhibit good electrical properties at high temperature. Nonstoichiometry ( $x \neq 1$ ) in these ceramics plays a certain role in improving their performances. Ma *et al.* [1] have studied the ionic conduction and nonstoichiometry in  $\text{Ba}_x\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{3-\alpha}$  ( $0.80 \leq x \leq 1.20$ ), discovering that  $\text{Ba}_{0.95}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{3-\alpha}$  has not only the highest conductivities (0.12 S/cm in dry air, 0.11 S/cm in wet air and  $6.7 \times 10^{-2}$  S/cm in wet hydrogen, at 1000 °C), but also the highest chemical stability. We have prepared  $\text{Ba}_x\text{Ce}_{0.8}\text{M}_{0.2}\text{O}_{3-\alpha}$  ( $x > 1, = 1, < 1$ ; M: Er, Tb) and studied their defect structure and ionic conduction, discovering the samples with  $x \neq 1$  have higher conductivities than those of the samples with  $x = 1$ , and the samples with  $x < 1$  have the highest chemical stability [2,3]. In our previous work, the ionic conduction and fuel cell performance of  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  ceramic were studied [4], and the results indicate that the sample is almost a pure protonic conduction at 600-1000 °C in wet hydrogen, a mixed conductor of proton, oxide ion and electron hole in wet air. The fuel cell using  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  as solid electrolyte can work stably, at 1000 °C with the maximum short-circuit current density and power output density of 346 mA/cm<sup>2</sup> and 80 mW/cm<sup>2</sup>, respec-

tively. For comparison, in the present study, perovskite-type  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{3-\alpha}$  was prepared and examined. The electromotive forces (EMFs) of gas concentration cells were measured, and the ionic transport numbers of the sample were thus obtained in wet hydrogen and wet air at 600-1000 °C. The conductivities were measured and the electrical conduction of the sample was investigated. The current density (*I*)-terminal voltage (*V*) performance of the hydrogen-air fuel cell using the sample as solid electrolyte was determined. All the above results were compared with those of  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ .

**II. EXPERIMENTAL SECTION**

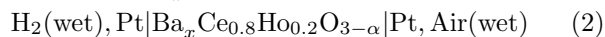
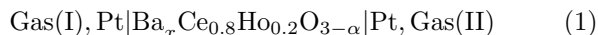
Ceramic samples of  $\text{Ba}_x\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  ( $x = 0.97, 1$ ) were prepared by the conventional solid-state reaction method using  $\text{Ba}(\text{CH}_3\text{COO})_2$ ,  $\text{CeO}_2$  and  $\text{Ho}_2\text{O}_3$  as starting materials [2]. Required amounts of starting materials were mixed in an agate mortar with ethanol and then calcined at 1250 °C for 10 h in the air. The calcined powders were ground in a ball mill with ethanol for 5 h and then passed through a sieve with 0.15 mm. The powder was pressed into pellets by hydrostatic pressing at  $2.7 \times 10^8$  Pa and sintered at 1650 °C for 10 h in the air. The obtained ceramics were made into thin discs with the diameter of 14 mm and the thickness of 0.5 mm, which were applied to determine the EMFs of gas concentration cells and *I-V* curves of the hydrogen-air fuel cells.

The samples phases were examined by powder X-ray diffraction analysis (XRD) using a nickel filtered  $\text{CuK}\alpha_1$

\* Author to whom correspondence should be addressed. E-mail: wmyqlg\_64@sina.com

radiation (Rigaku D/MAX-IIIC X-ray diffractometer). The conductivities were measured by AC impedance spectroscopy method over the frequency range of  $12-10^5$  Hz using a ZL5-Intelligent LCR measurer (made in Shanghai). The temperature dependency was measured for the two samples at 600-1000 °C in wet hydrogen and wet air.

For investigation of the ionic conduction and the performance of hydrogen-air fuel cells using the samples as electrolytes, the following gas concentration cells and hydrogen-air fuel cells were constructed:



where gas represents air, oxygen, hydrogen or water vapor. Wet gas: saturated with  $\text{H}_2\text{O}$  at the room temperature. Gasflow: 60 mL/min. The EMFs of cell (1) and  $I$ - $V$  curves of cell (2) were measured in the temperature range of 600-1000 °C.

### III. RESULTS AND DISCUSSION

#### A. Sample characterization

The powder XRD patterns of  $\text{Ba}_x\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  ( $x=0.97, 1$ ) ceramics showed a perovskite-type orthorhombic single-phase which corresponded to that of  $\text{BaCeO}_3$  (in JCPDS). The color of the sintered ceramics was dark yellow-green and the relative densities were higher than 95%. The experimental results proved that the two sintered ceramics were dense and could not be permeated by gases.

#### B. Protonic conduction under wet hydrogen

Protonic conduction in  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  ceramic under wet hydrogen was studied. The EMFs of the hydrogen concentration cell using the sample as solid electrolyte was measured at 600-1000 °C, and the protonic transport number ( $t_{\text{H}^+}$ ) was given by the ratio of the slope of each real line against that of each broken line at each temperature [5] (Fig.1). The total conductivity ( $\sigma$ ) of the sample under wet hydrogen was measured. The protonic conductivity ( $\sigma_{\text{H}^+}$ ) was calculated (Fig.2) from the formula:  $\sigma_{\text{H}^+} = \sigma t_{\text{H}^+}$  [5]. For the comparison, the protonic conduction in  $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\alpha}$  ceramic under wet hydrogen was also studied.

Figure 1 shows the EMFs of the hydrogen concentration cells using  $\text{Ba}_x\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  ( $x=0.97, 1$ ) as electrolytes at 600-1000 °C. In each experiment, hydrogen (101 kPa) and a mixture of hydrogen and argon were supplied to the anode and cathode compartments respectively. The water vapor pressure in both gases was kept constant ( $p_{\text{H}_2\text{O}} = 2.3$  kPa). The broken line stands for the theoretical values at each temperature, obtained based on Nernst's equation [5]. For

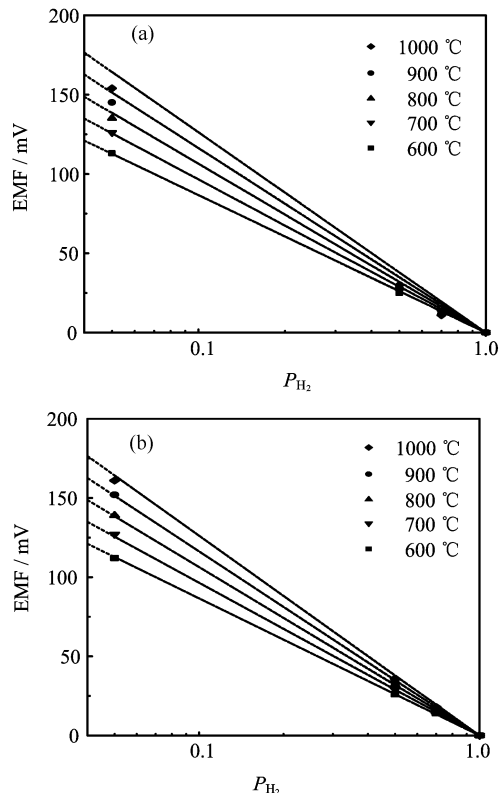


FIG. 1 EMFs of the hydrogen concentration cell:  $\text{H}_2(\text{wet}), \text{Pt|Ba}_x\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}\text{|Pt, H}_2\text{-Ar(wet)}$ . (a)  $x=0.97$ ; (b)  $x=1.0$ .

$\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ , the observed EMF values are almost in accordance with the theoretical ones at 600-1000 °C in wet hydrogen, its protonic transport number is 1 at 600-900 °C, 0.99 at 1000 °C, suggesting that  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  almost showed pure protonic conduction under the experimental temperatures. For  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ , when temperature was below 700 °C, the observed EMF values are in accordance with the theoretical ones, its protonic transport number is 1, but the observed EMF values are lower than the theoretical ones above 800 °C, and its protonic transport number is 0.99-0.96, indicating that  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  showed pure ionic conduction at 600-700 °C, but mixed conduction of proton and electron at 800-1000 °C. This may be due to that partial  $\text{Ce}^{4+}$  ions on the surface of  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  ceramic were reduced into  $\text{Ce}^{3+}$  ions in hydrogen at high temperature because of the lower alkaline caused by the BaO deficiency [6].

Figure 2 shows Arrhenius plots of protonic conductivities of  $\text{Ba}_x\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  ( $x=0.97, 1$ ) in wet hydrogen. It is seen from Fig.2 that  $\log(\sigma T)$  increases basically in linearity on the reciprocal of the temperature, indicating there is no phase change under the experimental conditions.  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  exhibits higher protonic conductivity than  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  at

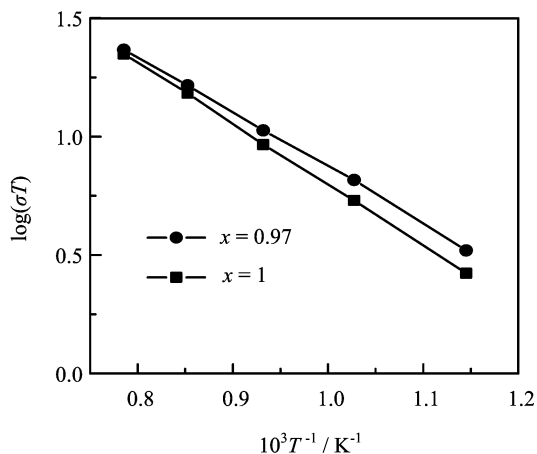
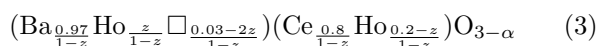


FIG. 2 Protonic conductivities of  $\text{Ba}_x\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  in wet  $\text{H}_2$  ( $p_{\text{H}_2\text{O}}=2.3$  kPa).

600-1000 °C. It may be correlated to their defect structures and oxidation-reduction behaviors [1,2,6-10]. In  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ ,  $\text{Ho}^{3+}$  mainly exist in  $\text{Ce}^{4+}$ -sites, some  $\text{Ho}^{3+}$  may transfer from  $\text{Ce}^{4+}$ -sites to  $\text{Ba}^{2+}$ -sites due to the  $\text{Ba}^{2+}$  deficiency, but still leaving the  $\text{Ba}^{2+}$  vacancy and the corresponding  $\text{O}^{2-}$  vacancy. Its defect structure is as follows:



where  $z$  and  $\square$  represent the amount of  $\text{Ho}^{3+}$  transferring from  $\text{Ce}^{4+}$ -sites to  $\text{Ba}^{2+}$ -sites and  $\text{Ba}^{2+}$  vacancy respectively. Oxygen vacancy concentration,  $\alpha$ , actually depends on  $z$ , that is,  $\alpha$  in  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  is greater than that in  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ , which enhances the ionic conductivities. Neglecting the water incorporation into the oxide ion vacancy,  $\alpha$  is 0.1 for  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ . For  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ ,  $\alpha$  exceeds 0.1 only when  $z < 0.0103$ , suggesting that  $\text{Ho}^{3+}$  mainly exist in  $\text{Ce}^{4+}$ -sites. Additionally, for the specimen with  $x=0.97$ , partial  $\text{Ce}^{4+}$  on the surface of the ceramic may easily be reduced into  $\text{Ce}^{3+}$  under high temperature and produce electronic conduction to some extent, and thus increase the total conductivity.

### C. Ionic conduction under wet air

The ionic conduction in the ceramic samples under wet air was studied employing the same method described in section B. At 600-1000 °C, the EMFs of the steam concentration cells and the oxygen concentration cells using the samples as solid electrolytes were measured, the results were shown in Fig.3 and Fig.4 respectively. The marks stand for the observed values ( $E_{\text{obs}}$ ), and the broken lines stand for the theoretical values ( $E_{\text{cal}}$ ) at each temperature. The protonic and oxide ionic transport numbers ( $t_i$ ) were thus obtained by the formula:  $t_i = E_{\text{obs}}/E_{\text{cal}}$  [5]. The total conductivity ( $\sigma_t$ ) of the samples under wet air was measured,

and protonic and oxide ionic conductivities ( $\sigma_i$ ) were determined by the formula:  $\sigma_i = \sigma_t t_i$  [5].

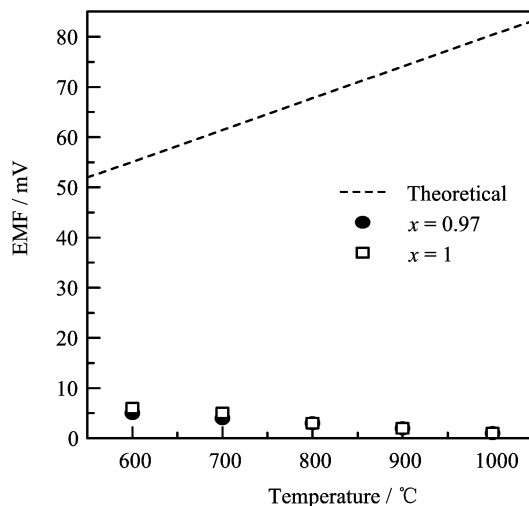


FIG. 3 EMFs of the steam concentration cell:  $\text{Air}(p'_{\text{H}_2\text{O}})|\text{Pt}|\text{Ba}_x\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}|\text{Pt}|\text{Air}(p''_{\text{H}_2\text{O}})$ .

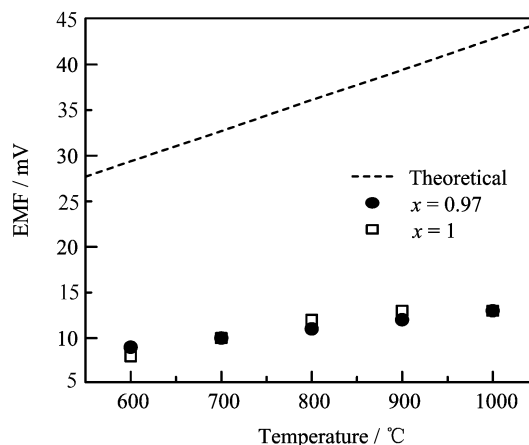


FIG. 4 EMFs of the oxygen concentration cell:  $\text{Air}(\text{wet})|\text{Pt}|\text{Ba}_x\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}|\text{Pt}|\text{O}_2(\text{wet})$ .

As shown in Fig.3, the EMFs of the water steam concentration cells of the two samples are close to each other, and are much smaller than the theoretical ones. For  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ , the protonic transport numbers are 0.01-0.11, but for  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ , 0.01-0.09, suggesting the samples have low protonic conduction under wet air at 600-1000 °C.

We can see from Fig.4 that the EMFs of the oxygen concentration cells based on the two samples are close to each other, and are much smaller than the theoretical ones at each temperature. For  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{3-\alpha}$ , the oxide ionic transport numbers are 0.30-0.31, but for  $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\alpha}$ , 0.27-0.33, indicating that the two samples exhibit poor oxide ionic conduction.

Figure 5 shows protonic and oxide ionic conductivities of  $\text{Ba}_x\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  ( $x=0.97, 1$ ) in wet air. It

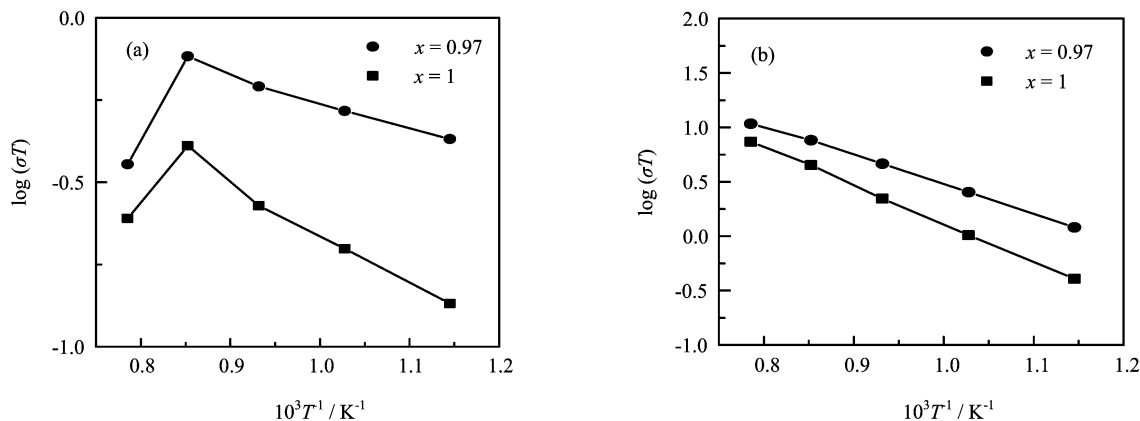


FIG. 5 Ionic conductivities of  $Ba_xCe_{0.8}Ho_{0.2}O_{3-\alpha}$  in wet air (a) protonic conductivities; (b) oxide ionic conductivities.

is clear that  $Ba_{0.97}Ce_{0.8}Ho_{0.2}O_{3-\alpha}$  has higher protonic and oxide ionic conductivities than  $BaCe_{0.8}Ho_{0.2}O_{3-\alpha}$ , which is similar to those in wet hydrogen. It may be due to the particular defect structure and the corresponding larger concentration of oxide ionic vacancy in  $Ba_{0.97}Ce_{0.8}Ho_{0.2}O_{3-\alpha}$  as discussed in section B. From Fig.5, we can see that the oxide ionic conductivities increase with the increasing temperature. The protonic conductivities increase with the increasing temperature at 600-900 °C, but decrease above 900 °C, and display a maximum at 900 °C. It may be ascribed to the effect of competition between an increase in the mobility of protonic carriers due to thermal activation and a decrease in their concentration due to loss of water [4,5].

#### D. Performance of hydrogen-air fuel cell

Figure 6 is  $I-V$  performance of the hydrogen-air fuel cell using  $Ba_{0.97}Ce_{0.8}Ho_{0.2}O_{3-\alpha}$  as solid electrolyte. A steady and stable current could be drawn from the cell, indicating that the ceramic diaphragm could serve as

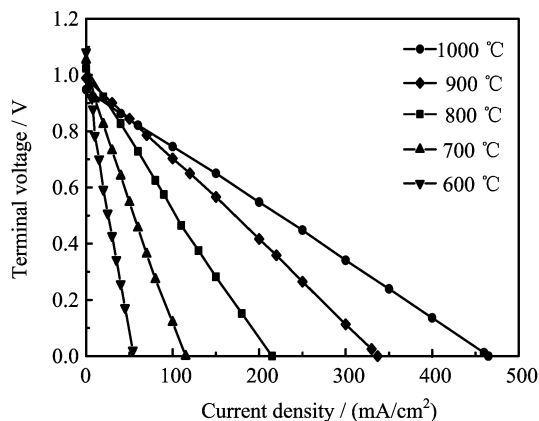


FIG. 6  $I-V$  characteristic curves for the fuel cell:  $H_2, Pt|Ba_xCe_{0.8}Ho_{0.2}O_{3-\alpha}|Pt, Air$ .

the solid electrolyte of a fuel cell. At 600-1000 °C, the relation between terminal voltage and current output is linear, suggesting the resistance of the solid electrolyte was the major factor of the cell performance. The open circuit voltage decreases with the increasing temperature. It means that the electronic transfer numbers increase and the ionic transfer numbers decrease with the increasing temperature. However, the current density increases with the increasing temperature, this may be explained by two aspects: (i) the protonic conductivity changes slightly whereas the oxide ionic conductivity improves markedly with the increasing temperature, which results in the increase of general ionic conductivity. (ii) the polarization effect at fuel electrode and air electrode decreases markedly with the increasing temperature. Thus the discharge performance improved [9]. The fuel cell using  $BaCe_{0.8}Ho_{0.2}O_{3-\alpha}$  as solid electrolytes has the similar discharge performance.

Figure 7 is current-voltage-power ( $I-V-P$ ) characteristic curves of the fuel cells:  $H_2, Pt|Ba_xCe_{0.8}Ho_{0.2}O_{3-\alpha}|Pt, Air$  ( $x=0.97, 1$ ) at 1000 °C. It is clear from Fig.7 that the fuel cell using  $Ba_{0.97}Ce_{0.8}Ho_{0.2}O_{3-\alpha}$

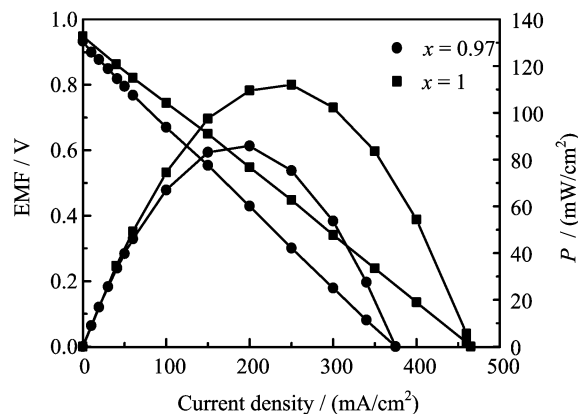


FIG. 7  $I-V-P$  characteristic curves for the fuel cell:  $H_2, Pt|Ba_xCe_{0.8}Ho_{0.2}O_{3-\alpha}|Pt, Air$  at 1000 °C.

as solid electrolyte produces higher short-circuit current densities and power output densities than those of  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  due to its higher protonic conductivities in wet hydrogen and higher ionic conductivities in wet air mentioned in section B and section C [11]. At 1000 °C, the maximum short-circuit current density and power output density of  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  are 465 mA/cm<sup>2</sup> and 112 mW/cm<sup>2</sup>, respectively.

#### IV. CONCLUSION

The sample of  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  is a single-phase of perovskite-type orthorhombic structure.  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  is almost a pure protonic conductor at 600-1000 °C in wet hydrogen, while  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  is mixed conductors of proton and electron due to its reduction in wet hydrogen above 700 °C. Under wet air, the two samples both exhibit low protonic and oxide ionic conduction. Conductivities of  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  is higher than those of  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  in wet hydrogen and wet air. The performances of the fuel cell using  $\text{Ba}_{0.97}\text{Ce}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$  as solid electrolytes are better than those of  $\text{BaCe}_{0.8}\text{Ho}_{0.2}\text{O}_{3-\alpha}$ . At 1000 °C, its maximum short-circuit current density and power output density are 465 mA/cm<sup>2</sup> and 112 mW/cm<sup>2</sup>, respectively.

#### V. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No.20171034) and the Natural Science Foundation of Education Department of Jiangsu Province (No.04KJD150218).

- [1] G. L. Ma, T. Shimura and H. Iwahara, *Solid State Ionics* **110**, 103 (1998).
- [2] L. G. Qiu, G. L. Ma and D. J. Wen, *Solid State Ionics* **166**, 69 (2004).
- [3] L. G. Qiu, G. L. Ma and D. J. Wen, *J. Rare Earths* **22**, 678 (2004).
- [4] L. G. Qiu, G. L. Ma and D. J. Wen, *Chin. J. Chem.* **23**, 1641 (2005).
- [5] N. Bonanos, *Solid State Ionics* **53-56**, 967 (1992).
- [6] D. Shima and S. M. Haile, *Solid State Ionics* **97**, 443 (1997).
- [7] G. L. Ma, H. Matsumoto and H. Iwahara, *Solid State Ionics* **122**, 237 (1999).
- [8] T. Shimura, G. L. Ma, H. Matsumoto, *et al.* *Electrochemistry* **68**, 409 (2000).
- [9] G. L. Ma, R. E. Gu, H. Shi, *et al.* *Acta Chim. Sin.* **59**, 2084 (2001).
- [10] J. Y. Fei, W. L. Xin, G. Z. Liang, *et al.* *Chin. J. Chem. Phys.* **16**, 425 (2003).
- [11] H. Iwahara, *Solid State Ionics* **77**, 289 (1995).