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Degradation of Some Ceria Electrolytes Under Hydrogen Contact Nearby Anode in Solid Oxide Fuel Cells (SOFCs)

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This work is concerned with thermodynamic analysis of the stability of some ceria electrolytes under contact with hydrogen gas nearby anode in fuel cells. It was considered the following types of ceria-electrolytes: pure ceria, strontium-doped ceria, calcium-doped ceria and calcium-bismuth-doped ceria. The equilibrium Log ($pH_2O/pH2$) *vs.* T diagrams were constructed for x = 0.1 and 0.01, where x is the fraction of initial ceria converted to Ce_2O_3 (proportional to the ratio between activities of Ce^{3+} and Ce^{4+} in the ceria electrolyte, which is proportional to the fraction of electronic conduction in the electrolyte at a given temperature). The predictions of the diagrams are as follows: (a) $Ce_{1.9}Ca_{0.1}Bi_{0.8}O_{5.1}$ and $Ce_{0.9}Sr_{0.1}O_{1.9}$ are less stable than pure ceria for the whole temperature range (from 0 to 1000 °C); (b) $Ce_{0.9}Ca_{0.1}O_{1.9}$ is more stable than pure ceria below about 650 °C for x = 0.1 and below about 400 °C for x = 0.01; (c) at each temperature in the considered range the pressure ratio $pH_2O(g)/pH_2(g)$ has to be higher than thermodynamically predicted in order to keep CeO_2 stable in the electrolyte contacting hydrogen gas. Thermodynamic predictions are entirely capable of explaining experimental data published on the subject (irreversible cell degradation in the case of SrO-doped ceria; weight loss from doped-ceria electrolyte above 700 °C; oxygen gas release during sintering of ceria).

Keywords: *ceria electrolytes, SOFCs, anode reaction, degradation of ceria*

1. Introduction

Fuel cells are expected to become the best solution for electric energy generation and electrical-vehicle by electrochemical energy conversion from hydrocarbon fuels, because of the higher conversion efficiency and lesser pollution. In this sense, efforts are applied worldwide for direct fueling fuel cells with hydrocarbon by means of in situ catalytic reforming of the same. Allied to the poisoning of the catalysts, there problems concerned with the attack of the CO and H_2 to the anode composite (e.g. nickel-solid oxide) when the solid oxide electrolyte used is ceria. This kind of electrolyte deserves attention from the viewpoint of attempting to reduce high temperature corrosion problems to current collector/interconnectors when fuel cells are operated using zirconia electrolytes (operation temperature in the range of 900 to 1000 °C). Ceria electrolytes are designed to allow solid oxide fuel cells being successfully operated at lower temperatures (500 to 800 °C), without too much decrease in ionic conductivity (which means loss in electrical current density or power density). This work deals with the problem of ceria electrolyte in the anode region of the fuel cells being affected by the hydrogen gas action, thereby suffering from loss electrical efficiency due to electronic conduction as a result of the Ce^{4+} to Ce^{3+}. More precisely, the behavior of ceria doped with Ca, Sr and their mixture is focused.

Hydrothermal synthesis of nanocrystalline codoped cerias (particle size in the range 15nm to 30nm) $Ce_{1-x}M_xBi_{0.4}O_{2.6-x}$ (where M = Ca, Sr e Ba; $0.01 \leq \times \leq 0.15$) appeared promising as solid electrolyte for fuel cells operating in the 500 to 800 °C temperature range and the highest oxygen ion conductivity provided by $Ce_{0,95}Ca_{0,05}Bi_{0,4}O_{2,55}$m, at 600 °C, was 1.7×10^{-2} $S.cm^{-1}$, while the maximum power density was 140 mW/cm^2 at 500 °C[1]. Li *et al.*[2] produced nanocrystalline (CeO2)(1-x)(BiO1.5) × (x = 0.0 to 0.5) under moderate hydrothermal conditions, 240 °C; a fluorite type cubic structure ceria was achieved

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when x < 0.5. Doshi *et al.*[3] showed that fuel cells based on doped ceria electrolyte may be operated at 500 °C, but improvement in the technology to manufacture thin film electrolyte is still necessary in order to get open circuit voltage of 0.97 to 1V. Another problem concerned with the doped ceria electrolyte is its decomposition by hydrogen gas during high temperature operation, generating Ce_2O_3, which imposes power losses to the fuel cell due to electronic conduction[4].

Cerias doped with rare earth metal oxides are also important options Sahibzada *et al.*[5] incorporated a dense film (5 to 10 µm) of $Ce_{0.9}Gd_{0.1}O_{0.95}$ by tape casting on Ni-YSZ anode substrate and investigated the behaviour of a hydrogen fuel cell in the temperature range from 550 to 650 °C, using $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathode, and obtained an open circuit voltage of 0.75 to 0.8V as well as power of 125 mW/cm at 650 °C and 30 mW/cm^2 at 550 °C; direct use of methanol in the anode was tested at 600 °C.

Maffei & Kuriakose[6] made planar solid oxide fuel cells with doubly doped ceria (with Gd and Pr) and tested at 700 °C. An argon -4%hydrogen gas mixture was used at the anode while air was used at the cathode.

Besides considerable electronic conduction, the doubly doped ceria showed a chemical reduction by hydrogen above about 700 °C.

Milliken, Guruswamy & Khandkar[7] obtained power densities > 250 mW/cm^2 at 700 °C, with stable performance during 15000 h, in individual fuel cells of samaria doped ceria electrolyte. Good efficiency of up to 42% was gotten when the fuel cell was operated with humid hydrogen.

Other studies on rare earth doped cerias were carried out by Murray, Tsai & Barnett[8], Maric *et al.*[9], Uchida, Osuga & Watanabe[10], Marina *et al.*[11], Ishihara *et al.*[12], Uchida, Suzuki & Watanabe[13] and Antonucci *et al.*[14], among others, which point out the relevant role to be played by doped ceria in solid oxide fuel cells.

The Research Group of Ogasawara *et al.*[15-18], at PEMM/COPPE/UFRJ, is carrying out developments in fuel cells with doped ceria electrolytes, and already concluded that it is possible to hydrothermally synthesize $Ce_{0,9}Ca_{0,10}O_{1,9}$ in autoclave at 220 °C for 4 h, at pH in the range from 13 to 14, and obtaining an electrolyte with ionic conductivity of 1.0×10^{-3} S/cm at 390 °C.

The present work deals with the thermodynamic analysis of the Ce-Ca-Bi-O-H_2-H_2O(g) system by constructing diagrams of pH_2O/pH_2 *vs.* temperature and comparing their predictions with experimentally known features..

2. Thermodynamic Data

The thermodynamic data used in this study were found in the Main Database of the HSC Chemistry for Windows 4.1, from Outokumpu Oy (Finland), licensed to the Metallurgical and Materials Engineering Department of COPPE/UFRJ. Those data referring to the key-species $Ce_{1.9}Ca_{0,1}Bi_{0,8}O_{5,1}$, $Ce_{0,9}Ca_{0,1}O_{1,9}$ and $Ce_{0,9}Sr_{0,1}O_{1,9}$, are displayed in Tables 1, 2 and 3, respectively.

3. Calculation and Interpretation of the Diagrams

The calculation was carried out by using the Chemical Reaction Module of the referred HSC Chemistry for Windows 4.1 Software, and the diagrams were mounted by hand. The important chemical reactions are the following:

$$CeO_2 + 0.5\ H_2(g) = 0.5\ Ce_2O_3 + 0.5\ H_2O(g) \tag{1}$$

$$Ce_{0,9}Ca_{0,1}O_{1,9} + 0.45\ H_2(g) = 0.45\ Ce_2O_3 + 0.1\ CaO + 0.45\ H_2O(g) \tag{3}$$

$$Ce_{0,9}Sr_{0,1}O_{1.9} + 0.45\ H_2(g) = 0.45\ Ce_2O_3 + 0.1\ SrO + 0.45\ H_2O(g) \tag{5}$$

$$Ce_{1,9}Ca_{0,1}Bi_{0,8}O_{5,1} + 0.95\ H_2(g) = 0.85\ Ce_2O_3 + 0.1\ CaBi_2O_4 + 0.2\ CeBi_3O_6 + 0.95\ H_2O(g) \tag{7}$$

It is defined x as the molar fraction of each doped ceria which decomposes under the action of the hydrogen gas. Consequently, (1-x) is the molar fraction of the referred doped ceria which remains unaltered, while Ce_2O_3 is derived by the same decomposition.

4. Presentation and Interpretation of the Diagrams

Figure 1 shows the $\log(pH_2O/pH_2)$ *vs.* temperature diagram of the cerias doped with calcia, strontia and calcia-bismuth oxide, for x = 0.1. Below a particular curve it's located the stability domain of Ce^{3+} cation, that is, of Ce_2O_3; so, the stability domain of ceria (CeO_2, that is, of Ce^{4+} cation) is located above the referred curve. Therefore, it may be observed that $Ce_{0,9}Ca_{0.1}O_{1,9}$ is only unique doped ceria more stable than the pure ceria below 650 °C.

Figure 2 shows the $\log(pH_2O/pH_2)$ *vs.* temperature diagram for the same system in the case of x = 0.01, which is notably more restrictive with respective to the maximum temperature of ceria stability under hydrogen than in the case of x = 0.1.

5. Final Discussion

It's worthwhile to note that these diagrams presented here are entirely new in the context of ceria electrolyte fuel cells.

The fraction of doped ceria which decomposes under action of hydrogen gas is directly proportional to the ratio ($a_{Ce}3+/a_{Ce}4+$) of the solid electrolyte. The cation Ce^{3+} is carrier of 1 electron in excess to that carried by the cation Ce^{4+}

Table 1. Thermodynamic data of the species $Ce_{1,9}Ca_{0,1}Bi_{0,8}O_{5,1}$: coefficients A, B, C and D of the constant pressure molar heat capacity as a function of temperature, enthalpies and entropies at 298.15K , as well as enthalpies and entropies of phase transformation.

Temperature Interval (K)	$H^\circ_{298.15K}$ or $\Delta H_{transform}$ kcal.mol^{-1}K^{-1}	$S^\circ_{298.15K}$ or $\Delta S_{transform.\ cal.mol}$$^{-1}$K^{-1}	$c_p^\circ = A + Bx10^{-3}T + Cx10^{5}T^{-2} + Dx10^{-6}T^{2}$ (cal.mol^{-1}K^{-1})			
			A	B	C	D
298.15-545	-566.424	46.311	34.206	14.942	-0.948	0.254
545-600	2.16	3.966	35.450	11.1	2.232	-0.508
600-720	0	9	34.841	11.902	2.232	-0.508
720-999	0.022	0.031	34.327	12.969	2.224	-0.995
999-1071	1.359	1.360	41.764	5.525	2.224	-0.995
1071-1112	2.480	2.314	41.422	5.525	2.224	-0.995
1112-1200	0.204	0.184	42.519	4.538	-2.224	-0.995
1200-1685.5	0	0	44.083	2.555	-1.742	-0.235

Table 2. Thermodynamic data of the species $Ce_{0,9}Ca_{0,1}O_{1,9}$: coefficients A, B, C and D of the constant pressure molar heat capacity as a function of temperature, enthalpies and entropies at 298.15K , as well as enthalpies and entropies of phase transformation.

Temperature Interval (K)	$H^\circ_{298,15K}$ or $\Delta H_{transform}$ kcal.mol^{-1}K^{-1}	$S^\circ_{298,15K}$ or $\Delta S_{transform.\ cal.mol}$$^{-1}$K^{-1}	$c_p^\circ = A + Bx10^{-3}T + Cx10^{5}T^{-2} + Dx10^{-6}T^{2}$ (cal.mol^{-1}K^{-1})			
			A	B	C	D
298.15-600	-250.359	14.957	13.241	3.915	-0.641	0.401
600-720	0	0	12.952	4.398	-0.641	-0.381
720-999	0.022	0.031	12.438	5.465	-0.649	-0.087
999-1071	0.644	0.644	15.961	1.939	-0.649	-0.087
1071-1112	1.175	1.096	15.961	1.939	-0.649	-0.087
1112-1755	0.204	0.184	17.058	0.952	-0.649	-0.087

Table 3. Thermodynamic data of the species $Ce_{0,9}Sr_{0,1}O_{1,9}$: coefficients A, B, C and D of the constant pressure molar heat capacity as a function of temperature, enthalpies and entropies at 298.15K , as well as enthalpies and entropies of phase transformation.

Temperature Interval (K)	$H^\circ_{298,15K}$ or $\Delta H_{transform}$ kcal.mol^{-1}K^{-1}	$S^\circ_{298,15K}$ or $\Delta S_{transform.\ cal.mol}$$^{-1}$K^{-1}	$c_p^\circ = A + Bx10^{-3}T + Cx10^{5}T^{-2} + Dx10^{-6}T^{2}$ (cal.mol^{-1}K^{-1})			
			A	B	C	D
298.15-600	-248.330	15.374	13.123	3.904	-0.682	0.373
600-820	0	0	13.223	4.388	-0.682	0.548
820-999	0.020	0.024	13.433	4.478	-0.649	-0.087
999-1050	0.644	0.644	16.956	0.952	-0.649	-0.087
1050-1071	0.178	0.169	17.143	0.952	-0.649	-0.087
1071-1685.5	1.175	1.096	17.125	0.952	-0.649	-0.087

and so it plays the role of an electronic conductor decreasing the electrical efficiency of the fuel cell. Therefore, to avoid the ceria decomposition under action of hydrogen gas is an important concern. In view of this fact, the diagrams developed here provide nice picture of the impact the degradation by hydrogen may have on a fuel cell operated with a hydrogen plus carbon monoxide mixture generated by in situ catalytic reforming of a hydrocarbon directly fed into the solid oxide fuel cell.

The decomposition of doped ceria electrolytes by hydrogen gas action during high temperature operation, generating Ce_2O_3, which imposes power losses to the fuel cell due to electronic conduction has been observed by Zhou[4]. Likewise, Maffei & Kuriakose[6] found degradation of planar solid oxide fuel cell composed by doubly doped ceria (with Gd and Pr) during tests at 700 °C, using an argon -4% hydrogen gas mixture at the anode. Good efficiency of up to 42% was gotten by Milliken, Guruswamy & Khandkar[7]

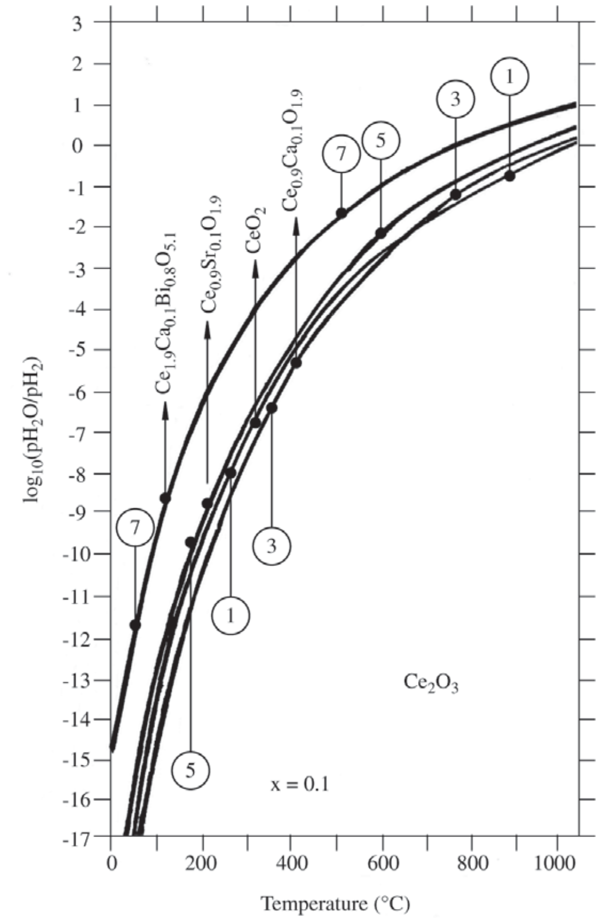

Figure 1. Diagram of $\log_{10}$ (pH_2O/pH_2) *vs.* Temperature (°C) for cerias doped with Ca, Sr and Bi; x = 0.1.

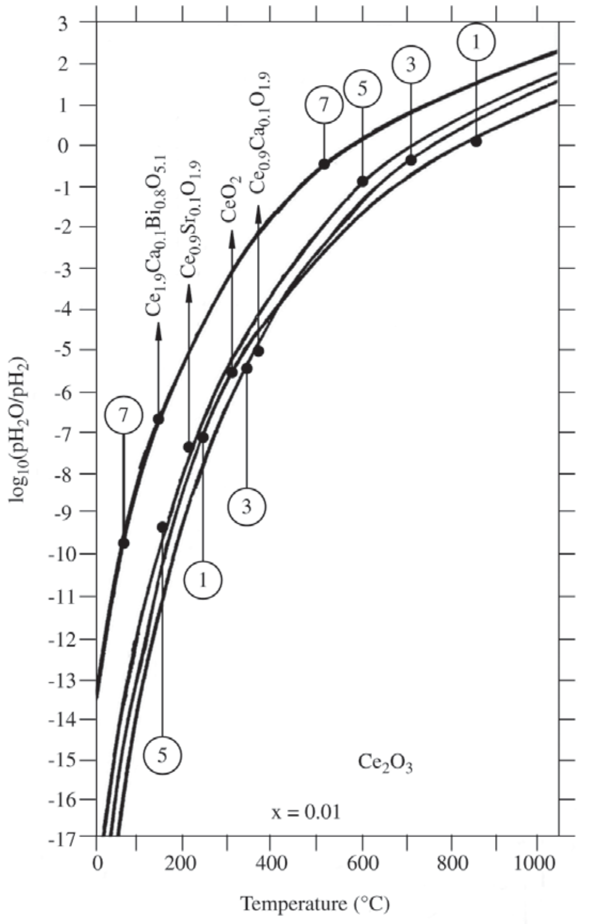

Figure2. Diagram of $\log_{10}$ (pH_2O/pH_2) *vs.* Temperature (°C) for cerias doped with Ca, Sr and Bi; x = 0.01.

when their fuel cell was operated with humid hydrogen (power densities > 250 mW/cm^2 at 700 °C, with stable performance during 15000 h, in fuel cells of samaria doped ceria electrolyte.

Therefore, the predictions of the diagrams developed here are consistent with experimentally observed facts, thereby constituting a good tool to improve better understanding of the ceria electrolyte stability nearby the anode in the hydrogen fuel cell.

6. Conclusions

- The stability domains of cerias doped with calcia, strontia and calcia-bismuth oxide were set up in a diagram of degree of oxidation of the hydrogen fuel gas *vs.* temperature;
- $Ce_{1.9}Ca_{0.1}Bi_{0.8}O_{5.1}$ and $Ce_{0.9}Sr_{0.1}O_{1.9}$ are less stable than pure ceria for the whole temperature range (from 0 to 1000 °C);
- $Ce_{0.9}Ca_{0.1}O_{1.9}$ is more stable than pure ceria below about 650 °C for x = 0.1 and below about 400 °C for x = 0.01;
- At each temperature in the considered range, the pressure ratio $pH_2O(g)/pH_2(g)$ has to be higher than thermodynamically predicted in order to keep CeO_2 stable in the electrolyte contacting hydrogen gas.

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