



Selection and study of basic layered cobaltites as mixed ionic–electronic conductors for proton conducting fuel cells



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ABSTRACT

High Temperature Steam Electrolysis using Proton Conducting Cells is a promising method for large-scale hydrogen production, but such system requires the development of new electrode materials ideally presenting Mixed Proton and Electron Conductivity. Different cobaltites were investigated in terms of durability and compatibility with the BaZr_{0.5}Y_{0.1}O₃ proton conducting electrolyte. REBaCo₂O_{5+δ} (RE = Pr, Nd, Sm, Gd, Y), YBaCo₄O₇, Ca₃Co₄O₉ and Ca₃Co₂O₆, were considered, among which the vacancy ordered perovskites were found to be the most stable in wet air. Oxygen vacancy formation and hydration properties of REBaCo₂O_{5+δ} were studied by iodometry and TGA in dry and wet atmospheres, respectively.

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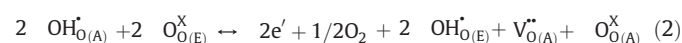
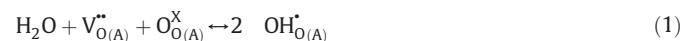
1. Introduction

Within the fuel cell family, solid oxide fuel cells (SOFCs) are very attractive systems due to their high efficiency for fuel to electricity transformation and the utilization of cheap materials for the electrode and electrolyte assembly [1]. For the same reasons, in countries where energy costs can be particularly low, e.g. in nuclear energy producing countries, high temperature steam electrolysis (HTSE) is considered as one of the best device for massive hydrogen production, based on thermodynamic and environmental considerations [2]. However, the commercialization of solid oxide cells (SOCs) has not already been achieved because of material issues, mostly due to their high temperature degradation. One way to avoid or limit such problems is to lower the operating temperature, so that metallic interconnects which are less expensive than ceramic interconnects can be used and chemical reactions or thermomechanical mismatch between cell components can be avoided [3]. Many research groups have focused on the development of low temperature O^{2−} conducting electrolyte cells (the classical SOCs) in which the main electrical loss is due to kinetic limitations at the air electrode (SOFC cathode or SOEC anode). For such purpose, mixed ionic and electronic conducting (MIEC) oxides have received a particular attention, especially as potential cathodes for intermediate

temperature solid oxide fuel cells (IT-SOFCs), since single phase compounds make possible the extension of the reaction zone to all the electrode material free surfaces [4].

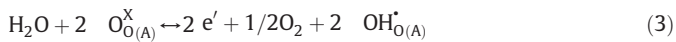
The next step in the development of SOCs will be probably through the use of proton conducting electrolytes that can operate at an even lower temperature than the previous ones (typically between 300 and 600 °C). Additionally, one advantage of using proton conducting cells (PCCs) for high temperature steam electrolysis stems from the production of intrinsically pure hydrogen (i.e. not mixed with H₂O), avoiding the costly step of gas drying [5]. For the same reasons as mentioned above, PCCs still require new materials able to dissociate oxygen (fuel cell) or water (electrolysis cell) at temperatures lower than 600 °C. It seems therefore reasonable to focus on mixed conducting materials and particularly mixed proton and electron conductors (MPECs) to benefit of maximum activity for the electrochemical half reaction.

Indeed, in the case of HTSE, two hypotheses of half reaction mechanism for water oxidation at the anode can be considered, depending if the electrochemical process is occurring at the anode–electrolyte interface (Eqs. (1) + (2)) or on the anode surface (Eqs. (3) + (4)) (note: for simplification, intermediate adsorption–dissociation–migration steps have been omitted):



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with $\text{OH}_{\text{O}}^{\bullet}$ being the proton defect described in the case of proton conducting electrolytes [6] and (A) and (E) indices referring to anode and electrolyte materials, respectively. In the first case, an efficient PCC air electrode should be ideally not only a good proton and electron conductor, but also a good oxygen vacancy conductor, which is not necessarily the case if the second hypothetical mechanism is taking place. As far as we know, there is no clear description of what is the exact electrode mechanism taking place at the air electrode, but the difference between two proposed schemes would remain mainly in the requirement for a material to be a suitable mixed proton electron conductor, i.e. the presence and mobility (or not) of oxygen vacancy to induce proton defect formation within the crystal structure. In a previous paper, a first study of material stability and water uptake in basic cobaltites was presented but with an emphasis on classical perovskite compounds [7]. For comparison purposes, it was decided to explore other oxygen vacant cobaltites with high oxide basicity (i.e. affinity to water). Double layered perovskite $\text{REBaCo}_2\text{O}_{5+\delta}$ (RE = Gd, Pr, Y, La, etc.) have been recently reported as good candidates for SOFC cathodes [8]. These materials possess an ordered structure in which a rare-earth and an alkaline earth cation occupy the A-site sub-lattice and oxygen vacancies are localized within the LnO_8 layers [5–8]. This growing interest provides from their high oxygen diffusion and surface exchange coefficients stating that layer-structured oxides are promising alternative materials for SOFC cathodes [9].

In the present work, five compounds of the oxygen vacant ordered perovskite family, $\text{REBaCo}_2\text{O}_{5+\delta}$ with RE = Gd, Nd, Pr, Sm and Y, were studied, as well as completely different and less studied structure types (i.e. YBaCo_4O_7 , $\text{Ca}_3\text{Co}_4\text{O}_9$ or $\text{Ca}_3\text{Co}_2\text{O}_6$) were selected for their layered structure. $\text{YBaCo}_4\text{O}_{7+\delta}$ (YBCo1147) has been recently considered as a potential electrode material in high temperature cells taking into account its high oxygen mobility, oxygen storage capacity as well as high cobalt content (catalytically active) [10]. In the Ca–Co–O system, oxygen deficient $\text{Ca}_2\text{Co}_2\text{O}_5$ compound cannot be obtained via thermal treatments in air and a mixture of two different materials is generally obtained: $\text{Ca}_3\text{Co}_4\text{O}_9$ (CaCo349) and $\text{Ca}_3\text{Co}_2\text{O}_6$ (CaCo326), which were better considered in this study [11].

After synthesis and structural characterization of the materials, we embarked on the analysis of stability of all compounds under laboratory and wet air in the 400–600 °C temperature range, as well as their reactivity with the selected electrolyte material $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ (BZY91), that is considered as a compromise between sufficiently high proton conductivity and low sensitivity to CO_2 [12–14].

2. Experimental

All compounds were prepared through solid state reaction using manual grinding in acetone of Co_3O_4 (Alfa Aesar 99.9985%), BaCO_3 (Alfa Aesar 99.95%), CaCO_3 (Alfa Aesar, 99.99%) and/or RE_2O_3 (RE =

Gd, Nd, Pr, Sm and Y – Alfa Aesar REacton® grade, 99.9%), thermogravimetrically assayed or thermally pre-treated, and weighted in stoichiometric proportions. After decarbonation at 1000 °C for 12 h, the intermediate mixtures were ground, pressed into pellets and heated in air at different temperatures for 12 h before being slowly cooled down to obtain the monophasic oxide materials. Only calcium compounds were thermally treated at a lower temperature (900 °C) due to their instability to higher temperatures [11] (Table 1).

The $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ electrolyte powder was synthesized by the nitrate polyacrylamide gel (NPG) method using controlled source of $\text{ZrO}(\text{NO}_3)_2$ (Aldrich 99.5%), BaCO_3 (Alfa Aesar 99.5%) and $\text{Y}(\text{NO}_3)_3$ (Alfa Aesar 99.9%) as precursors. Nitrate salts of the desired cations were first dissolved in deionized water and the barium carbonate was reacted with nitric acid to obtain a nitrate solution. Obtained solutions were then mixed together in presence of citric acid (Alfa Aesar, 99.5%) using a citric acid:cation ratio of 3:1. Appropriated amounts of acrylic acid (Fluka, 99%) as monomer and N,N'-methylene diacrylamide (Fluka, 99%) as cross-linking reagent were then introduced. Polymerization reaction was initiated by adding two drops of hydrogen peroxide. The as-formed gel was heated in a microwave oven to obtain a xerogel, which was in turn manually ground and heated in air for 1 h at 700 °C to eliminate most of the organics, or convert them into carbonates. As-prepared powder was finally mixed and ground manually before being treated at 1200 °C for 10 h in air.

The stability of the different electrode compounds was performed for 350 h in operating conditions that are typical for proton conducting systems: $T = 600$ °C in laboratory air and $T = 400$ °C in a $p_{\text{H}_2\text{O}} = 0.2$ atm, corresponding to air passing through water at $T = 60$ °C. This last choice was fixed considering that proton incorporation in most of relevant conducting oxides takes place in the temperature range of 300–400 °C.

Reactivity between electrode and electrolyte materials was performed mixing the two oxide powders in a 50:50 weight ratio and then pressed into pellets. The resulting samples were heated for 3 h at a so-called electrode sintering temperature T_s , previously determined by dilatometry measurements using a high temperature dilatometer (SETARAM Setsys Evolution TMA). Into details, the melting temperature T_m of the studied samples was preliminarily established by trial and error in a furnace operating in air. Then each sample was heated up at a rate of 5 °C·min⁻¹ from room temperature to $T_s = T_m - 20$ °C. The temperature was maintained for 1 h and cooled down to room temperature at the same rate (5 °C·min⁻¹). Electrode sintering temperatures were deduced from dilatometric curves as the beginning of sintering corresponding to neck formation between grains (sintering first step). The same dilatometric curves were also used to determine thermal expansion coefficients (TECs) in air.

Phase purity, reactivity and stability of the synthesized compounds were checked by X-ray powder diffraction (XRD). Diffraction data were recorded using a Brüker “D8 Advance” powder diffractometer operating in Bragg–Brentano reflection geometry with a $\text{CuK}\alpha$ radiation. The data were collected at room temperature by step scanning (0.02° by step) over the angular range $5^\circ \leq 2\theta \leq 110^\circ$; structural refinement was carried out by the Rietveld method using the Fullprof Suite program [15]. Phase stability was characterized comparing the deduced lattice parameters, considering the estimated standard deviations σ provided by the Rietveld refinement results. Structural refinement for the incommensurate compound $\text{Ca}_3\text{Co}_4\text{O}_9$ was performed by the Le Bail method using the JANA program [16].

Cobalt oxidation states were determined by iodometric titration. For this purpose, ~50 mg of each powder was preliminary dried for 1 h in dry air at 800 °C with a slow cooling down to room temperature (1 °C·min⁻¹). Such treatment was used to fix the oxygen vacancy content to the thermodynamical level corresponding to room temperature, without introducing water in the oxygen vacant sites. The sample was then placed in a three-neck flask and air was removed from the system using a continue argon flow. Gas outlet was connected to two bubblers

Table 1
Summary of thermal treatments used for selected cobaltites.

Formula	Reference	Temperature cycles
$\text{GdBaCo}_2\text{O}_{5+\delta}$	GBCo	1000 °C/12 h + 1100 °C/12 h × 2
$\text{SmBaCo}_2\text{O}_{5+\delta}$	SBCo	1000 °C/12 h + 1200 °C/12 h × 2
$\text{NdBaCo}_2\text{O}_{5+\delta}$	NBCo	1000 °C/12 h + 1200 °C/12 h × 2
$\text{PrBaCo}_2\text{O}_{5+\delta}$	PBCo	1000 °C/12 h + 1100 °C/12 h × 2
$\text{YBaCo}_2\text{O}_{5+\delta}$	YBCo	1000 °C/12 h + 1100 °C/12 h × 2
YBaCo_4O_7	YBCo1147	1000 °C/12 h + 1200 °C/12 h
$\text{Ca}_3\text{Co}_2\text{O}_6$	CaCo326	900 °C/24 h + 900 °C/72 h
$\text{Ca}_3\text{Co}_4\text{O}_9$	CaCo349	900 °C/24 h + 900 °C/72 h

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