Perovskite cathodes for NaBH$_4$/H$_2$O$_2$ direct fuel cells

D.M.F. Santos[a,b,*], T.F.B. Gomes[a], B. Šljukić[a], N. Sousa[b], C.A.C. Sequeira[a], F.M.L. Figueiredo[b]

[a] Materials Electrochemistry Group, CeFEMA, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisbon, Portugal
[b] CICECO, Dep. Engª. Materiais e Cerâmica, Universidade de Aveiro, 3810-193 Aveiro, Portugal

ABSTRACT

Perovskite-type oxides are evaluated as cathodes for hydrogen peroxide (H$_2$O$_2$) reduction in direct borohydride fuel cells (DBFCs). The study is conducted on button-type ceramic electrodes of LaCoO$_3$ (LC), La$_{0.84}$Sr$_{0.16}$CoO$_3$ (LSC), La$_{0.8}$Sr$_{0.2}$Fe$_{0.8}$Co$_{0.2}$O$_3$ (LSFC), and La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSM), thus avoiding cross-contributions of carbon or nickel catalyst supports. Cyclic voltammetry shows that LSM has the highest activity for H$_2$O$_2$ reduction in alkaline solution, with the other three materials showing minimal (LC) to none (LSC, LSFC) electroactivity. The data also suggest that only LC and LSM are stable within the tested potential window, although the alteration of the samples surface is apparent in scanning electron microscopy images collected after the electrochemical measurements. The analysis of LSM by chronopotentiometry in light of the Sand equation indicates ca. 1 electron involved in the H$_2$O$_2$ reduction. A demonstration DBFC employing a single phase LSM ceramic cathode yields a peak power density of 8.2 mW cm^{-2} at 28 mA cm^{-2}, at 45 °C. This value is about 60% of that obtained with a commercial platinum foil electrode, which is a notable feature and demonstrates the potential of LSM as an alternative low cost cathode for DBFCs.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The direct borohydride fuel cell (DBFC) is a particularly interesting technology that uses an alkaline solution of sodium borohydride (NaBH$_4$) as a fuel fed directly to the anode, overcoming the transportation problems usually associated with hydrogen (H$_2$). Moreover, DBFC reactions occur in alkaline media, where in principle non-precious metal electrocatalysts can be used without major performance loss [1]. The borohydride (BH$_4^-$) oxidation at the DBFC anode proceeds according to Eq. (1), with a standard electrode potential (E^0) of -1.24 V vs. standard hydrogen electrode (SHE).

$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^- \quad (1)$$
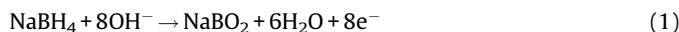
The product of this reaction is sodium metaborate (NaBO$_2$), inert and non-toxic, and can be recycled back to NaBH$_4$ [2]. Typically, the cathodic reaction in DBFCs is the oxygen (O$_2$) reduction but lately there has been much interest in using hydrogen peroxide (H$_2$O$_2$) as the oxidant. In that case, the cathodic process is described by Eq. (2).

$$H_2O_2 + 2e^- \rightarrow 2OH^- \quad (2)$$

Accordingly, the overall cell reaction can be written as Eq. (3).

$$NaBH_4 + 4H_2O_2 \rightarrow NaBO_2 + 6H_2O \quad (3)$$

The E^0 of 0.87 V vs. SHE for the direct reduction of H$_2$O$_2$ (Eq. (2)) is higher than that for O$_2$ reduction (0.40 V vs. SHE). Consequently, direct H$_2$O$_2$ reduction in the direct borohydride/peroxide fuel cell (DBPFC) yields larger theoretical cell voltages (2.11 to 3.01 V, depending on the pH) and specific energy (17 Wh g^{-1}) compared to those of the DBFC (1.64 V and 9.25 Wh g^{-1}). The reported significant increase of power density of a fuel cell with H$_2$O$_2$ as oxidant results from a lower activation barrier and hence faster kinetics of two-electron H$_2$O$_2$ reduction compared to the four-electron O$_2$ reduction [3]. Additional benefit of using H$_2$O$_2$ as oxidant comes from the fact that it is liquid and therefore its storage, transport, handling and controllable feeding to a fuel cell is easier than in the case of O$_2$ gas.

Still, H$_2$O$_2$ as oxidant in fuel cells has some drawbacks as it is prone to spontaneous decomposition into O$_2$ and H$_2$O in the presence of some metals and it is unstable at higher temperatures [9]. Furthermore, fuel cell membrane can deteriorate in the presence of such strong oxidant as H$_2$O$_2$. In general, the main operational issues of the DBPFC are the hydrolysis and thus incomplete BH$_4^-$ anodic electrooxidation [4] and the

* Corresponding author.
E-mail address: diogosantos@tecnico.ulisboa.pt (D.M.F. Santos).

mentioned chemical decomposition of H_2O_2 at the cathode [5]. Therefore, the development of anode and cathode electrocatalysts having high selective catalytic activities for BH_4^- oxidation and H_2O_2 reduction, respectively, has been a key point in DBPFC research [6–11]. Platinum-based catalysts, similarly to gold, palladium and silver, possess good catalytic activity for H_2O_2 reduction reaction (HPRR) but have the disadvantage of high cost [9].

Perovskite-type materials, with general chemical formula ABO_3 where A is a lanthanide or an alkaline earth metal and B is a transition metal, are known to be good electrocatalysts for the oxygen reduction reaction (ORR) in fuel cells and other energy conversion devices, both at low and high temperatures [12–17]. Only few examples of their use in DBFC technologies have been reported, despite their acceptable ORR activity and BH_4^- tolerance in membraneless DBFCs [18,19]. Subsequent reports have confirmed the potential of $La_{1-x}Sr_xCoO_3$ [20] and $LaNi_{0.8}Co_{0.2}O_3$ [21], as cathodes for regular BH_4^-/O_2 DBFCs. Examples of perovskite-type cathodes in DBPFCs are not known, but the few and recent studies concerning the H_2O_2 electroreduction on perovskite electrodes suggest a potentially interesting electrocatalytic performance of $La_{1-x}Sr_xMnO_{3\pm\delta}$ [22,23], $LaNiO_3$ [24], $La_{1-x}Ca_xCoO_{3-\delta}$ [25], and $LaCoO_3$ [23], with the manganites displaying somewhat higher activity [23]. To the best of our knowledge, the HPRR on ferrites has not been assessed so far.

These studies are usually based on optimised electrode designs consisting of mixtures of the catalyst powders with carbon (of various kinds and in proportions approaching 50 vol.%) and an organic binder, which in some cases are pressed onto nickel foam current collectors [15,16,26], themselves also being able to catalyse the reaction. While it has not been demonstrated for the HPRR, there is growing evidence that the addition of carbon to transition metal oxides (e.g., $LaCoO_3$ and $La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$) can enhance the electrocatalytic activity for the ORR in alkaline media by up to one order of magnitude. The underlying mechanism seems to be the electroreduction of O_2 to H_2O_2 on the carbon, which is then decomposed by the oxide [27,28]. This means that the identification of the exact role of the oxides on the performance of these otherwise composite electrodes comprising the carbon and the transition metal oxide particles, implies the knowledge of the behaviour of the oxides themselves. This aspect, certainly hidden by the best performance of the carbon-containing electrodes, remains unexplored in the literature, with few and very recent known reports [27,28].

The investigation of the complex relationships between the perovskite composition and their intrinsic electrocatalytic properties for the HPRR is of extreme importance to rationalise and optimise this type of electrodes, since the vast compositional variety potentially offered by the perovskite structure is difficult to cover on a basis of "synthesise and check". Here we present an electrochemical study of four different perovskite-based materials, namely $LaCoO_3$ (LC), $La_{0.84}Sr_{0.16}CoO_3$ (LSC), $La_{0.7}Sr_{0.3}MnO_3$ (LSM) and the ferrite $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_3$ (LSFC) with the objective of assessing the effect of the transition metal on the electroreduction of H_2O_2, and their performance as cathodes in a DBPFC. The study involves the characterisation by cyclic voltammetry and chronopotentiometry of button electrodes made from dense ceramic pellets to avoid cross-effects of other factors, namely porosity or the mentioned contribution of additional components, such as carbon or nickel supports. Finally, we compare the performance of two equivalent laboratory DBPFCs, one with a commercial platinum foil cathode, and another with the most electroactive perovskite oxide, which is a highlighted contribution of this work.

2. Experimental

2.1. Preparation and characterisation of the electrodes

Commercial powders of the four tested perovskites ($LaCoO_{3-\delta}$, $La_{0.84}Sr_{0.16}CoO_{3-\delta}$, $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-\delta}$ and $La_{0.7}Sr_{0.3}MnO_{3\pm\delta}$, all from Seattle Specialty Ceramics, now Praxair Specialty Ceramics) were shaped into discs by applying uniaxial pressure (70 MPa) in order to obtain powder compacts ($\sim$8 mm in diameter and $\sim$1–2 mm thick) with a fractional density equal or higher than 50% of theoretical value. These compacts were sintered in air at 1425 °C to obtain ceramic samples with fractional density higher than 92%, thus free from percolating porosity. Silver paint (SPI, high purity) was used to glue each ceramic disc to a copper wire, with a thin glass tube protecting the wire. The discs were then mounted in an epoxy resin in a proportion of 5 parts of resin (EpoxiCure Epoxi Resin 20-8130-032) to 1 part of hardener (EpoxiCure Epoxi Hardener 20-8132-008). Prior to the electrochemical measurements the surface of the electrodes was polished using SiC abrasive papers (Struers) of decreasing grit sizes (1200, 2400, 4000) until reaching perfectly smooth surfaces. The geometric area of the electrodes was determined to be 0.35 cm^2.

The surface and the cross-section of the ceramic electrodes before and after the electrochemical measurements were observed by scanning electron microscopy (SEM) on a Hitachi SU-70 microscope equipped with Bruker QUANTAX 400 energy-dispersive X-ray spectroscopy (EDS) detector. The structural studies were carried out on X-ray diffraction (XRD) patterns collected on the surface of the ceramics with a Rigaku Geigerflex D/Max-C series diffractometer using CuK radiation and $2\theta = 3°\ min^{-1}$. The patterns were analysed with PowderCell v2.4 [29] by refining the scale factor, zero shift, background, lattice parameters and peak profile parameters. Two series of patterns were collected, one on the surface of freshly polished samples and another after the electrochemical measurements.

Finally, the room temperature electrical conductivity (σ) of the ceramic pellets was confirmed by 2-probe AC method. The pellets were painted with a commercial silver paste (Algar) on opposite surfaces, and placed on an alumina jig with platinum (Pt) wires to measure the electrical resistance (R) with an Agilent 2980A meter using a test signal amplitude of 100 mV and a frequency range between 20 Hz and 2 MHz. The impedance of the short-circuited cell was subtracted to the measurements in order to correct for the resistance of the wires, and also to minimise the effect of the inductance in the platinum wires. The R values were estimated as corresponding to the high frequency intercept with the real axis. The conductivity was obtained through $\sigma = L(RS)^{-1}$, where S is the area of the electrodes and L is the thickness of the pellets. The results, presented in Table 1, were found to be in good agreement

Table 1

Electrical conductivity, lattice parameters and unit cell volume (indexed on R-3c space group) estimated from the XRD patterns before and after the electrochemical measurements.

Electrode		a, b / Å	c / Å	V / Å^3	Electrical Conductivity / S cm^{-1}
LC	before	5.426(6)	13.061(8)	333.11	0.048
	after	5.428(0)	13.049(1)	332.96	
LSC	before	5.431(7)	13.245(1)	338.42	0.832
	after	5.431(1)	13.261(3)	338.76	
LSFC	before	5.442(0)	13.239(5)	339.56	0.029
	after	5.445(5)	13.238(4)	339.97	
LSM	before	5.504(9)	13.362(6)	350.68	0.117
	after	5.504(8)	13.362(1)	350.66	