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Enhanced durability of a cost-effective perovskite-carbon catalyst for the oxygen evolution and reduction reactions in alkaline environment

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ABSTRACT

The design of a bifunctional air electrode able to carry out both the oxygen reduction and evolution reactions in an alkaline environment is essential for the progress of new-generation energy conversion and storage devices. Alkaline systems allow the use of non-noble metals, which favors a considerable reduction of the system cost. In this work, a cost-effective perovskite, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$, has been investigated as bifunctional catalyst in a 6 M KOH alkaline solution. The perovskite was mixed with an experimental carbon black, characterized by a graphitic structure and a specific surface area of $220 \text{ m}^2 \text{ g}^{-1}$. The perovskite-carbon composite was compared to a Pd/C catalyst (employing the same carbon black as support). Generally, bifunctional catalysts are subjected to high electrochemical potentials, particularly during the oxygen evolution. In order to assess the stability of the bifunctional catalyst, several accelerated degradation tests were performed. Results proved that the perovskite-carbon composite showed good performance for both reactions, in particular for the oxygen evolution. Furthermore, it also presented enhanced stability vs. Pd/C when subjected to degradation tests, maintaining a constant potential over time, even working at high current densities (80 and 125 mA cm^{-2}). This material is envisaged as a very promising bifunctional catalyst, in particular in terms of durability.

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Introduction

Energy conversion and storage devices such as reversible fuel cells, metal–air batteries, and water electrolyzers are governed by the kinetics of two reactions: the oxygen reduction

(ORR) and the oxygen evolution (OER) [1–7]. In alkaline media, the kinetics for these reactions are faster than in acidic media [8,9]. Still, finding a stable and performing bifunctional catalyst is a great challenge to resolve. Many kinds of bifunctional catalysts have been studied in the last decades [2,3,10–16], being noble metals and their oxides the most active

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[1,3–6,8,9,14,17–19]. However, their high cost hinders their application at large scale [20–22]. Pd-based catalysts have been recently investigated as bifunctional catalysts with good performances. Alegre et al. proved its better suitability as bifunctional catalyst in comparison to Pt supported on carbon [23]. McKerracher et al. tested a Pd/C catalyst as air-cathode in a one-cell iron–air battery. Pd/C managed to cycle over 1000 cycles at a current density of 10 mA cm^{-2} [10]. Non-noble catalysts such as transition metal oxides, carbonaceous materials and inorganic–organic composites are very promising and have received a great deal of attention lately in recent literature [1–4,7,11,20,21,24]. Among them, perovskite oxides have emerged as a new class of highly efficient cost-effective catalysts for the oxygen electrocatalysis in alkaline media [1,21,22,25–28]. In spite of their attractive bifunctional catalytic activity, their performance is mainly hindered by their low electrical conductivity and limited surface area [1,26]. For this reason, they are usually combined with carbonaceous materials [26,29–33].

Another issue to take into account for this kind of devices is their durability. The oxygen evolution reaction occurs at high potentials ($>1.4 \text{ V}$ vs. RHE), which means extremely oxidative conditions, where most catalysts, especially the ones based on carbon, rapidly degrade [8,26,34–37]. Highly resistant carbons are then mandatory. In the field of fuel cells, some carbon materials such as carbon nanotubes, carbon nanofibers, graphene, etc, have shown enhanced resistance to corrosion [38–45].

In this work, a perovskite-based catalyst was investigated as bifunctional catalyst for both the ORR and the OER. To improve both the low conductivity and surface area of the perovskite, an experimental carbon black provided by Imerys Graphite & Carbon was employed. This carbon black is characterized by a good electric conductivity, graphitic structure (which is expected to favor a proper resistance to corrosion) and a specific surface area around $220 \text{ m}^2 \text{ g}^{-1}$ [10]. This work was carried out within the framework of a European Project, Necobaut (New Concept of Metal-Air Battery for Automotive Application based on Advanced Nanomaterials, Grant agreement no: 314159). The same carbon black had already been used in the past as the support for a Pd-based catalyst, which showed a good performance and stability as the air electrode in an iron–air battery [10,12]. In this work, the carbon black acts more as a conductive additive than as support for the perovskite. Given the physico-chemical characteristics of both the perovskite and the employed carbon black, a good resistance towards corrosion for this catalyst is expected. The activity and stability of the catalyst were assessed at high electrochemical potentials, simulating the conditions of a metal–air battery.

Experimental

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$, from now on LSFCE, was synthesized by the solid-state reaction method, using oxides and carbonates of the corresponding metals as precursors, as described in Ref. [46]. LSFCE was mixed with an experimental carbon black (named as C) supplied by Imerys Graphite & Carbon. Materials were mixed in iso-propanol in a ball-milling at 100 rpm for 2 h

in a 1:1 ratio (% weight). For the sake of comparison, the same carbon black was employed as support for Pd nanoparticles. Pd/C was synthesized as described in Ref. [10] and used as internal benchmark material. Pd/C has been widely studied for the ORR in alkaline media [10,12,14,17,23,47,48]. Briefly, an acidic solution of $\text{Na}_6\text{Pd}(\text{SO}_3)_4$ was added to a slurry of the carbon black dispersed in water. The amount of Pd-sulfite was calculated to reach a final loading of 30 wt.% of Pd on the carbon support. Then, the Pd sulfite complex solution was decomposed by H_2O_2 to obtain the colloidal form of PdO_x/C , subsequently reduced in H_2 stream at room temperature ($23 \text{ }^\circ\text{C}$) to form the 30 wt.% Pd/C catalyst.

A Philips X-pert 3710 X-ray diffractometer with Cu $K\alpha$ radiation operating at 40 kV and 20 mA was employed to analyze the crystalline structure and the crystallite size. Scanning Electron Microscopy (SEM) analysis were carried out with a FEI XL30 SFEQ microscope operated at 25 kV. Transmission Electron Microscopy analyses were performed in a FEI CM12 transmission electron microscope. Samples were dispersed in isopropyl alcohol and deposited on carbon film-coated Cu grids that were subsequently introduced in the microscope chamber.

The electrochemical analyses were performed in a half-cell connected to an Autolab potentiationstat/galvanostat (Metrohm). A gas diffusion working electrode (GDWE) of 0.5 cm^2 was prepared by depositing the catalytic ink (composed of a 67 wt.% of the catalyst and a 33 wt.% Nafion[®] ionomer) on a gas diffusion layer (LT 1200 W ELAT, E-TEK). The catalyst loading was of ca. $1 \pm 0.05 \text{ mg cm}^{-2}$ when using LSFCE and 0.3 mg cm^{-2} when using Pd/C. A high surface area platinum mesh and an Hg|HgO were employed as counter-electrode and reference electrode, respectively. The electrolyte was a 6 M KOH aqueous solution, prepared from high-purity reagents (Sigma–Aldrich). The catalytic activity towards the oxygen reduction and the oxygen evolution reactions was investigated by linear sweep voltammetry (LSV) from 0.3 to 1.2 V vs. RHE and from 1.2 to 2 V vs. RHE respectively, at a scan rate of 5 mV s^{-1} . The stability of the perovskite-based catalyst was analyzed by different durability tests: charge/discharge cycles and chronoamperometries at different current densities flowing O_2 through the gas-diffusion working electrode during the whole experiment.

Results and discussion

Fig. 1 presents the XRD patterns with the corresponding Miller indexes (JCPDS 89-1268 for the LSFCE and JCPDS 46-1043 for Pd) for both catalysts, LSFCE/C and Pd/C. Crystallite sizes were determined by the Scherrer's equation. Pd/C presented a crystallite size of 3.4 nm (calculated from the (2 2 0) peak at around 68°), whereas the LSFCE/C presented a crystallite size of 28 nm, calculated from the main peaks, (1 1 0), (2 0 0) and (2 1 1). The type of synthesis of the perovskite oxide (at high temperatures) leads to the formation of large crystallites; whereas the synthetic route based on sulfite complexes for the noble metal based catalyst, allows obtaining small crystallites.

Fig. 2 shows the TEM micrographs for both the perovskite (as-obtained from the synthesis) and the employed carbon

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