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Dual role of carbon in the catalytic layers of perovskite/carbon composites for the electrocatalytic oxygen reduction reaction

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ABSTRACT

Perovskite oxides are promising materials for the ORR in alkaline media. However, catalytic layers prepared from perovskite powders suffer from high Ohmic losses and low catalyst utilization. An addition of carbon to the catalytic layers greatly improves the performance of the electrodes in the ORR. In this work composite thin film electrodes comprised of a perovskite oxide (either $LaCoO_3$ or $La_{0.8}Sr_{0.2}MnO_3$) and pyrolytic carbon of the Sibunit family were investigated in aqueous 1 M NaOH electrolyte using cyclic voltammetry and rotating disc electrode (RDE) method with the objective to unveil the influence of carbon on the catalyst utilization and on the ORR electrocatalysis. By systematically varying the oxide to carbon ratio we arrive to the conclusion on the dual role of carbon in composite electrodes. On the one hand, it is required to improve the electrical contact between perovskite particles and the current collector, and to ensure maximum utilization of the perovskite surface. On the other hand, carbon plays an active role in the ORR by catalyzing the O_2 reduction to H_2O_2. Composite electrodes catalyze the $4e^-$ ORR in contrast to carbon which is only capable of catalyzing the $2e^-$ reduction. For $LaCoO_3$ composite electrodes, carbon is responsible for the catalysis of the first steps of the ORR, the role of $LaCoO_3$ being largely limited to the hydrogen peroxide decomposition and/or reduction. For $La_{0.8}Sr_{0.2}MnO_3$ composite electrodes, along with the catalysis of the chemical decomposition and/or reduction of H_2O_2 produced on carbon, the perovskite also significantly contributes to the first steps of the ORR. The results of this work suggest that the ORR on the carbon and the oxide components of composite cathodes must be considered as coupled reactions whose contributions cannot be always separated, and that neglecting the contribution of carbon to the ORR electrocatalysis may lead to erroneous values of the catalytic activity of perovskite materials.

1. Introduction

The cathodic oxygen reduction reaction (ORR) is one of the most important processes in energy conversion systems such as fuel cells and metal-air batteries. The sluggish kinetics of the ORR is largely responsible for the voltage losses in proton exchange membrane fuel cells (PEMFC) and other types of low temperature fuel cells [1,2]. Therefore numerous studies are focused today on the development of new electrocatalysts for the ORR [2–4]. During the last decade the research has been mainly focused on the ORR in acid electrolytes due to the rapid development of PEMFCs. However, the advent of anion exchange membranes with high conductivities and satisfactory stabilities has boosted the interest towards the ORR in alkaline media.

The early studies of the ORR in aqueous alkaline electrolytes were performed on metal electrodes and date back to 1960s [5–7]. It was suggested that likewise the ORR in acidic electrolytes, in alkaline media the reaction may either follow a “direct” $4e^-$ (Eq. (1)) or a “series” pathway. The former involves the rupture of the O—O bond at initial steps, while the latter occurs through formation of HO_2^-/H_2O_2[1] (Eq. (2)). The peroxide intermediate can either diffuse away from the electrode, or be further reduced to OH^- in an electrochemical reaction (Eq. (3)). Alternatively, it may decompose into O_2 and H_2O in a chemical reaction (Eq. (4)). It is obvious that each of the equations below comprises a number of elementary steps which are still not fully understood.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (2)$$

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[1] Depending on the pH; p*K*a (H_2O_2) = 11.7 [8].

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$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (3)$$

$$H_2O_2 \rightarrow O_2 + 2H_2O \quad (4)$$

In contrast to the ORR in acidic media, which occurs at a reasonable rate only on noble metal electrodes, the ORR in alkaline media is catalyzed by a wider range of materials, including oxides [9–11], and carbon materials [12,13]. It was already clear from the early studies that transition metal oxides can catalyze either the “direct” pathway (Eq. (1)), or the electroreduction of peroxide (Eq. (3)) and/or its decomposition (Eq. (4)). Electrocatalytic activity of oxides in the H_2O_2 reduction (Eq. (3))/decomposition (Eq. (4)) has motivated many researchers to use them for improving the electrocatalysis of the ORR on carbon, typically supporting only the $2e^-$ reaction (Eq. (2)) at reasonable overvoltages [12,13].

In this work, perovskite oxides are studied as the ORR electrocatalysts in alkaline media in view of their potential applications in alkaline fuel cells with solid polymer electrolytes (SAFC). The perovskite structure ABO_3 can incorporate almost any metal cation either in A or in B position thanks to some tolerance to the distortions of the structure [14,15]. Thus, the properties of perovskite-based catalysts can be tuned by varying the composition of oxides, offering vast possibilities for electrocatalysis. Here we focus on $LaCoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$, which have demonstrated high catalytic activity in the ORR and OER (oxygen evolution reaction) [16–19].

Various electrode configurations have been applied to study the ORR/OER electrocatalysis on perovskites, including pellets [16,17,20], gas-diffusion electrodes [21–25], films obtained by painting the oxide slurry on a metal foil [26,27], or by spreading oxide particles and a binder, with or without carbon, on a glassy carbon support [18,28–31]. The thin film approach is compatible with the rotating disc (RDE) [28] and the rotating ring disc electrode (RRDE), the advantage compared to the gas-diffusion electrode consisting in a more reliable separation of kinetic and mass transport contributions. While pellets allow to avoid binders or other additives, their disadvantage lies in the high porosity and concomitant internal diffusion complications. For example, Bockris and Otagawa [32] estimated the roughness factor of perovskite pellets prepared by solid state synthesis as ca. 1000. Moreover, electrode formulations containing perovskites alone usually suffer from high Ohmic losses, posing problems for the ORR investigation but also for practical applications of perovskite materials as fuel cell cathodes.

Addition of carbon powders significantly improves the conductivity of oxide-based electrodes. Several studies have proven that carbon is required in order to increase the electrocatalytic efficiency of oxide materials [23,25]. However, an appreciable catalytic activity of carbon in the ORR in alkaline media brings up a question on the separation of contributions from the two components in these composite materials. Recent studies of the ORR on perovskite oxides neglect the contribution of carbon into the ORR kinetics, even if the latter is added to the thin film electrodes [28,29]. Therefore, the objective of this work is to unveil the role of carbon in perovskite/carbon composite cathodes, and to verify the correctness of conventional approaches to quantify the activity of perovskites by either neglecting or subtracting the contribution of carbon to the ORR kinetics. In order to achieve this goal, we vary systematically the oxide to carbon ratio and study electrochemical and electrocatalytic properties of thin film composite electrodes using cyclic voltammetry and the RDE method. The results of this work suggest that the ORR on the carbon and the oxide components of composite cathodes must be considered as coupled reactions whose contributions cannot be always separated. Thus, either neglecting or subtracting the contribution of carbon to the ORR electrocatalysis may lead to erroneous values of the catalytic activity of perovskite materials.

2. Materials and methods

2.1. Synthesis and characterization

Ceramic samples of $LaCoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$ were synthesized with the sol–gel method described in Ref. [33] using polyacrylamide gel. Samples were annealed in air at 650 °C for 1 h, and milled in a planetary mill in the presence of ethanol for 3 h at 120 rpm using WC balls. The phase purity of compounds was verified by X-ray powder diffraction recorded with Huber G670 Image plate Guinier diffractometer (CuKα1 radiation, curved Ge monochromator, image plate detector). Unit cell parameters were refined by the full profile Rietveld analysis using the GSAS program package [34,35].

The morphology of the samples was analyzed by scanning electron microscopy (SEM), while the elemental distribution of the composite electrodes was studied using the energy-dispersive X-ray spectroscopy (EDX) and the elemental mapping methods (Jeol 6007F). The specific surface area of powders was determined by Brunauer, Emmett and Teller (BET) method (Micromeritics).

2.2. Electrode preparation

In this work, the effect of the quantity of carbon at a constant loading of perovskite (91 $\mu g\ cm_{geo}^{-2}$) and the quantity of perovskite at a constant loading of carbon (37 $\mu g\ cm_{geo}^{-2}$) on the ORR were studied. Carbon of the Sibunit family (BET surface area 65.7 $m^2\,g^{-1}$) was chosen for its high purity, avoiding reactions catalyzed by impurities, and high electrical conductivity [36–38]. The desired amounts of the oxide and carbon powder were mixed together (Table 1). Milli-Q water (18.2 MΩ cm, Purelab) was added to get a desired suspension of the powder: 0.67 $g\,L^{-1}$ of perovskite for the samples with the constant amount of perovskite, and 0.27 $g\,L^{-1}$ of carbon for the samples with the constant amount of carbon. The suspension was then treated in an ultrasonic bath during 30 min to break down agglomerates and disperse particles. A glassy carbon (GC) RDE (0.07 cm^2 geometric area, Autolab) was successively polished with 1.0, 0.3 and 0.05 μm alumina slurry (Escil) to get a mirror finish. 3.2 μL of the catalyst suspension was taken under sonication to keep a homogeneous mixture, drop cast onto the GC support following the procedure adapted from Schmidt et al. [39], and dried under N_2. This last operation – deposition and drying – was repeated three times in order to get a homogeneous coverage of the electrode and to improve the reproducibility. After drying, 2 μL of an alkaline AS-4 ionomer from Tokuyama Company (0.011 wt.% solution in water) was added as a binder to improve the stability of the thin layer electrode. In order to better identify the contribution of carbon, electrodes containing only carbon (no perovskite) and ionomer were prepared following the same procedure and the quantities as indicated in Table 1.

The thickness t of the catalytic layer was estimated using Eq. (5):

$$t = m_1/(\pi r^2 \rho_1) + m_2/(\pi r^2 \rho_2) \quad (5)$$

Here m_1 and m_2 stand for the mass of the perovskite oxide and carbon, respectively; ρ_1 and ρ_2 for the density of the perovskite oxide and carbon, respectively; r is the radius of the RDE (0.15 cm). The powder densities of materials used in this study were estimated as 0.65 and 0.4 $g\,cm^{-3}$ for perovskite oxides and the Sibunit carbon, correspondingly.

Pt/C (40 wt.% Pt on carbon black, Alfa Aesar) was utilized as a benchmark of the ORR activity. The surface area of Pt particles on the electrode was estimated using the coulometry of the hydrogen underpotential deposition and found to be 1.34 cm^2.