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CoMn-LDH@carbon nanotube composites: Bifunctional electrocatalysts for oxygen reactions

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ABSTRACT

In the present work, a set of five Layered Double Hydroxides, LDH, containing Co and Mn derived electrocatalysts was prepared for the oxygen electrode, evaluating their performances in ORR and OER. A LDH with a Co/Mn ratio of 4, CoMn4, was the reference electrocatalyst of the set, presenting the typical hydrotalcite structure with a trace of $MnCo_2O_4$, with a surface area of $76\,m^2\,g^{-1}$. HNO_3 oxidized carbon nanotubes (CNT_HNO_3) and CNT_HNO_3 with a low content of carboxylic acids (CNT_ HNO_3tt350), were incorporated into the CoMn4 synthesis, obtaining CoMn4@CNT_HNO_3 and CoMn4@CNT_HNO_3tt350 with surface areas of 111 and $167\,m^2\,g^{-1}$, respectively. According to X-ray diffraction (XRD), the oxide phase of CoMn4@CNT_HNO_3 is composed by a mixture of LDH with $MnCo_2O_4$, while the low%COOH on the carbon surface promoted the synthesis of LDHs as the only oxide structure at CoMn4@CNT_HNO_3tt350. Moreover, after a thermal treatment of the latter electrocatalyst, the LDHs were totally converted into $MnCo_2O_4$.

All electrocatalysts showed to have activity over both oxygen reactions when the KOH solution was saturated with O_2. A detailed ORR study showed that the LDH structures mixed with CoMn oxides, present at CoMn4@CNT_HNO_3, play a relevant role in ORR, exhibiting an onset potential, E_{ORR}, of -0.274 V. On the other hand, CoMn4@CNT_HNO_3tt350 led to a four-electron mechanism for ORR, similar to the Pt/C standard. The best OER potential (0.636 V) was also obtained for CoMn4@CNT_HNO_3tt350. Regarding the oxygen electrode bifunctionality, a good balance between ORR and OER was observed for the CoMn4@CNT_HNO_3tt350_N_2 composite.

1. Introduction

The growing demand for energy, together with the limited availability of fossil fuels and their harmful environmental impacts, encourages the development of low-cost and less-polluting energy generation/storage devices based on renewable sources [1,2]. However, the intermittent nature of these energy resources may compromise the delivery of electricity at full time. The design of efficient energy storage/conversion devices is becoming a target to achieve the efficiency needed for real working conditions [1,3]. Fuel cells are seen as a viable alternative, especially for portable technologies and transport applications [4], since the electrical energy is produced by means of an electrochemical reaction between a fuel (typically hydrogen) and an oxidant (oxygen from the atmosphere) [5]. A fuel cell combined with an electrolysis cell is denominated a Unitized Regenerative Fuel Cell, URFC. This device, working in the electrolysis mode, allows storing the intermittent electricity generated by renewable sources by converting water into H_2 and O_2; the hydrogen produced is stored on-site for subsequent consumption with the device working in the fuel cell mode, when there is a demand of energy [6].

The energy conversion and storage at URFC are driven by four electrochemical reactions, where the oxygen reactions occur at the cathode, while the hydrogen reactions occur at the anode. In the electrolysis mode at URFC, the excess of electricity produced by the renewable sources is converted to chemical energy by means of two electrochemical reactions, the hydrogen and oxygen evolution reactions (HER and OER), producing H_2 and O_2, respectively. In the fuel cell mode, the chemical energy is converted into electricity when the renewable sources are unable to produce enough electricity to meet the needs of consumers. In this case, both gases are consumed by the respective electrochemical reaction: the oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR) [6]. Since the

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kinetics of the oxygen reactions are very slow compared to the hydrogen processes, leading to considerable electrochemical overpotential requirements, the development of oxygen electrocatalysts is of crucial importance to bring these technologies to a competitive commercial standing [7–9].

Traditionally, Pt and IrO_2 or RuO_2 and their alloys have been employed as electrocatalysts in ORR and OER, respectively, due to their relatively low overpotential and high current density. However, Pt- and Ir/Ru-based electrocatalysts suffer from low stability, high cost and they are limited in nature [7,10].

Composite metal oxides incorporating two or more transition metal elements, including simple and mixed-metal oxides, and hydro(-oxy) oxides have been studied extensively during the last few years. Layered Double Hydroxides (LDH), also known as hydrotalcite-like compounds or anionic clays, are composed of brucite-like layers in which a fraction of divalent metal cations, coordinated octahedrally by hydroxyl groups, has been replaced isomorphously by the trivalent metal cations, giving positively charged layers. These compounds can be represented by the following general formula $[M^{II}_{1-x}M^{III}_{x}(OH_2)]^{x+}[A^{n-}_{x/n}\cdot yH_2O]^{x-}$ where M^{II} and M^{III} are divalent metal cations, (e.g. Mg^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, or Zn^{2+}) and trivalent metal cations (e.g. Al^{3+}, Cr^{3+}, Ga^{3+}, In^{3+}, Mn^{3+} or Fe^{3+}), respectively, A^{n-} is a n-valent anion and the value of x is equal to the molar ratio $M^{2+}/(M^{2+} + M^{3+})$ and is generally in the range 0.2–0.33 [10–13].

Manganese oxides, MnO_x, are among the most promising non-precious metal ORR electrocatalysts [14–16], since they have high stability against corrosion and relatively high catalytic activity [7]. On the other hand, many studies show that cobalt oxides and hydroxides have good catalytic activities for OER [9,17–19]. Therefore, many articles have studied the combination of these two metal oxides as a bifunctional electrocatalyst for the two considered reactions [7,20–23].

Herein, we report the synthesis and characterization of low cost bifunctional electrocatalysts for both oxygen reactions, ORR and OER, based on the cobalt and manganese Layered Double Hydroxides structures. The LDHs structure, due to the possibility of incorporating mixed metal ions into layers with several compositions, can also be converted into the corresponding mixed metal oxides (MMOs) with a uniform M^{2+} and M^{3+} distribution by thermal treatment. In addition, oxidized CNTs were added during the LDHs synthesis, not only to compensate for their low electronic conductivity, but also to increase the surface area and, consequently, the catalytic activity of the resulting composite for both reactions.

2. Experimental section

2.1. Materials and reagents

Manganese (II) acetate tetrahydrate, Mn(CH3COO)3·4H2O (99.0%, Acros Organics), cobalt (II) nitrate hexahydrate, $Co(NO_3)_2{\cdot}6H_2O$ (99.0%, Aldrich), sodium hydroxide, NaOH, (98.5%, José Manuel Gomes dos Santos, Lda.) and sodium carbonate, Na_2CO_3 (99.8%, Panreac) were used in the synthesis of the LDH electrocatalysts. Commercial multi-walled carbon nanotubes (95%, Nanocyl-3100) were oxidized with nitric acid, HNO_3 (65%, Sigma-Aldrich). The 20 wt% Pt/C (Printex80) electrocatalyst is the standard electrocatalyst used in this work, which was prepared according to the procedure described by Rocha et al. [24].

2.2. Preparation of the electrocatalysts

The LDH precursor was prepared according to the procedure described by Wang et al. [20], with some convenient adaptations. This methodology has two defined steps based on separate nucleation and aging of the structures. Typically, the nucleation step starts with a salt solution (an aqueous solution containing $Mn(CH_3COO)_3{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$, with a Co/Mn molar ratio of 4:1, with a total cation concentration of 0.2 M) and an aqueous basic solution, with equal volume to the salt solution, containing NaOH and Na_2CO_3, whose concentrations were calculated based on the following expressions: $[CO_3{}^{2-}] = 2.0\ [Mn^{3+}]$ and $[OH^-] = 1.6\ ([Co^{2+}] + [Mn^{3+}])$ [20]. Both solutions were simultaneously added at room temperature, under continuous stirring, and the pH of the resulting solution was measured. Then, the obtained suspension was aged at 60 °C during 6 h, allowing the growth of the layers and the corresponding intercalation of water and carbonate molecules. Once finished the aging step, the solution was washed with deionized water to remove all the excess of base and dried at 60 °C overnight. The resulting electrocatalyst, denominated CoMn4, is the starting material for the remaining electrocatalysts presented in this work.

The CoMn4@CNT_HNO_3 composite was prepared considering a 50% oxide phase and 50% carbon material proportion. The carbon nanomaterial used in this work was carbon nanotubes oxidized in liquid phase with HNO_3 7 M, CNT_HNO_3, according to Gonçalves et al. [25], in order to create anchoring sites for the growth of LDH. First, the free spaces present at CNT_HNO_3 were filled with water, using the traditional incipient wetness impregnation method, and subsequently added to the salt solution; the nucleation and aging steps were reproduced according to the methodology used for the CoMn4 synthesis, yielding the CoMn4@CNT_HNO_3 sample.

In order to evaluate the effect of the acid oxygen groups, namely carboxylic acids, CNT_HNO_3 were submitted to a thermal treatment at 350 °C, under N_2 atmosphere, during 4 h, yielding the CNT_HNO_3tt350 sample. CoMn4@CNT_HNO_3tt350 was prepared using the same procedure of the CoMn4@CNT_HNO_3 sample.

Well dispersed mixed oxide electrocatalysts were prepared using a controlled thermal treatment of the LDHs. For that purpose, CoMn4 and CoMn4@CNT_HNO_3tt350 were submitted to a thermal treatment at 350 °C, under N_2 atmosphere, during 4 h. The resulting electrocatalysts were CoMn4_N_2 and CoMn4@CNT_HNO_3tt350_N_2, respectively.

2.3. Characterization of the electrocatalysts

X-ray diffraction (XRD) measurements were taken using an X-ray diffractometer (PANalytical X′Pert PRO) with Cu Ka (λ = 1.54 nm). A voltage with an intensity of 50 kV was used, and the current intensity was 40 mA. The results were collected in the 2θ range between 10° and 90°, with a speed of $0.017°\ s^{-1}$.

Transmission Electron Microscopy (TEM) characterization was performed using a LEO 906E instrument, with operating voltage of 120 kV. The samples were previously dispersed in ethanol with the assistance of ultrasounds, and a drop of this suspension was deposited in a copper grid with formvar film.

Thermogravimetic (TG) analyses of the electrocatalysts were performed on a Netzsch STA 409PC apparatus. Samples of the electrocatalysts were heated to 350 °C at $5\ °C\ min^{-1}$ under N_2 atmosphere.

The textural parameters were determined from the N_2 adsorption isotherms at −196 °C, using a NOVA 4200e analyser of Quantachrome Instruments. Samples of all the electrocatalysts (about 100 mg) were previously degassed at 120 °C for 5 h. The specific surface areas were calculated by applying the BET equation (S_{BET}) to portions of the isotherms within the $0.05 < P/P^o < 0.30$ relative pressure range.

In addition, elemental analysis (EA) was performed on Elementar instrument, model rapid Micro cube.

2.4. Electrochemical studies

Electrochemical measurements were carried out on an Autolab electrochemical workstation (Eco Chemie B.V.), controlled by NOVA v1.10 software, with a conventional three electrode cell. A glassy carbon rod (2 mm diameter) and Ag/AgCl (sat. KCl) electrodes were used as counter and reference electrode, respectively. About 1 mg of electrocatalyst was ultrasonically suspended in a water, ethanol and