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GRAPHENE-BASED ELECTROCATALYSTS WITH ENHANCED PERFORMANCE TOWARDS OXYGEN REDUCTION REACTION DECORATED WITH COBALT, IRON AND/OR TITANIUM

Giovanni Lemes[1], José Manuel Luque-Centeno[1,3], Elena Pastor[2], María Victoria Martínez-Huerta[3], David Sebastián[1], María Jesús Lázaro[1*]

[1]*Instituto de Carboquímica. CSIC, C/ Miguel Luesma Castán nº 4 50015, Zaragoza, Spain.*
[2]*Instituto de Materiales y Nanotecnología, Universidad de La Laguna, Apdo 456, 38200, La Laguna, Spain.*
[3]*Instituto de Catálisis y Petroleoquímica (CSIC), Marie Curie 2, 28049 Madrid, Spain.*

*Presenting author's e-mail: mlazaro@icb.csic.es

Introduction

The development of non-noble metal electrocatalysts towards the oxygen reduction reaction (ORR) is a key step to launch fuel cells (FCs) into the market. Carbon-based materials, such as graphene, have been proposed as an alternative to platinum group metals (PGMs) at the cathode of FCs because they are inexpensive, widely available and active towards ORR. The modification of reduced graphene oxide (rGO) structure by doping procedures with heteroatoms (N, P, S, B) and with earth-abundant metals creates structural defects which can enhance the ORR activity[1]. In particular, the creation of active sites formed by Me-N-C species (Me = Co/CoO, Fe, Ti, Mn, etc.), is highly related with an enhancement in the catalytic activity towards the ORR[2].

Materials and Methods

In order to compare the influence of the synthesis method, catalysts have been prepared following two different routes. Graphene oxide (GO) has been prepared from graphite by a modified Hummers' method. Cobalt chloride (II), iron chloride (II) and titanium n-butoxide (IV) have been used as metallic precursors. For the first set of catalysts, a two-step synthesis has been used (henceforth R1). Firstly, N-doped graphene (NrGO) has been synthesized by a thermal treatment of GO with urea at 800 ºC. In the second step, NrGO was decorated with iron and/or cobalt by reduction of metal precursors with sodium borohydride at room temperature followed by thermal annealing at 800 ºC. For the second set of catalysts, a direct annealing method has been carried out (R2)[2]. GO, metal precursors and urea were thermally annealed at 800 ºC in a single step synthesis. Composites synthetized following R1 have been labelled as NrGO-Co-R1, NrGO-Fe-R1 and NrGO-CoFe-R1, and the ones prepared by R2 have been labelled as NrGO-Co-R2, NrGO-Ti-R2 and NrGO-CoTi-R2.

Results and Discussion

The structures of the catalysts were investigated by XRD (not included). The X-ray diffraction patterns have demonstrated that all composites exhibit the diffraction peak at a 2Θ of 26.6º associated to graphitic carbon (002), revealing the effective GO reduction. Metallic cobalt was obtained regardless the synthesis route in the monometallic Co catalysts (NrGO-Co-R1, NrGo-Co-R2) as well as in NrGO-TiCo-R2 and NrGO-FeCo-R1. NrGO-Fe-R1 presents metallic iron and FeN crystalline phases. Besides, the catalyst NrGO-FeCo-R1contains Co, Fe and Co-Fe

alloy according to XRD. Regarding catalysts containing Ti, NrGO-Ti-R2 and NrGO-TiCo-R2 have showed two different TiO_2 structures, corresponding to anatase and rutile phases.

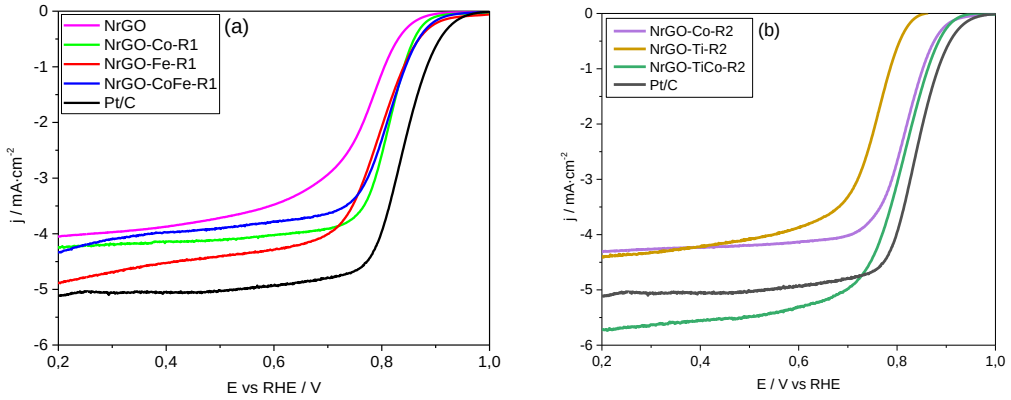

Figure 1. Electrochemical behaviour towards ORR recorded at 1600 rpm in oxygen saturated NaOH 0.1 M electrolyte for catalysts synthetized by (a) R1 and (b) R2. Scan rate: 2 mV s^{-1}.

In order to determine the catalytic activity of synthetized composites, linear voltammetries have been performed between 1.0 V and 0.2 V (vs. RHE) for ORR (Figure 1). In all composites prepared with cobalt or iron, the electrocatalytic activity is improved in comparison with the NrGO catalyst, in contrast with monometallic Ti exhibiting poorer performance. Composites decorated with monometallic cobalt (NrGO-Co-R1 and R2) have showed similar results for the ORR, having the same onset potential of 0.9 V and a value of diffusion limiting current near to -4.3 mA cm^{-2}. Comparing bimetallic composites, the formation of Co-Fe alloy does not enhance the performance of the catalysts in comparison with the monometallic counterparts. On the other hand, the catalyst prepared using titanium and cobalt has demonstrated a good electrochemical behaviour than Co-based catalysts, approaching the activity of a commercial Pt/C catalyst.

Conclusions

Two different synthesis methods have been successfully used to produce NrGO with non-noble metals with no significant differences between them. Attending to the metal, the use of cobalt and iron nanoparticles improves the catalytic performance in comparison with titanium composite or the bare NrGO. However, the use of titanium in combination with cobalt appears to significantly favour the electrocatalytic behaviour of the composites in comparison with the cobalt-iron composites.

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