

# Bifunctional electrocatalysts based on N-Doped graphene and modified with Ti and Co for unitized regenerative fuel cells

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## Objectives and Novelty

The increasing demand of energy that humanity had suffer in the last times, added to the global warming expanse associated to the fossil fuels used as main energy source, have made that the humanity has to afford one of its highest challenges: the search for new sources of sustainable energy. Currently, the use of electrochemical energy conversion systems like fuel cells (FC) and electrolyzers (PEM) have been raised as good candidate to solve this problem. These kinds of devices are so important than some government agencies have proposed some strategies in order to develop the use of green H<sub>2</sub> as alternative for the generation of electrical energy. In this sense, some strategies like the pickups stabilised by the European Union as “European Green Deal” or “EU Hydrogen Strategy” remarks the importance of contribute to the improvement of these technologies in order to reach a more sustainable future.

To accomplish these targets, low temperature unitized regenerative fuel cells (URFC) are a promising technology for storing energy via hydrogen. A URFC consists of a single device capable of working as a FC and WE, in such a way that only one of the modes is operational in time. With these devices is possible to generate hydrogen by the electrolysis of water supplied by renewable energies, its storage and its use directly in the URFC to obtain electricity when necessary. However, development of these technologies has its main limitation in the oxygen electrode reactions, which are the oxygen reduction (ORR) and evolution (OER) reactions, whose high overpotential in both reactions (1.23 V vs RHE) make necessary the use of catalysts based on noble metals which increase significantly the cost of manufacture. To solve this, in the last decade the efforts have been focused in the use of carbon-based materials as catalysts combined with early transition metals, creating a new range of materials named *composites*, whose high conductivity, availability and stability make them good candidates to substitute actual noble metal-based catalysts as Pt or Ir.

For this reason, the aim of this doctoral thesis is the design and optimization of a synthesis method which allow the obtention of *composites* prepared by combining nitrogen doped graphene with Ti and Co nanoparticles. This work has been focused in the optimization of some parameters as the precursor mixture preparation, in order to obtain different N-doped graphene structures, and the pyrolysis

temperature and time for the thermal reduction step.

## Results

The *composites* synthesis starts with the preparation of a precursor mixture based on graphene oxide, urea and a metallic precursor (NrGO). In the first part of this work, monometallic Ti *composites* have been prepared by pyrolyzing the above mixture at 800 °C at different duration times (1h, 2h and 3h). Physicochemical characterisation have shown a very similar chemical composition with a metal amount around 20 – 30 wt.%. The nitrogen has been successfully incorporated into titanium *composites*, but decreases with pyrolysis time. It is observed the presence of TiO<sub>2</sub> anatase and rutile in all composites. In addition, *composites* annealed at low temperatures show the formation of Ti-N species and mixed oxides of Ti<sup>3+</sup>. Electrochemical characterization has been carried out using a three electrodes system in alkaline environment. Comparing all Ti-based *composites* can be demonstrated that the combination of graphene doped with Ti oxide nanoparticles have achieved much better electrocatalytic performance than bare N-doped graphene and Ti-based graphene without N species. Activity towards OER have showed similar results, where Ti-based catalysts have shown higher current than N-doped graphene *composite*, confirming that addition of Ti increase the catalytic performance of materials[1]. The metal effect has been investigated substituting Ti by Co. Co-based material has been prepared using similar synthesis conditions used to obtain the best bifunctional Ti catalyst. Results show that Co and Ti *composites* have similar metal and nitrogen loading with no remarkable changes in the physicochemical characterization. According to the electrochemical characterization, Co *composite* have shown better activity towards ORR and OER than Ti *composites*. In addition, the electrochemical stability is significantly improved by using cobalt in the *composite*[2].

The study of the combined effect of Ti and Co oxides mixed with N-doped graphene has been prepared using an atomic relationship 1:1 of Ti-Co precursors. In addition, the effect of the pyrolysis time and temperature has been studied at 700 and 800 °C for 1, 2 and 3 hours. Physicochemical characterisation has confirmed the introduction of N, Co and Ti in the *composite*. The use of different techniques as XRD, XPS and HAADF-STEM has demonstrated that the main metallic phase in those *composites* annealed at 700 °C are combined structures of CoTiO<sub>3</sub>, while

in the catalysts annealed at 800 °C, Co and Ti oxides are presented as separately phases. Electrochemical characterization has revealed that catalysts annealed at 800 °C and low processing times have the best performance for both reactions, indicating that the presence of separate Co and Ti oxides promotes the formation of active sites. The stability of the catalysts for the ORR and OER show that catalysts synthesized at 800 °C are quite stable than those synthesized at 700 °C[3].

A second group of materials have been prepared with the aim of increase the specific BET area of the *composites*. In these materials, the synthesis method has been modified to obtain a new N-doped graphene structure called *cryogel* (NGA). In addition, the influence of the Co precursor has been studied employing three different Co salts:  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Cl),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Nit) and  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (Ac). The absorption isotherms obtained for the new *composites* have shown an increased BET area with an increase of 100  $\text{m}^2/\text{g}$  compared with reduced graphene-based *composites*. Chemical composition determined by ICP-OES revealed that the metal amount and distribution are affected by the employed Co precursor, meanwhile, nitrogen amount is equal in all bimetallic *composites*. Crystalline phases determined by XRD are very similar than founded in the catalysts pyrolyzed at 800 °C in the previous study. XPS results reveals that all bimetallic *cryogels* have similar properties, where N-pyridinic is the predominant nitrogen specie. Electrochemical measures performed by the same methods than the previous studies have revealed that the bests bifunctional catalysts are TiCo/NGA-Ac and TiCo/NGA-Nit, suggesting that using counterions with higher sizes as  $\text{NO}_3^-$  and  $\text{CH}_3\text{COO}^-$  allows the formation of higher number of active sites.

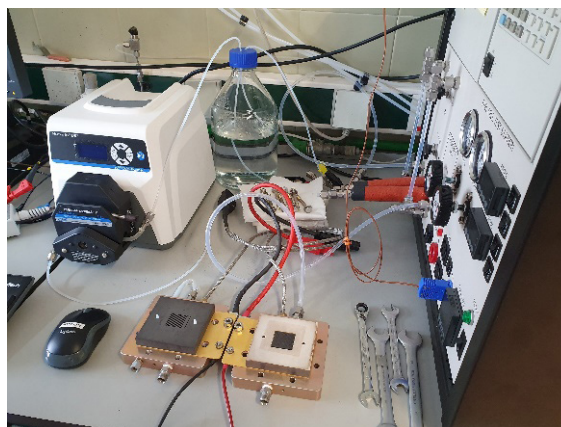
To compare the electrochemical behaviour of the best catalysts, the final part of this work has been the study of the bifunctional behaviour in a prototype URFC (**Figure 1**). Catalysts have been sprayed in a carbon substrate and employed as oxygen electrode using a Fumion® FAA-3-50 as anionic alkaline membrane and a Pt/C (40%) electrode as hydrogen electrode. Measures on FC mode show that the best catalysts have been the TiCo/NGA-Ac and TiCo/NrGO-800-1h. In electrolyser mode, the best catalysts have been TiCo/NGA-Ac, with better performance than Pt/IrO<sub>2</sub> commercial catalysts, demonstrating that those catalysts prepared with N-doped graphene *cryogels* as carbon phase have the best bifunctional performance[4].

## Conclusions

In this study, a simple, fast and reproducible method has been designed for the obtention of catalysts based on N-doped graphene and Co and isolated materials as TiO<sub>2</sub>. This synthesis method can be used to the obtention of different formulation of materials, with different metallic phases and carbon-based materials, obtaining active catalysts for ORR

and OER in all cases.

In addition, the postulated method has allowed the study of physicochemical properties of different materials which have helped to understand which active sites are more important to obtain catalysts for the oxygen electrode in a URFC.



**Figure 1.** Prototype URFC system used to determine electrocatalysts activity.

## Related Publications

- [1] J. M. Luque-Centeno, M. V. Martínez-Huerta, D. Sebastián, S. Pérez-Rodríguez, and M. J. Lázaro, "Titanium Dioxide/N-Doped Graphene Composites as Non-Noble Bifunctional Oxygen Electrocatalysts," *Ind. Eng. Chem. Res.*, vol. 60, no. 51, pp. 18817–18830, Dec. 2021, doi: 10.1021/acs.iecr.1c02896.
- [2] J. M. Luque-Centeno, M. V. Martínez-Huerta, D. Sebastián, G. Lemes, E. Pastor, and M. J. Lázaro, "Bifunctional N-doped graphene Ti and Co nanocomposites for the oxygen reduction and evolution reactions," *Renew. Energy*, vol. 125, 2018, doi: 10.1016/j.renene.2018.02.073.
- [3] J. M. Luque-Centeno, M. V. Martínez-Huerta, D. Sebastián, J. I. Pardo, and M. J. Lázaro, "CoTiO<sub>3</sub>/NrGO nanocomposites for oxygen evolution and oxygen reduction reactions: Synthesis and electrocatalytic performance," *Electrochim. Acta*, vol. 331, 2020, doi: 10.1016/j.electacta.2019.135396.
- [4] D. Sebastián, G. Lemes, J. M. Luque-Centeno, M. V. Martínez-Huerta, J. I. Pardo, and M. J. Lázaro, "Optimization of the catalytic layer for alkaline fuel cells based on fumatech membranes and ionomer," *Catalysts*, vol. 10, no. 11, 2020, doi: 10.3390/catal10111353.

Full Thesis can be downloaded from <https://digital.csic.es/handle/10261/244352>