

Development of Electrodes for fuel cells Pt-free load

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Abstract:

Direct methanol fuel cells, DMFCs, have a great interest due to their applications in the development of devices for portable energy applications due to their ability to produce electricity using methanol as fuel. These systems are environmentally friendly. Nevertheless, the methanol crossover from the anode to the cathode through the electrolytic membrane, the poisoning of the catalyst and the cost of these systems are some of the problems. One of the responsible of the high cost of these systems is the use of platinum, Pt, for the development of the electrodes.

The objective of this work is to develop catalysts Pt-free. Materials based on FeCo solid solutions are synthesized by the combustion method and characterized for their further application as anode catalysts in DMFC. In addition, a post-treatment in reactive environments has been carried out the aim of improving the metal solution. The prepared materials have been morphological, structural and electrochemically characterized to test their activity towards methanol oxidation. Further, the catalytic layer composition has been designed to prepare electrodes by spray, in such a way that the slurry can be homogeneously sprayable on the surface of the carbon paper gas diffusion layer. The catalyst and electrodes have been studied to know if they are good candidates as anode of DMFCs, and to modify the synthesis and/or the different processes to improve their activity.

Keywords:

DMFC; electrocatalyst; Pt free; catalytic layer; combustion synthesis.

1. Introduction

The development of the society has increased the consumption of energy. The high cost of energy, the lack of resources and the pollution among others, make urgently to seek and develop new and renewable energies [1,2]. Fuel cells, which convert chemical energy into electrical energy via electrochemical reactions on the electrode surface are a promising alternative and clean energy resource [3-5].

Direct methanol fuel cells, DMFCs, have a great interest due to their high energy density, high conversion efficiency, low operating temperatures, low emissions of toxic substances [4] and also to their applications in the development of devices for portable energy applications [6-8]. Moreover, these systems are environmentally friendly, have easy operation and simple construction [4,9]. However, the crossover of methanol from the anode to the cathode through the electrolytic membrane, sluggish oxidation kinetics and the durability and deteriorating catalyst performance are some factors which have restricted the commercialization of DMFC tools [1]. Another problem is the high cost of the catalysts due to the use of Nobel metals like platinum. Consequently, it is necessary to reduce the cost of fuel cell catalyst and enhance their lifespan.

As catalysts in DMFC are commonly supported on conductive and porous membranes being this another important fact. It is well known that supported metal catalysts show improved stability and higher activity compared to unsupported bulk metal catalysts. Surface area, porosity, electrical conductivity, electrochemical stability, and surface functional groups characterise a support [5,10]. In this sense, carbon materials have been used as catalyst support due to remarkable properties, such as good electronic conductivity, better stability and environment friendliness. There are several materials such as mesoporous carbon, carbon black, carbon quantum dots, carbon nanotubes, carbon nanofibre, graphene and other carbon forms such as carbon nanosheet, nanohorns, nanosphere as electrocatalyst support have been reported [11].

In order to diminish or avoid the use of platinum in fuel cells several low-platinum catalyst, Pt-C or free Pt catalyst have been developed including Pt-based alloying, Pt-based nanostructure design and supports-enhanced methods [10,12-17]. Alloying Pt with more abundant and cheaper 3d-transition metals (such as Fe, Co, Cu, Ni) is considered as a facile strategy for heightening the electrochemical properties of [18-20].

Combustion synthesis is an effective, low-cost method for production catalysts and nanocarries by solid state and solution combustion [21,22]. The exothermicity of the redox chemical reaction is used to produce the material. Depending on the nature of reactants different methods has been developed [22].

The objective of this work is to develop catalysts Pt-free. Materials based on FeCo solid solutions are synthesized by the combustion method and characterized for their further application as anode catalysts in DMFC. Further, the catalytic layer composition has been designed to prepare electrodes by spray, in such a way that the slurry can be homogeneously sprayable on the surface of the carbon paper gas diffusion layer. The prepared materials have been morphological, structural and electrochemically characterized to teste their activity towards methanol oxidation.

2. Experimental

2.1. Sample preparation by combustion method

To prepare the catalysts have been used are used iron (II) nitrate and cobalt and cobalt (II) nitrate as precursors. Urea has been chosen as fuel to maintain or modify the balance of valences. To obtain different local conditions during combustion different amounts of fuel have been employed. The nominal compositions formulated for the catalysts are $\text{Fe}_x\text{Co}_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$).

2.2. Structural and morphological characterization

The structural identification was performed by XRD with a Bruker to D8 Advance (CuK α radiation, 30 mA, 50kV). For composition determination was used EVA Application V6.0 program with PDF-2 Database sets 1-46.

2.3. Electrochemical measurements

Catalytic activity of the prepared powders towards methanol oxidation reaction was analysed by CV in a three-electrode cell (CE: Pt sheet, RE: Ag/AgCl and the material ink onto a glassy carbon tip as WE), at 25°C. Using HClO₄ 0.1M + CH₃OH 0.5M as electrolyte. All data are collected in a I-V curve by AUTOLAB PGSTAT302N, firstly the samples have been activated, and measurements have been recorded at 50 mV/s from -0.1 to 1.3 V vs Ag/AgCl.

3. Results and discussion

Combustion synthesis exhibit four more or less rapid stages depending on raw materials (Fig. 1). The ignition temperature achieved allows obtaining, in a short time, the crystalline phases of the nanopowder material with porous structure. That phenomenon accelerates the kinetic reaction that is why this is the stage that controls the global process.

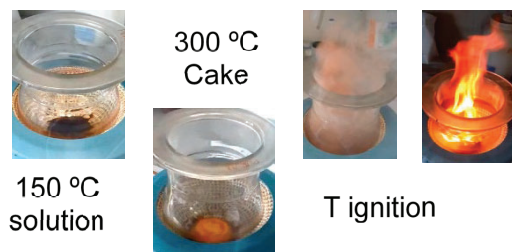


Figure 1. Scheme of urea synthesis processes.

Figure 2 shows that a mixture of oxides is obtained directly from the combustion with stoichiometric urea, observing small amounts of mixed oxides of iron and cobalt when different proportions of them are used to prepare the distinct nominal compositions.

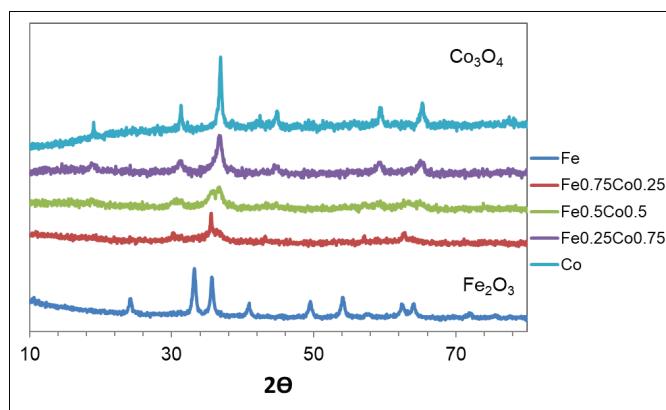


Figure 2. XRD of $\text{Fe}_x\text{Co}_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1$) prepared by combustion synthesis with stoichiometric urea.

While in Fig. 3 it can be seen how the variation in the proportion of fuel makes it go from having Co_3O_4 to obtaining CoO .

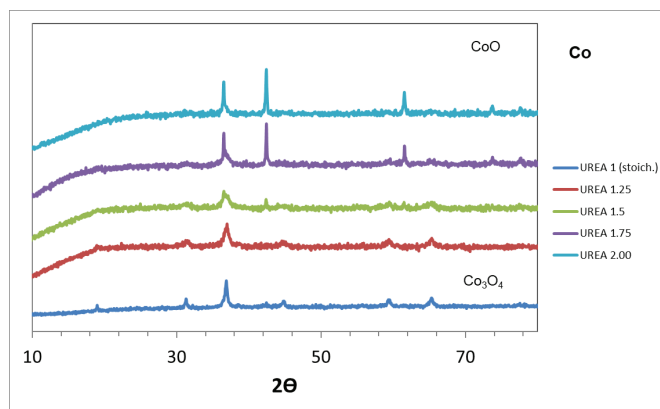


Figure 3. XRD of $\text{Fe}_x\text{Co}_{1-x}$ ($x=0$) prepared by combustion synthesis with different ratios of urea.

By varying the stoichiometry of urea, in the case of $x=0.25, 0.5, 0.75$, the concentration of the mixed oxides of iron and cobalt increases.

Regarding the preliminary electrochemical measurements carried out, it has been observed that when iron or cobalt oxide is found alone there is no activity against methanol oxidation. But this activity begins to appear, although slightly, as the iron-cobalt mixture appears in the catalyst formulation.

4. Conclusions

The ignition stage of the combustion synthesis determines the final crystallographic and morphological properties of the powders due to the number of gases released in that condition and both the atmosphere and the local synthesis temperature. The combustion method has been studied tailoring the properties of the final product based on the raw mixture used. It has been proven that final features and electrochemical behaviour is different, mainly due to the different crystalline phases achieved in the synthesis.

The higher electrochemical activity is related to the crystal structure, the microstructure and morphology of the material. And these differences are directly related with time of reaction, local temperature and oxygen partial pressure reached.

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