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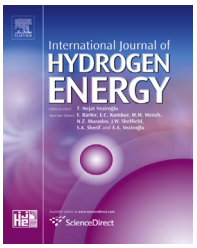

Electrocatalysis on metal carbide materials

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ABSTRACT

This paper will provide a review of the recent work done by our group on the synthetic routes to prepare metal carbide and nitride materials, which are proposed as alternative to actual materials used as supports and catalysts in fuel cells. With this end, the proper physicochemical and spectroelectrochemical characterization of these materials is reported. Additionally, the electrochemical behavior in absence and presence of carbon monoxide, hydrogen, methanol and ethanol in acidic media up to 70 °C is scrutinized. Experiments realized on Mo_2C are described along the manuscript to exemplify the main achievements.

Introduction

Fuel cells (FCs) are devices that convert chemical energy into electrical energy through electrochemical reactions, similar to batteries. However, a fundamental difference between FCs and batteries is that FCs consume reactant from an external source, which must be replenished, whereas in batteries electric energy is chemically stored internally in the electrodes, that is, fuel cells produce electricity while the fuel is supplied and converted at the electrodes, which act as catalysts for the electron transfer reactions [1]. Furthermore, FC systems are not limited by the Carnot efficiency because no combustion occurs, and consequently a higher efficiency may be achieved than in systems operating on internal combustion [1,2].

Hydrogen proton exchange membrane fuel cell (HPEMFC), direct methanol fuel cell (DMFC) and direct ethanol fuel cell (DEFC) are the most common FCs that are emerging as promising candidates for automobile industries and portable electronics due to their high power density and portability [1–3]. However, there are still technical impediments that remain for large-scale commercialization. Major limitations of FC technology are [1–4]: i) the high cost and low abundance of the principal catalytic materials (Pt and Ru); ii) the low stability owing to corrosion of conventional carbon supports under chemical and electrochemical oxidation conditions; iii) slow kinetics for the electrooxidation of alcohol; iv) slow kinetics for the electroreduction of oxygen; v) poisoning of the catalytic active sites by strongly adsorbed CO; and iv) mixed potential due to the crossover of the alcohol through the electrolyte from the anode to the cathode.

Thus, elaborate exploration and rational design of low cost materials with high efficiency and durability will have a significant impact on making these promising energy technologies commercially viable. The latter can be achieved by

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investigating new materials or by modifying the current catalysts. In this context, potential alternative electrocatalysts and/or electrocatalyst supports are transition metal carbides and nitrides [5–10]. The great interest of these materials resides in their similar electronic structure near Fermi's level of the Pt-group metals [11]. Moreover, these materials were reported to be chemically stable in acidic media and resistant to poisoning, as well as, to have excellent mechanical durability and to possess high electrical conductivity [6,8,10,12].

Despite the many advantages of these materials, main drawback includes their thermodynamic instability in the oxidative FC environment. Indeed, they are eventually transformed to transition metal oxides, which for most metals is the only thermodynamically stable compound under FC conditions [13–15]. In this context, metal transition oxides appear to be potentially suitable as electrocatalyst supports as better dispersion of the active phase (e.g. Pt) in association with a promotional effect were reported [8,14,16–18]. However, transition metal oxides are almost insulators, and therefore, it becomes necessary to appropriately modify their nature to produce catalysts with suitable conductivity and reactivity.

Having this in mind, our Group undertook an investigation to develop novel core–shell carbide/nitride particles, with a reduced-M core (M = metal transition (oxy)carbide/nitride) and a small metal oxide-shell (2–3 nm). In this way, materials with high conductivity and activity, as well as, with enhanced dispersion and interaction of the active phase were developed.

Herein we report the proper use of transition metal carbides and nitrides in an electrochemical media, as well as, the work done to enhance the catalytic activity toward benchmark reactions such as the electrooxidation of CO, hydrogen, methanol and ethanol. With this end, experiments performed on Mo_2C material will be used to illustrate the above described.

Synthesis and physicochemical characterization

In general terms there are two main routes described in the literature to synthesize transition metal carbides and nitrides, i.e. physical and chemical approaches [5,6,8,19]. The first one includes the use of plasma, laser and vapor deposition techniques. The second tactic comprises reactions of the metal precursor with sources of carbon (e.g. coal, gaseous hydrocarbons, urea, etc.) or nitrogen (e.g. N_2, NH_3, urea, etc.) into a reactor (with or without pressure) at elevated temperatures (600–2000 °C). The last route is handier and allows the synthesis of a broad range of products, although the morphological control is tricky and small changes in the procedure induce modifications in the desired compound. Commercial transition metal carbides and nitrides are available and are commonly produced by the chemical route. Main drawbacks of commercial materials are the presence of high amount of coal and undesired second phases, as well as, the high particle size.

We employed commercial TiC, TiN, TiCN, Mo_2C, WC, W_2C and synthesized Mo_2C, W_2C and TiO_xC_y materials [14,20–28]. An example includes the synthesis of nanometric Mo_2C particles by slight modification of the standard carbothermal method [29]. Briefly, an appropriate amount (e.g. 1.8 g) of molybdenum oxide precursor (MoO_3, 99.5% Sigma–Aldrich) is dissolved in the correct volume of ammonium hydroxide solution (e.g. 30 mL of 15% of NH_4OH solution, 99.99% Sigma–Aldrich) under stirring at room temperature ("Sample A"). "Sample B" consists of an appropriate amount (e.g. 0.15 g) of carbon black (Vulcan® XC 72R) dissolved in a correct volume (e.g. 30 mL) of ethanol (CH_3CH_2OH, Merck p.a.) under sonication. After that, "Sample A" is added drop by drop into "Sample B" under stirring at room temperature and later the temperature is raised up to 60 °C until a dry powder is achieved. Then, the sample is grounded in a mortar and subsequently introduced in a tubular furnace under a H_2/N_2 (5 vol.%) flux (140 mL min^{-1}), in which a ramp of 5 °C min^{-1} from room temperature to 800 °C is applied. The highest temperature (800 °C) is maintained during a period of 10 h, and after that, the temperature is cooled down to room temperature under the same conditions.

Fig. 1 compares X-ray diffraction pattern of two samples synthesized (small: 0.1 g (blue) and large: 2 g (green) bench scale production) with a commercial one (Sigma–Aldrich). Average metal crystallite size was calculated using the Scherrer' equation. It can be established that pure molybdenum carbide with crystallite size smaller than 20 nm is reached even at large-bench scale production. The rise of particle size with the scale production can be understood from the system properties that depend on quantity of material that may change as the system increases in size. In this context, several factors such as reaction kinetics, chemical equilibrium, material properties or thermodynamics may change during the rise of the production scale. On the other hand, it is remarkable that crystallite size of commercial molybdenum carbide is much higher (50 nm) than those synthesized by the carbothermal reduction procedure.

Transmission electron microscopy (TEM) images were obtained from a HRTEM Jeol JSM 6300 operating at an accelerating voltage of 200 kV. Fig. 2 shows the TEM images for commercial and synthesized Mo_2C materials. The particle size values of commercial material achieved from TEM are much higher than those acquired by XRD. In this sense, the Scherrer

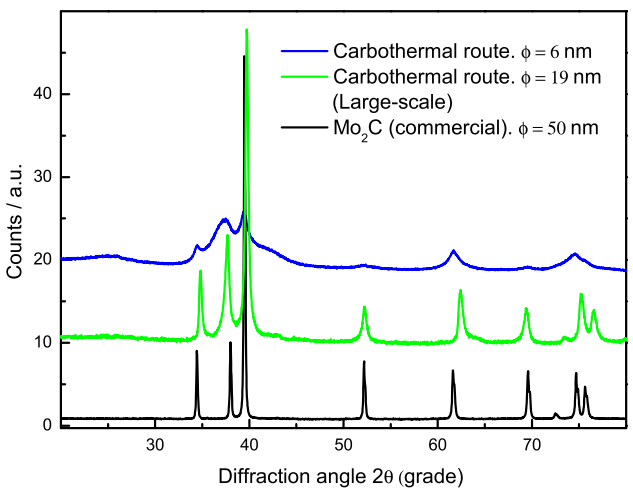

Fig. 1 – XRD patterns of synthesized and commercial Mo_2C materials.

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