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Preparation and characterisation of Ti oxide based catalyst supports for low temperature fuel cells

S. Siracusano, A. Stassi, E. Modica, V. Baglio, A.S. Aricò*

CNR-ITAE Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", Via Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy

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ABSTRACT

Bare and doped Ti-oxides were prepared by using various synthesis routes and investigated in terms of structure, morphology and electrochemical properties for application as catalyst supports in low temperature fuel cells. A crystalline Anatase phase was obtained for most of the doped and undoped Ti-oxide supports after an air treatment in a range 300°–600 °C. Rutile structure was observed for treatments at higher temperatures. BET surface area varied as a function of the preparation route, the doping agent and the thermal treatment. BET surface area decreased passing from bare TiO₂ to Ta-doped TiO₂ and further decreased in the presence of Nb doping. A sulphite complex route allowed to achieve crystalline materials with crystallite domain sizes of about 3–4 nm upon thermal treatment at 400 °C. The corresponding BET surface area for TiO₂ was around 250 m²/g whereas it decreased to 175 m²/g for the doped support. Electrochemical oxidation tests at 1.4 V RHE showed that oxide supports were significantly more stable in terms of electrochemical corrosion than conventional carbon black supports used in fuel cells. This comparison was extended to Ti-suboxides with Magneli phase obtained by high temperature reduction. The latter material appeared also very stable but characterised by low surface area (about one order of magnitude lower than bare TiO₂) due to the high temperature treatment. Oxygen reduction reaction studies (ORR) showed that suitable performance can be achieved in the presence of a proper combination of electronic conductivity and dispersion for the oxide supported catalyst nanoparticles.

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1. Introduction

Development of catalyst supports in the field of fuel cells is relevant in relation to both catalyst stability and performance. The physico-chemical properties of the support influence catalyst dispersion, metal-support and ionomer interaction, conductivity within the catalytic layers etc. [1–5].

High utilisation of Pt electrocatalysts is achieved by supporting nanosized metal particles on a high surface area

conducting support. The support provides a physical surface for the dispersion of Pt nanoparticles as needed to obtain high electrochemically active surface area. General degradation phenomena for carbon black supported catalysts regard Pt nanoparticles agglomeration, Pt dissolution and reprecipitation, occurrence of electrically isolated Pt particles and specifically Ru dissolution at the anode in direct methanol fuel cells (DMFCs). These phenomena reduce the durability of the catalysts causing a failure of the fuel cell system [4–6].

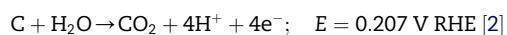
* Corresponding author. Tel.: +39 090624237; fax: +39 090624247.

E-mail addresses: arico@ita.e.cnr.it, antonino.arico@ita.e.cnr.it (A.S. Aricò).

To stabilise anode and cathode catalysts in polymer electrolyte (PEM) and direct methanol fuel cells, one of the main strategies concerns with utilisation of oxide supports in order to stabilise the metallic active phase through a strong metal-support interaction (SMSI) [6–8] and development of appropriate highly graphitic carbonaceous supports [2]. The first approach reduces electrochemical corrosion phenomena e.g. dissolution and metal particle growth, which in most cases are promoted by the degradation of carbonaceous supports; whereas, in the second approach, the aim is to get advantage of the good stability of graphitic basal planes in the potential window of PEMFC and DMFC operation [9,10] as well as to combine good stability with high BET surface area and conductivity which are needed to obtain high performance in fuel cells. Accordingly, selection of stable carbon supports is essentially based on resilience to corrosion, proper BET surface area, conductivity and surface graphicity index. Similar pre-requisites are requested to non-carbonaceous supports, however, in the latter case a good crystallinity is included in the selection criteria (instead of graphicity index used for carbonaceous supports) especially with regard to the chemical stability in the super-acid environment of proton exchange membrane fuel cells.

For non-carbonaceous supports, the activity of the present work was focused on the preparation of doped Ti-oxide and Ti-suboxide supports with tailored morphologies. The approach was concerning the colloidal and sol–gel preparation procedures for the synthesis of spherical nanoparticles. Doping of Ti-oxides by using Ta and Nb was necessary to increase electronic conductivity.

For carbon blacks the main corrosion process is reported below:



From the oxidation charge i.e. the current integrated during the time of the experiment, carbon loss or carbon transformation into CO_2 by effect of water can be easily estimated from the Faraday law.

For non-carbonaceous supports such as Ti oxides, no clear electrochemical corrosion mechanisms have been individuated in the literature [6,7]. However, an oxidation charge is also recorded in these cases and it may be associated with, double layer discharging effects, surface reactions, oxidation of sub-stoichiometric species within the support (e.g. from Ti^{3+} to Ti^{4+}) which may cause erosion and dissolution. As an example, the presence of Ti^{3+} species is essential to provide proper electronic conductivity. Formation of Ti^{3+} is promoted by doping with Ta^{5+} , Nb^{5+} species to maintain the electro-neutrality within the crystallographic structure or it is induced by high temperature reduction (Magneli phase). In this regard, it appears appropriate to evaluate the electrochemical stability as inversely related to the oxidation charge and it is important to normalise this parameter by sample weight and possibly by BET surface area. In fact, BET is an important parameter that governs the feasibility of achieving high dispersions for the active metal phase on the support. Although several promising oxide supported fuel cell catalysts have been studied in the literature [7–24], no significant efforts have been made to identify clear guidelines for selecting

an oxide catalyst support as well as to correlate the preparation procedures and physico-chemical characteristics to the properties relevant for fuel cell applications. It is worth noting that beside fuel cells, electro-catalysts based on Ti-oxide supports may find application in PEM electrolysis and regenerative fuel cells in relation to the oxygen reaction process [25–29].

In this work, an investigation of chemical, structural, surface and morphology properties of oxide catalyst supports prepared by various chemical routes is carried out. The approach was addressed to provide a guideline for the identification of the most promising supports that were characterised in terms of electrochemical stability, in-situ conductivity and capability to enhance the dispersion of a Pt metal phase used in the oxygen reduction process. Beside bare TiO_2 , highly doped TiO_2 e.g. a $\text{Ti}_{0.75}\text{Ta}_{0.25}\text{O}_2$ and $\text{Ti}_{0.75}\text{Nb}_{0.25}\text{O}_2$ were studied. Their formulation was selected based on the fact that they have only a slightly different nominal fraction of Ti^{3+} species than conventional Ti sub-oxides such as Ti_4O_7 also used in this study for comparison.

2. Experimental

2.1. Oxide support preparation

2.1.1. Complexation method

This consisted in a complexation of Ti, Ta or Nb ions with a chelating agent and successive decomposition of the complex to form a colloidal suspension giving rise to an amorphous oxide after flocculation. Ethylenediaminetetraacetic acid (EDTA) was used as complexation agent due to its capability to act as chelating specie for the transition metal ions. The reaction mixture of metal ions and complexation agent was maintained at a pH \sim 5 at 80 °C for 1 h. Decomposition of the formed organic complex with metal ions was carried out by using H_2O_2 at 80 °C in aqueous solution. The amorphous material was thereafter treated at various temperatures in the range 300°–600 °C. Ti sub-oxides were also obtained by the same preparation approach but using as thermal treatment a reduction in H_2 at 1050 °C.

2.1.2. Pechini process

In this procedure ethylene glycol and citric acid were dissolved in water for 20 min at room temperature. Afterwards, TiCl_4 was added and the solution was maintained under ultrasounds at 90 °C until it was dried. This material was treated at high temperatures as above.

2.1.3. Sulphite complex route

Ti and Ta sulphite complexes were prepared by reaction of Ti and Ta chloride salts (TiCl_4 and TaCl_5) with dithionite at 70 °C in aqueous solution. Thereafter, these complexes were mixed in proper amounts in acidic solution to achieve a Ti/Ta = 3:1 atomic ratio in the final oxide support and decomposed in the presence of H_2O_2 to form a colloidal suspension giving rise to an amorphous oxide after flocculation. Amorphous Ti-oxides were thermally activated at various temperature in the range 300°–600 °C and analysed in terms of surface area and crystalline properties.

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