Journal of Power Sources 243 (2013) 826–830

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

High surface electrochemical support based on Sb-doped SnO_2

M.P. Gurrola [a], M. Guerra-Balcázar [b], L. Álvarez-Contreras [c], R. Nava [b], J. Ledesma-García [b,*], L.G. Arriaga [a,*]

[a] Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Parque Tecnológico Querétaro, C.P. 76703 Querétaro, México
[b] División de Investigación y Posgrado, Facultad de Ingeniería, Universidad Autónoma de Querétaro, C.P. 76010 Querétaro, México
[c] Centro de Investigación en Materiales Avanzados (CIMAV), Laboratorio Nacional de Nanotecnología, C.P. 31109 Chihuahua, México

HIGHLIGHTS

- ATO support is prepared by sol–gel with dodecylamine as template.
- The resulting powder has the highest specific surface area until now reported.
- Electrical conductivity value is comparable to the typically used carbon.
- ATO support showed great stability to high overpotentials in acid media.
- ATO has strong potential for using in several electrochemical applications.

ARTICLE INFO

Article history:
Received 10 April 2013
Received in revised form
13 June 2013
Accepted 13 June 2013
Available online 22 June 2013

Keywords:
ATO support
Sol–gel
Carbon support
Electrochemical stability

ABSTRACT

Sb-doped SnO_2 (ATO) support is prepared by sol–gel method in the presence of dodecylamine as template. The synthesized powder presents the highest specific surface area until now reported (216.7 $m^2\ g^{-1}$) with high electrical conductivity (0.202 S cm^{-1}). The durability test accomplished by cyclic voltammetry in acid media (100 cycles between 0 and 1.7 V vs NHE) demonstrates that the ATO support maintains significantly its stability and the performance of the tested electrocatalyst compared to Vulcan XC-72. The ATO material is a promising support that can be used in several electrochemical applications where the use of carbon is not suitable.

1. Introduction

Tin dioxide, SnO_2, belongs to the family of transition metal dioxide compounds with rutile structures. SnO_2-supported Pt and Pd metals are interesting catalyst systems for various reactions, such as the low-temperature oxidation of CO and methane [1,2]. SnO_2 has also been proposed as a support material for fuel cell and electrolysis electrocatalysts because of its chemical properties; it adsorbs OH species at low potentials and/or induces an electronic effect with Pt catalysts [3,4]. Undoped tin dioxide is a wide bandgap semiconductor ($E_g \approx 3.6$ eV) with electrical resistivity varying from 10 to 10^6 Ω cm, depending on the temperature and the stoichiometry of the oxide [5]. The electrical resistivity was found to drastically decrease to 10^{-2}–10^{-3} Ω cm upon doping SnO_2 with Sb^{+5} [6–8]. Other materials have been investigated such as Ebonex® and used as a catalyst support for the oxygen reduction and evolution reaction [9–12]; however, a major detriment for use in practical support applications resides in its low surface area compared to Vulcan XC-72[13].

Recent studies have shown the potential use of ATO material. Santos et al. [14] electrodeposited platinum microparticles on Sb-doped SnO_2 (ATO) thin films and tested their activity for methanol electro-oxidation. The crystallite size of ATO-supported Pt was in the range of 8.5–12 nm. These results suggest than tin oxide can be a good matrix for Pt (or Pt alloys) catalyst dispersion for applications in DMFC. Lee et al. [15] deposited Pt colloidal particles on ATO nanoparticles with various degrees of Pt loading and investigated their electrocatalytic activity and stability for methanol and ethanol oxidation reactions. The electrical conductivities of undoped and Sb–SnO_2 were 0.0028 and 0.11 S cm^{-1},

* Corresponding authors.
E-mail addresses: janet.ledesma@uaq.mx (J. Ledesma-García), larriaga@cideteq.mx (L.G. Arriaga).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.06.078

respectively. The specific surface area of the ATO from a BET analysis was 99.7 $m^2\ g^{-1}$. To our knowledge Sb–SnO_2 has a surface area less than 100 $m^2\ g^{-1}$ lower than Vulcan XC-72. Hagemeyer et al. [16] investigated a variety of methods for the preparation of high-surface-area tin oxide. BET analysis of the surface area showed values between 43 and 100 $m^2\ g^{-1}$ by a variety of methods after calcinations in the temperature range of 300–500 °C, indicating the presence of mesopores in the ATO support [17]. The synthesis of ATO with a high surface area (up to 100 $m^2\ g^{-1}$) is a primary requirement for its use as a catalyst/electrocatalyst support for different chemical and electrochemical reactions such as oxygen evolution reaction by water. The support provides a physical surface for the dispersion of small particles of the active phase, which is necessary for achieving high surface area and to provide good electronic conductivity. Besides, a high stability at the anodic potential is required. A variety of techniques have been used to synthesize tin oxide nanoparticles, including Sol–gel technique [7] that has attracted the most attention for the preparation of Sb-doped SnO_2 because of several advantages, such as excellent homogeneity, ease of controlling the doping level, ability to coat large areas and complex shapes and a low processing cost [18–20]. In this work, Sb-doped SnO_2 (ATO) support was prepared by a novel route Sol–gel method in the presence of dodecylamine as template, resulting in a powder with high specific surface area (216.7 $m^2\ g^{-1}$) and electrical conductivity (0.202 S cm^{-1}).

2. Experimental

2.1. Synthesis of ATO

ATO begins with the synthesis of the precursor solution using Tin (IV) *tert*-butoxide (Aldrich, ≥98%), anhydrous ethanol (Aldrich, ≥99.7%), HNO_3 (Aldrich), dodecylamine (Aldrich, ≥99%), distilled water and antimony (III) ethoxide (Aldrich) in a tri-necked flask. All of the chemical reagents used in this experiment are of analytical grade. Sn^{4+} and Sb^{3+} precursors in a molar ratio of 90:10 (Sn:Sb) are mixed in ethanol under an inert atmosphere (N_2) by magnetic stirring for 30 min. The final pH value of this solution is 2.5. Subsequently, for the hydrolysis reaction, the solution was added to 0.1 M nitric acid aqueous solution as the catalyst and 84 mM dodecylamine as surfactant, with a gelation time (t_g) of 4 h at 5 °C. Then, the resulting gels were kept at room temperature for one day, filtered and subsequently washed with deionized water at 80 °C. After the resulting gel powder was crushed in an agate mortar, it underwent thermal processing, starting at $T = 110$ °C for 18 h at heating rate of 2 °C min^{-1}. After at $T = 500$ °C for 12 h at heating rate of 1.5 °C min^{-1}.

2.2. Physicochemical characterization

XRD was performed on the dry support powders of ATO using an X-pert MPD Philips diffractometer that used the Kα line of copper

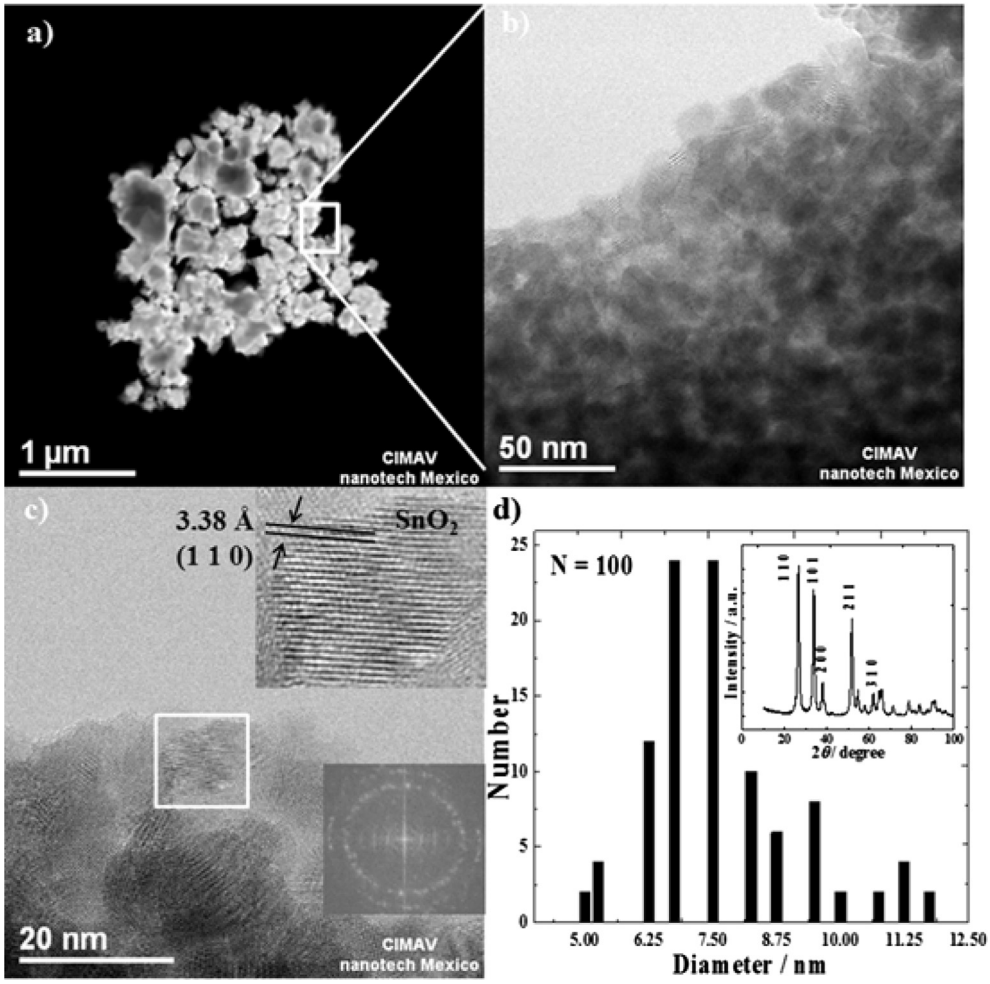

Fig. 1. TEM micrographs of ATO support and particle size distribution analysis of ATO calcinated for 12 h at 500 °C. d) Inset X-ray diffraction pattern of Sb-doped SnO_2 (ATO).