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SnO_2 coated Ni particles prepared by fluidized bed chemical vapor deposition

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Abstract

A Fluidized Bed Metal–Organic Chemical Vapor Deposition (FB-MOCVD) process was developed for the growth of tin oxide thin films on large hollow Ni particles. Tetraethyl tin was used as tin source and dry air both as fluidization gas and oxidant reagent. The SnO_2 films were grown in a FBCVD reactor under reduced pressure (13.3 kPa) in the temperature range of 633–663 K. A series of specific experiments was carried out to optimize the design of the reactor and to determine the range of experimental parameters (flow rate, pressure, temperature) leading to good fluidization of the large hollow Ni particles used as base material. The SnO_2 films deposited on particles exhibited a dense nodular surface morphology similar to that previously observed on flat substrates. The relative thickness of the films was determined by EDS analyses and the real values were measured by SEM on cross-sections of particles. The SnO_2 films exhibit satisfactory thickness uniformity from one particle to another in the same batch and from run to run. XRD studies revealed that the films exhibited good crystallinity with the cassiterite structure. Traces of NiO were found at the SnO_2/Ni interface. Finally, the SnO_2 CVD coated-Ni particles were used as anodes in an electrochemical cell. The potential limit of oxygen evolution measured was that of the SnO_2 layer despite the initial porosity of the hollow Ni particles inherent to their preparation. This work is the first step towards the preparation of high specific surface area electrodes.
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1. Introduction

Tin oxide thin films have important applications due to their semi-conductive properties and to their optical transmission. The main application concerns gas sensors, owing to the strong dependence of the conductivity of the films on the ambient atmosphere and on the temperature [1,2]. Recent works deal with the development of SnO_2 films as electrochemical materials. SnO_2 thin films have been successfully used as anode material in an electrochemical process for the depollution of organic compounds in wastewater. Conventional anodes, such as Pt, Ti/IrO_x, Ti/RuO_2 and Ti/PbO_2, give relatively low current efficiencies in contrast to the SnO_2 anode, which not only gives high current efficiency, but also allows quasi complete total organic carbon (TOC) elimination [3,4]. Furthermore, the electrochemical method for wastewater treatment is easy to control and its efficiency could be significantly increased by the use of electrodes with a higher specific surface area.

Thin films of SnO_2 have been deposited by a variety of techniques including reactive sputtering [5], spray pyrolysis [6], evaporation [7], sol–gel [8], pulsed Laser deposition [9], plasma-assisted chemical vapor deposition [10] and thermal chemical vapor deposition (CVD). Among these techniques, CVD has meaningful advantages such as its capacity for large area growth, precise control of thickness and superior conformal coverage. The use of labile organometallic molecules allows deposition of thin films at low temperatures that most inorganic substrates can tolerate.

The aim of this work was to prepare specific electrodes by metal–organic chemical vapor deposition of SnO_2 on Ni particles in a fluidized bed reactor (FB-MOCVD). In previous

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works we have reported optimal CVD conditions for the growth of SnO_2 on flat substrates [11–13]. SnO_2 thin films were grown by MOCVD at 653 K and 13.3 kPa using tetraethyl tin ($SnEt_4$) as molecular precursor with a mole fraction of 10^{-3} and oxygen as oxidant reagent [13]. In the present work, the deposition of SnO_2 was done on hollow Ni particles in a fluidized bed reactor. The use of a fluidized bed reactor has great advantages for the CVD technique [14]. One of the most important features is the relatively large heat and mass transfer rates. Consequently, the temperature and the gas composition in the bed are more homogeneous than in a conventional CVD reactor. By setting the global parameters of the process (T, P, flow rates and mole fraction of the reactants), the local growth conditions are well controlled and the fluidization phenomena lead to a good thickness uniformity of the coatings.

2. Experimental

Calculations and several series of specific experiments were performed to design and to build the fluidized bed CVD reactor used for SnO_2 deposition. The process is related to the MOCVD process previously developed for coating flat substrates [11–13]. Basically, $SnEt_4$ was used as tin source and dry air both as fluidization gas and oxidant.

2.1. Selection and preparation of the substrate

The substrate was chosen (i) to provide a high electrocatalytic efficiency and (ii) to be easily fluidized in the CVD reactor. The first requirement results from the application for these coated particles: the substrate coated by SnO_2 will be immersed in an electrochemical reactor as anode material for the depollution of wastewater [15]. Consequently, its density must be higher than that of water. Furthermore, the diameter of the particles used as substrates must be large enough to offer both the high surface area required for an efficient organic degradation and sufficient electrical conductivity to use the material as an anode. Titanium is frequently used as base material for electrode fabrication and CVD of SnO_2 films on Ti plates have already been reported [16]. However, Ti particles are quite expensive and preliminary fluidization attempts were not satisfactory. Taking into account economical factors in addition to the above requirements, Ni appeared to be a good candidate. Indeed, it has been used as an electrode material in various electrochemical processes [17].

Regarding the second item, the particles to be coated must be fluidized homogeneously to carry out a reliable CVD process. However, fluidization of large particles under reduced pressure is difficult and generally tends to operate in the slugging regime [18]. As a result, a good compromise was the use of hollow Ni particles as substrates, 2.17 mm in mean diameter and 2160 kg m^{-3} in density. These particles belong to the D group according to the Geldart classification [19]. The typical behavior ascribed to the D group is a rapid increase of the bubble size with the bed height, which causes strong interactions between the bubbles themselves and the reactor walls. Such flow conditions promote the formation of slugs, which are usually described as square-nosed slugs or solids slugs [20].

The hollow Ni particles underwent various treatments before their use as substrates in the FBCVD process. They were degreased with trichloroethylene and acetone and dried at 353 K for 10 min. Part of the particles were separated and precoated with a thin layer of IrO_x deposited by dip-coating [21]. The process involved the following steps: the Ni particles were dipped in an isopropanol solution of $IrCl_4$ (15 wt.%), the solvent was evaporated at 353 K for 10 min and the samples were heated in air at 773 K for 5 min. The above operations were repeated three times to improve the uniformity and the thickness of the IrO_x coating. Finally, the particles were annealed in air at 773 K for 1 h.

2.2. Design of the fluidized bed CVD reactor

The reactor was designed to avoid or to limit slugging behavior. It is known that increasing the reactor diameter changes the total slugging regime towards wall slugs then axisymmetric slugs, as frequently observed in systems with small particle sizes [22]. However, an increase in the reactor diameter requires a higher tetraethyl tin flow rate and, consequently, higher consumption of the metal–organic precursor. A reactor diameter of 5 cm was found to be a good compromise because of the relatively high cost of the molecular precursor.

The distributor at the bottom of the reactor was a porous or perforated plate serving both as support for the bed of granular material and as a uniform diffuser of the gas stream through the bed. A high porosity plate generally reduces the slugging behavior [23]. In this work, the gas distributor was a perforated stainless steel plate with a porosity of 30%. For some experiments, a half cone-shaped stainless steel piece (5 cm diameter) was placed on a part of the gas distributor to produce a spouted bed regime.

The MOCVD set-up is depicted in Fig. 1. The decomposition and oxidation reactions of $SnEt_4$ took place in a fluidized

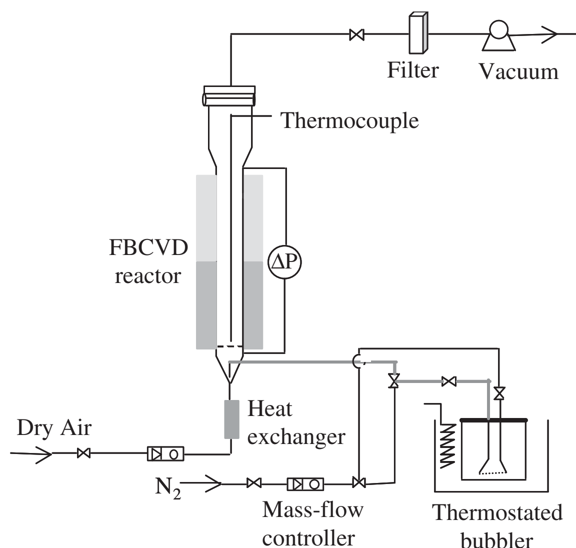

Fig. 1. Schematic representation of the FBCVD reactor.

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