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Preparation and characterization of Nb-doped TiO_2 nanoparticles used as a conductive support for bifunctional $CuCo_2O_4$ electrocatalyst

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Abstract

Nb-doped TiO_2 powders with various Nb contents (0%, 5% and 10%) were prepared using a sol–gel process and annealed at 450, 650 and 1050 °C with the aim to be used as a conductive support for bifunctional electrocatalysts in rechargeable metal-air batteries, substituting the more conventional carbon particles which slowly corrode at high potentials during cell recharge. X-ray diffraction analyses revealed that niobium hinders the anatase–rutile transformation and prevents the grain growth, which is important to achieve a conductive support with high specific surface area. X-ray photoelectron spectroscopy measurements have shown that the powders possess surface $Ti^{4+}$and Nb^{4+}species, and that the $Nb_{0.05}Ti_{0.95}O_2$ (1050 °C) sample also contains $Ti^{3+}$and Nb^{5+} ions. Composite film electrodes containing $CuCo_2O_4$ particles (60 w/w%), $Nb_{0.05}Ti_{0.95}O_2$ or Vulcan XC72R or Ebonex powder (25%), and poly(vinylidene fluoride-*co*-hexafluoropropylene) (15%) were formed on the glassy carbon disk surface of a rotating ring-disk electrode and studied for both the O_2 evolution and O_2 reduction reactions in 1 M KOH solution and O_2-saturated 1 M KOH solution, respectively. Rutile $Nb_{0.05}Ti_{0.95}O_2$ (1050 °C) powder was chosen owing to its larger overpotential for H_2 evolution (detrimental to the performance of bifunctional electrodes) and its low and stable anodic activity, whereas anatase $Nb_{0.05}Ti_{0.95}O_2$ (450 °C) powder was mainly selected due to its higher specific surface area. The results have shown that the $Nb_{0.05}Ti_{0.95}O_2$ powders are more suitable than Vulcan XC72R for use as a conductive support material, based on the higher electrode intrinsic current densities recorded for O_2 evolution and reduction reactions.
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1. Introduction

Secondary metal-air batteries are promising power sources for portable electric devices or electric vehicles due to their high theoretical (*e.g.*, 1085 Wh kg^{-1} for a Zn-air battery) as well as practical (60–150 Wh kg^{-1} for a Zn-air battery) specific energies, and also due to the low cost and low toxicity of the materials involved. The development of this type of battery is however impeded by different lacks, such as a viable bifunctional air electrode, which consists in a material able to reduce as well as generate oxygen in alkaline electrolytes. The corrosion resistance and the activity for both O_2 reduction (cell discharge) and O_2 evolution (cell recharge) at the air electrode have to be improved, in order to achieve typical long-term utilization.

Air electrodes are often made of a porous carbon structure (carbon black and/or graphitized carbon black powders) covered or mixed with the catalyst [1]. The use of carbon supports provides a good electronic conductivity and a physical surface for dispersion of small catalyst particles, which is necessary for achieving high surface areas, and diminishes the catalyst loading. However, the oxygen evolution reaction (OER), as the oxygen reduction reaction (ORR), is irreversible and during cell recharge at high

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potentials, the kinetically slow carbon corrosion reaction (Eq. (1)) at the air electrode could proceed irreversibly [1]:

$$C + 6OH^- \rightarrow CO_3^{2-} + 3H_2O + 4e^- \quad (1)$$

damaging the carbon support, which may lead to significant deterioration of the cell performance. Also, it has been well demonstrated that whereas the current efficiency for oxygen evolution of a cobalt oxide-catalyzed acetylene black electrode is increased severalfold relative to that for the uncatalyzed black sample, the rates of the corrosion processes are also accelerated [2,3]. Therefore, the development of a more anodically stable catalyst support is mandatory for rechargeable metal-air batteries.

Titanium based materials play an important role in electrochemistry owing to their high conductivity and/or high stability. Numerous electrochemical studies have been done on the conductive Magneli phases with the general formula Ti_nO_{2n-1} ($4 \leqslant n \leqslant 10$), such as Ti_4O_7 and Ti_5O_9, two main components of commercial Ebonex® (Atraverda Ltd., UK) [4]. Ebonex possesses a high electrical conductivity of about ~1000 S cm^{-1} and is electrochemically stable, with very high overpotentials for hydrogen and oxygen evolution, in acid and alkaline solutions [5]. Titanium based oxides have been investigated as catalyst support materials for different applications, showing promising results: (i) Ebonex electroplated with PbO_2 electrocatalyst for ozone formation in acid and neutral electrolytes [6], (ii) TiO or Ti_4O_7-supported Ru or RuO_2 thin layers as electrocatalysts for the OER in acid medium [7], (iii) Ebonex-supported Pt or Ni electrocatalysts for the oxidation of simple aliphatic and aromatic alcohols [8], (iv) Ebonex and pure Ti_4O_7-supported mixed metal catalysts containing Pt, Ir, Ru, Rh and Os, employed in unitized regenerative fuel cells as bifunctional O_2 catalysts [5], and (v) Ti_4O_7-supported Pt electrocatalysts for polymer electrolyte fuel cells [9].

Recently, Chen et al. [5] have found that Pt–Ir–Ru catalysts supported on conductive rutile $Nb_{0.1}Ti_{0.9}O_2$ have better electrochemical stability in sulfuric solution than those supported on Ebonex, particularly at high anodic potentials and under oxygen gas-enriched conditions. In addition to increase the oxide electronic conductivity, the doping of TiO_2 with Nb allows retarding the anatase to rutile phase transformation and impedes grain growth [10], which might lead to enhanced powder specific surface areas. To our knowledge, the electrochemical behavior of Nb-doped TiO_2 ($Nb_xTi_{1-x}O_2$) used as an electrocatalyst support material over a wide potential range involving water electrolysis, in alkaline medium, has not been reported. In the present paper, we first synthesized and characterized the conductive support consisting of nanocrystalline Nb-doped TiO_2 with various Nb contents (0%, 5% and 10%) and thermally treated at three different temperatures (450, 650 and 1050 °C). Then, we report the electrochemical behavior (window of electrochemical stability and ORR), in Ar- or O_2-saturated 1 M KOH solutions, of several composite film electrodes, based on mechanically mixed $Nb_xTi_{1-x}O_2$ particles with poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP), formed on the glassy carbon disk surface of a rotating ring-disk electrode (RRDE). Finally, in order to evaluate the performance of these oxides as bifunctional electrocatalyst support materials in 1 M KOH solution, the O_2 reduction and O_2 evolution activities of composite film electrodes containing $CuCo_2O_4$ (as the electrocatalyst) [11,12] and $Nb_xTi_{1-x}O_2$ or Vulcan XC72R (a commonly used conductive support) or Ebonex are compared.

2. Experimental

2.1. $Nb_xTi_{1-x}O_2$ powder preparation and characterization

Powdered undoped and Nb-doped TiO_2 were synthesized through a sol–gel route procedure similar to that reported in the literature [10,13]. A volume of 8 mL (27 mmol) of titanium tetraisopropoxide, $Ti(OiPr)_4$ (Acros Organics, 98+%), and an appropriate volume (340 μL (5% Nb in Nb/Ti atomic ratio to get the $Nb_{0.05}Ti_{0.95}O_2$ solid solution) or 680 μL (10% Nb in Nb/Ti atomic ratio to get $Nb_{0.1}Ti_{0.9}O_2$)) of niobium ethoxide (Acros Organics, 99.95%) were dissolved in 92 mL of anhydrous denatured ethanol (Anachemia) under Ar in a glove box. To this alkoxide solution, concentrated HNO_3 (EMD, ACS) was added dropwise under vigorous stirring, under Ar (out of the glove box), until a transparent solution was observed; this solution was then added dropwise to a 1:1 ethanol/water solution. Gellification of the sols (white filamentous gel) was obtained by adding dropwise concentrated NH_4OH (Fisher Scientific, ACS) under vigorous stirring under Ar. Afterwards, the liquid was filtered to obtain a precipitate which was dried at 100–110 °C and calcined (450, 650 and 1050 °C) for 2 h under air atmosphere in a tubular furnace (Lindberg/Blue M, model TF55035A) to form the $Nb_xTi_{1-x}O_2$ samples.

Titanium and niobium contents in $Nb_x\ Ti_{1-x}O_2$ powders were determined using an Yvon Jobin Horiba model JY2000 inductively coupled plasma-atomic emission spectrometer (ICP-AES), and by energy dispersive X-ray (EDX) analyses (EDAX detector, model Sapphire, integrated into a Hitachi S-4300SE/N scanning electron microscope).

Powdered $CuCo_2O_4$ was synthesized using a sol–gel method described in a previous paper [11]. In summary, a xerogel powder was first obtained from the evaporation, at 40 °C and under atmospheric pressure, of a slightly acidified ethanolic solution containing stoichiometric amounts of copper and cobalt nitrate salts, being refluxed for 4 h. The xerogel was ground in a mortar and annealed at 350 °C for 3 h under air atmosphere to form the oxide powder.

X-ray diffraction (XRD) patterns of the $Nb_xTi_{1-x}O_2$ powders were obtained from a D5000 Siemens diffractometer with a Co $K\alpha_1, \alpha_2$ radiation ($\lambda\alpha_1 = 1.7890$ Å) and a silicon detector. Diffractograms were recorded for 2θ ranging