Electrosynthesis of Ce–Co Mixed Oxide Nanotubes with High Aspect Ratio and Tunable Composition

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An electrochemical synthetic route is developed to produce cerium-cobalt mixed oxide nanotubes with tunable composition. The process consists of a template-assisted electrogeneration of base from a cerium-cobalt nitrate solution of different compositions. From scanning electron microscopy studies it is seen that Ce–Co oxide nanotubes of high aspect ratio and ordered structures are formed. Energy-dispersive X-ray analysis shows a linear relationship between the solution and the oxide composition [Ce/(Ce + Co) atomic ratio].

*c* Electrochemical Society Active Member.

Abstract

Cerium oxide and cobalt oxides have attracted the interest of several researchers due to their potential application in several technological fields (electrochromism, lithium batteries, catalysis, etc.). Ceria has been used as a promoter in the so-called “three-way catalytic” for the control of toxic emission from automobile exhaust. The promotion consists of the enhancement of the noble metal dispersion, as well as stabilization of the supporting medium toward thermal sintering. A direct catalytic effect of CeO2 in chemical processes such as water–gas shift reaction or NO decomposition has been also evidenced. Concerning Co3O4, several papers have reported on its beneficial role in the oxidation of carbon monoxide and methane. Recent works have demonstrated that the addition of ceria to cobaltic oxide allows cocatalyst production, with better performances with respect to pure Co3O4 in terms of higher thermal stability and catalytic activity. Ceria-based electrolytes are the most promising alternative to yttria-stabilized zirconia as a fast ionic conductor for solid oxide fuel cells, with the advantage of a lower operating temperature. In recent years the increased interest in these materials has lead to many investigations aimed at studying efficient processes for the fabrication of ceria powders as well as to improve their sinterability. According to Ref. 19 and 20, the addition of a small amount of cobalt oxide to ceria can lead to microspheres, such as one-dimensional nanostructures, which can be obtained by a direct catalytic effect of CeO2 in chemical processes such as water-gas shift reaction or NO decomposition. Energy-dispersive X-ray analysis shows a linear relationship between the solution and the oxide composition [Ce/(Ce + Co) atomic ratio].

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Introduction

Ceria has been used as a promoter in the so-called “three-way catalytic” for the control of toxic emission from automobile exhaust. The promotion consists of the enhancement of the noble metal dispersion, as well as stabilization of the supporting medium toward thermal sintering. A direct catalytic effect of CeO2 in chemical processes such as water–gas shift reaction or NO decomposition has been also evidenced. Concerning Co3O4, several papers have reported on its beneficial role in the oxidation of carbon monoxide and methane. Recent works have demonstrated that the addition of ceria to cobaltic oxide allows cocatalyst production, with better performances with respect to pure Co3O4 in terms of higher thermal stability and catalytic activity.

Ceria-based electrolytes are the most promising alternative to yttria-stabilized zirconia as a fast ionic conductor for solid oxide fuel cells, with the advantage of a lower operating temperature. In recent years the increased interest in these materials has led to many investigations aimed at studying efficient processes for the fabrication of ceria powders as well as to improve their sinterability. According to Ref. 19 and 20, the addition of a small amount of cobalt oxide to ceria results in much lower sintering temperature, higher shrinkage rates, larger particles, and generation of OH− ions according to Eq. 1

$$\text{NO}_2^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_3^- + 2\text{OH}^- \quad [1]$$

Electrogeneration of base is a well-established, low-cost technique for the preparation of metal oxides and hydroxides starting from the metal nitrate solution. It has been recently demonstrated that this method can be extended to the preparation of 1D metal oxide and hydroxide nanostructures by using an AAM template. In this article we report on the possibility of using the same electrochemical route for the synthesis at room temperature of cerium oxide, cobalt oxide, and cerium-cobalt mixed oxhydroxide NTs with a tunable Ce/Co ratio. Moreover, we show how the use of an AAM as a template for the direct synthesis of these materials allows ordered and high-aspect-ratio arrays of high-quality NTs to be obtained.

Experimental

Commercial AAMs (Anodicisc-60 Whatman, average pore diameter 200 nm, porosity 43%) were employed as a template. Gold was sputtered on one side of the membrane to serve as the conductive layer. The AAM was supported in a holder in order to delimit the electrode area exposed to the solution (2.54 cm2). The electrodeposition process was carried out in aqueous 0.05 M Ce(NO3)3 (pH 4.1) and/or 0.05 M Co(NO3)2 (pH 4.8) solutions by applying a constant current density of 1 mA cm−2 with a multichannel potentiostat. A classic three-electrode cell was employed with the AAM as the working electrode, a dimensionally stable anode electrode as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The AAM/NT samples were sometimes chemically etched in 0.1 M NaOH in order to remove the alumina host. Thermal treatment of AAM/NT samples was realized in an oven at 500°C in air.

Morphology and quality of the NTs were investigated using a Philips XL30 ESEM scanning electron microscope (SEM). Energy-dispersive X-ray analysis (EDX) was also performed in order to identify the elements in the deposited materials and to determine their composition. X-ray analysis of composite AAM/NT arrays was realized by a Philips X-Ray Generator (model PW 1130) and a PW (model 1050) goniometry. The identification was performed according to the International Centre for Diffraction Data (ICDD) cards available.

Results and Discussion

As previously shown, the mechanism of electrogeneration of base is an electrochemical method for the deposition of metal oxides and/or hydroxides involving the cathodic reduction of nitrate ions and generation of OH− ions according to Eq. 1

$$\text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$$

with consequent local increase of pH sufficient to induce the chemical precipitation of many metal hydroxides and/or oxides at the electrode/solution interface, according to the reaction
Peaks that can be assigned to CeO$_2$ cerium nitrate solution NTs soon after preparation. The broad feature in the spectra arises at pH 4.8 and with $\text{[NO}_3^-\text{]} = 1 \times 10^{-6}$ M the equilibrium potential for the reduction of nitrate ion to nitrite ion is +0.16 V, corresponding to the following overall cathodic process:

$$2\text{Ce}^{4+} + 4\text{OH}^- \rightarrow 2\text{Ce}^{3+} + 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$$

which is operating during the electrodeposition, presumably in parallel with the nitrates reduction, leading to the direct Ce(IV) precipitation.

After thermal treatment some peaks relative to Ce(OH)$_3$ seem to disappear (see Fig. 3b), indicating Ce(III) oxidation to Ce(IV) by oxygen. The transformation is evidenced also by a change in the color of the AAM/NTs from yellow-brown to light yellow.

In contrast, the nanostructures grown from pure Co(NO$_3$)$_2$ solution seem to be amorphous or scarcely crystalline (see Fig. 2e). The evident blue-green color of the samples soon after the electrodeposition suggests the presence of Co(III) into the AAM pores. Looking at the X-ray analysis performed on the same samples after thermal treatment (500°C, 4 h, air), some peaks attributed to cubic Co$_3$O$_4$ (ICDD card no. 42–1467) appear, in agreement with the black color of the annealed samples (Fig. 3a).

Concerning the Ce–Co mixed oxides containing electrodeposits, the only scarcely visible diffraction peaks are those attributed to CeO$_2$ and Ce(OH)$_3$ (see Fig. 2b–d). Moreover, a gradual decrease and widening of the peak intensity is observed with the decrease of
Ce/Co ratio in the electrolyte. These findings agree with previous results found for thin-film Ce/Co oxide, where the presence of CeO₂ nanocrystals in Ce–Co mixed oxide amorphous matrix has been evidenced. In the same paper IR adsorption spectra of the Ce/Co composite films reveal a new peak, not present in the spectra of pure CeO₂ or Co(OH)₂, assigned to Ce–O–Co bridging vibration. This result suggests that the deposit is a mixed oxide and not an aggregate of CeO₂ and Co(OH)₂.

The XRD patterns recorded for thermal treated Ce/Co mixed NTs did not show any appreciable difference with respect to those relating to as-prepared samples. This indicates that up to this temperature the mixed NTs keep their amorphous structure.

The SEM side views (Fig. 4) of pure Ce(OH)₃/CeO₂ (Fig. 4a), Ce/Co mixed oxides (Fig. 4b), and pure Co(OH)₂ (Fig. 4c) NTs after removal of the AAM template show that the tubes are continuous and uniform throughout the entire length and are arranged roughly parallel to each other. The typical morphologies of NTs are better evidenced in Fig. 5. SEM measurements reveal that the NTs have internal diameters of ~200 nm and lengths of ~30 to 50 μm, corresponding to a high aspect ratio of 150–250.

According to experimental findings collected with several metal nitrate solutions, we believe that the formation of hollow interior nanostructures is related to the morphology of the Au layer sputtered on the AAM template, as will be discussed in a forthcoming paper.

In Fig. 6a we report the typical EDX spectrum relating to mixed Ce–Co oxyhydroxide NTs. As shown in Fig. 6b, a quite linear relationship between the EDX Ce/(Ce + Co) atomic ratio revealed into the deposits as a function of Ce/(Ce + Co) atomic ratio in the electrodeposition solution (total concentration 0.05 M metal nitrate). Each point is averaged on at least four measurements.
the NTs and the Ce/(Ce + Co) in the electrodeposition bath has been revealed, suggesting that the deposit formation is not influenced by the nature of the cation, but it depends on the relative amount of Co\(^{2+}\) and Ce\(^{3+}\) present in the electrolyte. This is expected for an oxyhydroxide formation precipitation mechanism not controlled by OH\(^-\) concentration, which is kept high by the electrochemical process.

Conclusions

Cerium oxyhydroxide, cobalt hydroxides, and Ce-Co mixed oxyhydroxide NTs were successfully prepared at room temperature by a template-assisted process via electrogeneration of base. The NTs are continuous and uniform throughout the entire length and are arranged roughly parallel to each other. According to the morphological analysis performed by SEM, the NT internal diameter is \(\sim 200\) nm, while their length is approximately 30–50 \(\mu\)m, corresponding to a high aspect ratio of 150–250. The NT diameter, thickness, and density can be also tuned in a wide range of values by simply changing the AAM template morphology.\(^{37}\) The Ce-Co mixed oxyhydroxide NTs have a variable composition with a Co/Ce ratio very close to that of the electrodeposition solution. This aspect makes the AAM template-assisted electrodeposition a very powerful technique for tailoring the composition of the growing mixed oxide nanostructures. Moreover, in the specific case of Ce-Co mixed oxyhydroxide employed as catalyst, NTs-embedded AAM can be directly used as catalyst, because alumina is usually used as catalyst support for high-temperature applications.\(^{38}\)

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References