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A Sol–Gel Route for the Synthesis of $Bi_2Ru_2O_7$ Pyrochlore Oxide for Oxygen Reaction in Alkaline Medium

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In this investigation, $Bi_2Ru_2O_7$ pyrochlore-type oxide was prepared using the Pechini process. We employed a sol–gel route, in which a solution of Ru(III) and Bi(III) in a mixture of citric acid and ethylene glycol was heated to form a polymeric precursor, followed by an annealing at higher temperatures during various periods. The oxide obtained was identified by X-ray diffraction analysis. The results revealed that the formation of homogeneous oxide with a single pyrochlore structure phase occured at or above 650°C. Sample powders consisted of fine grains with homogeneous morphology and an average size of about 0.5 μm. This new preparation procedure yielded an electrode material with improved electrochemical activity compared to those elaborated through conventional methods. © 2001 Academic Press

Key Words: **$Bi_2Ru_2O_7$ pyrochlore-type oxide; Pechini process; sol–gel route; electroactivity.**

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1. INTRODUCTION

Several simple and mixed metal oxides have been often considered for various electrocatalytic applications. Unfortunately, their practical applications have been limited by relatively low electronic conductivities and small surface areas. Over the past two decades, a series of mixed metal oxides with the pyrochlore structure has been discovered (1). The materials, which are described by the general formula $A_2[Ru_{2-x}A_x]O_{7-y}$, where $A = $ Pb or Bi, $0 \leq x \leq 1$ and $0 \leq y \leq 0.5$, have demonstrated high catalytic activity for oxygen reduction as well as for oxygen evolution, and have emerged as possible candidates for use in secondary metal–air batteries (2). These compounds have also promoted the selective electrooxidation of certain organics (3). The electrochemical activity of this mixed oxide type is believed to be related to variable oxidation states available for ruthenium, and consequently to oxygen stoichiometry (4). These attracting properties account for the recently renewed interest in the study of ruthenium pyrochlores (5–7).

In literature, these types of catalysts were usually prepared using traditional solid-state reactions (8, 9) involving mechanical mixing of oxides and/or carbonates followed by high-temperature heating and extended grinding. This synthetic method, which requires long-range diffusion of reactants, may result in heterogeneous distribution of the constituting elements and nonuniform grain growth. Results obtained with catalysts synthesized by the alkaline solution technique (2, 7, 10) were impressive and provided evidence for pyrochlore oxide catalysts with high surface areas but with uncertain bulk or surface structures. Sol–gel synthesis methods of these pyrochlore-type oxides were still lacking, and there is a great need to develop convenient and inexpensive mild chemistry routes. The latter, which is the target of a number of material syntheses, involves transformation of a solution into a gel by ion polymerization, and yields compounds with higher surface areas and very narrow particle size distributions (11, 12). Thus, preparation of mixed oxide electrocatalysts for oxygen reaction by this technique seems very promising.

The aim of the present work is to prepare $Bi_2Ru_2O_7$ oxide using a sol–gel method, namely the so-called Pechini process, and to define the proper experimental conditions of synthesis.

2. EXPERIMENTAL

2.1. *Synthesis*

The bismuth–ruthenium pyrochlore was synthesized by following a procedure similar to that used for other metal oxide powders such as $LaMnO_3$ perovskite (13) and $LiMn_2O_4$ spinel (11). The process involves the dissolution of a metal chloride and a metal oxide in a mixture of a weak hydroxy carboxylic acid, such as citric acid, and a polyol,

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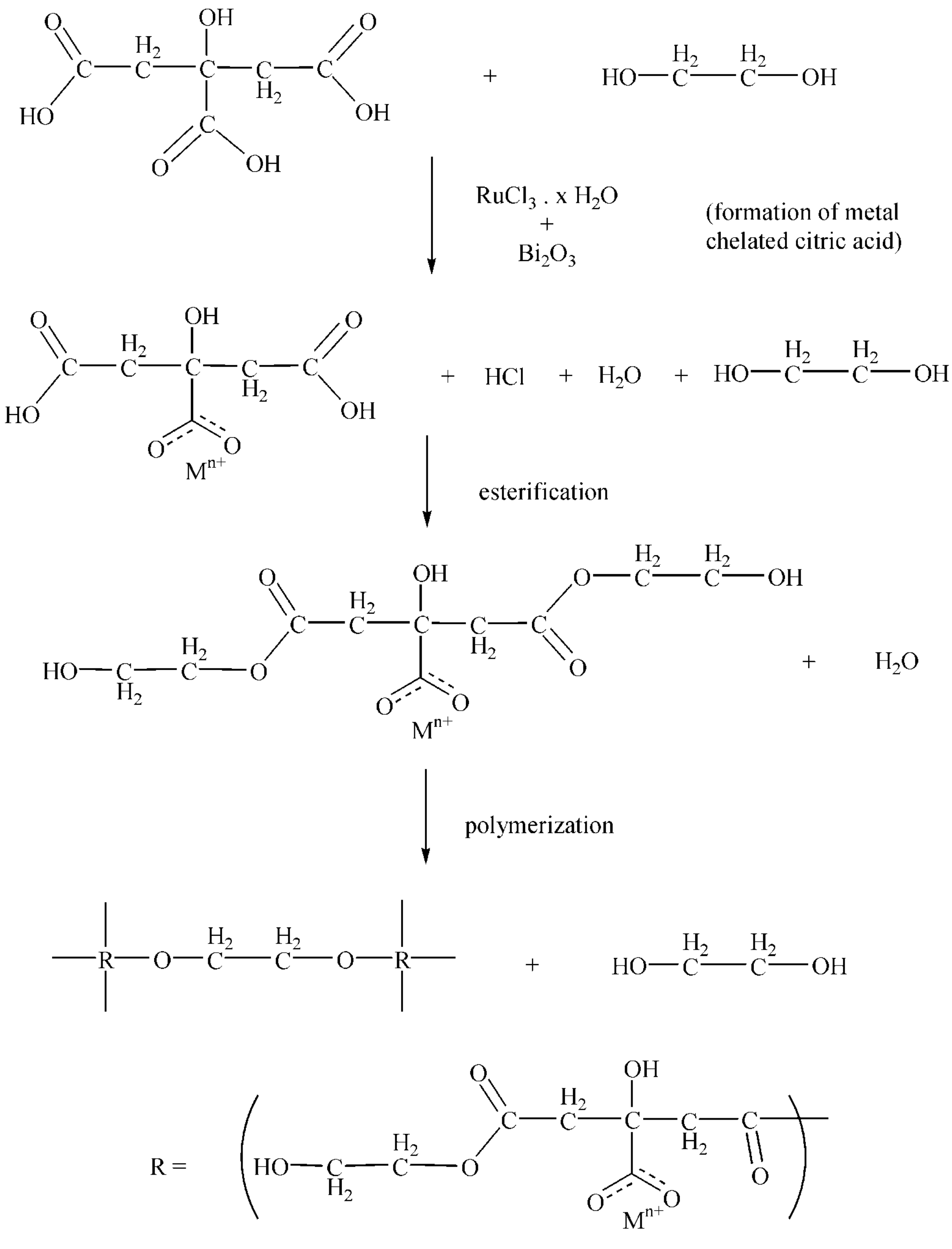
such as ethylene glycol. Previous work on this process has suggested that three basic reactions, i.e., formation of metal chelates, esterification, and polymerization, occur during the formation of the polymeric precursor (14), as shown in the following scheme:



A clear solution was obtained by heating a mixture of citric acid and ethylene glycol (1:4 molar ratio) at 90°C for 20 min. $RuCl_3.3H_2O$ (Lancaster synthesis, ref. 0421) and Bi_2O_3 (Aldrich, ref. 22, 389-1) were added in the appropriate amounts. The resulting solution was further heated at 140°C to induce esterification and remove excess of ethylene glycol. The viscous solution was vacuum dried at 180°C to yield an organic polymer precursor. Black powders were obtained by heating in air the precursor, at temperatures ranging from 580 to 760°C, during various periods. Calcination at higher temperatures and/or for longer periods resulted in monophased pyrochlore structure samples.

Because the oxygen stoichiometry was not quantified, the oxide thus produced will be denoted hereafter by the formula $Bi_2Ru_2O_7$.

The bonds involved in the different constitutional groups for the precursor (carboxyl groups) as well as for the final product (metal-oxygen bendings) were qualitatively checked by means of infrared spectroscopy analysis.

It is worth noting that a synthesis following an equivalent procedure, using propionic acid (15, 16), did not yield the desired product.

2.2. *Characterization Methods*

The precursor and the final product were analyzed by means of infrared spectroscopy. The spectra were recorded by using a Nicolet Avatar 320 FT-IR instrument with a KBr pellet technique.

Thermal gravimetric analysis (TGA) was performed on a TGA 7 Perkin Elmer thermogravimetric analyzer. The polymeric precursor was heated at a rate of 10°C/min in 1 atm oxygen gas flow.

X-ray diffraction (XRD) studies of the oxide powders were carried out on a Siemens D-500 diffractometer with a Guinier-Wolf chamber using cobalt $K\alpha$ radiation ($\lambda = 0.1789$ nm) and a quartz monochromator. The XRD patterns were recorded in the 20–80° 2θ range at a scanning rate of 0.05°/s.

The oxide morphology was determined by scanning electron microscopy (SEM), using a JEOL scanning electron microscope.

The surface area of the powders was measured with a Sorpty 1750 Carlo Erba instrument by the BET method, using nitrogen gas absorption at liquid nitrogen temperature.

The electrochemical experiments for O_2 reactions were performed using a PJT 120-1 Tacussel potentiostat–galvanostat and a PE 8116 Sefram recorder. Electrodes (1 cm^2) were obtained by painting, with an oxide suspension in isopropanol, a polyisobutylene foil (Nikolaus Branz, Berlin) charged with graphite of the type used in the battery industry (16). In that case, the carbon material acts only as a substrate. This latter, before being coated, was mechanically polished with sand paper (grade 1200) and then degreased with acetone. The counter electrode used was a Pt plate with large surface area. A mercury/mercurous oxide electrode (Hg/HgO, 1 mol/dm^3 KOH) was used as the reference electrode.

3. RESULTS AND DISCUSSION

3.1. *Thermal Gravimetric Analysis*

Figure 1 displays a typical thermal gravimetric analysis scan of the polymeric precursor. This sample exhibits two closely consecutive stages of decomposition. The first, occurring in the 200–380°C range and evaluated at 35% weight loss, corresponds to evaporation of ethylene glycol and water traces. The second step in the process, ranging from 380 to 600°C, with 30% weight loss can be explained by the decomposition of the metal citrate complex and the residual organics. This behavior was found to be typical for the pyrolysis of certain citrate precursors (17, 18). It can be inferred from these data that the final product may only be obtained by annealing at temperatures equal to or higher than 600°C.

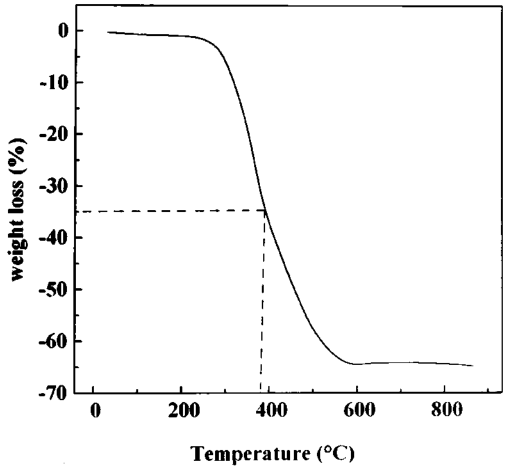


FIG. 1. TGA plot of the polymeric precursor under 1 atm O_2 gas flow. Heating rate 10°C/min.

3.2. *X-Ray Diffraction Analyses*

$Bi_2Ru_2O_7$ samples were prepared under different conditions: at temperatures ranging from 580 to 760°C during 24 h, and at a fixed temperature of 650°C for different heating periods. The corresponding XRD patterns of the oxide powders are gathered in Figs. 2a and 2b, indicating that the single-phase $Bi_2Ru_2O_7$ pyrochlore (matching the JCPDS ASTM files No. 45-0881 and No. 26–222, 19) could be obtained only for heating temperatures equal to or higher than 650°C during at least 24 h. Otherwise, small additional peaks appeared, revealing the presence of Ru- and Bi-based secondary phases. In fact, careful analysis of the 2θ positions of such peaks indicates the presence of $Bi_{12}Ru_{0.15}O_{18.3}$ as a secondary phase (JCPDS ASTM file No. 44–190). A similar observation was also reported by Takeda *et al.* (20) and Varfolomeev *et al.* (21) on $Bi_2Ru_2O_7$ samples synthesised using the solid-state reaction method.

The degree of crystallinity of powders increases slightly with the annealing temperature. The values determined for the d_{hkl} interplanar distances are in good agreement with those reported for samples with the same chemical composition obtained by conventional methods (22). The patterns of the monophased samples obtained at 650, 700, and 760°C during 24 h, are indexed in a cubic unit cell and the corresponding lattice parameter, calculated using the Peracel Program (23), is equal to 0.9330 ± 0.0030 nm. This value is

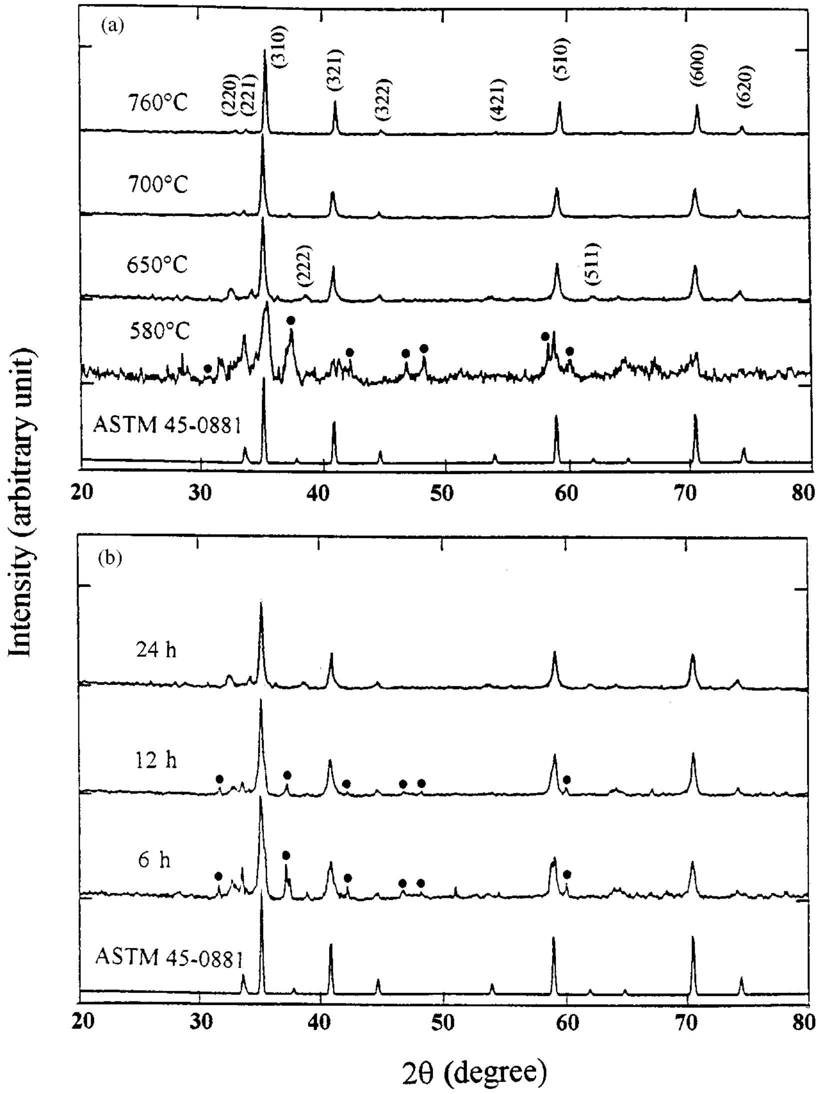


FIG. 2. X-ray patterns obtained for the $Bi_2Ru_2O_7$ samples annealed at (a) different temperatures, during 24 h; (b) at 650°C, during 6, 12, and 24 h. (●) Indicates the presence of the secondary phase.

very close to that reported for oxygen over stoichiometric $Bi_2Ru_2O_{7.3}$ oxide ($a = 0.9302$ nm) (22).

3.3. Morphology and Specific Surface Area

The scanning electron microphotograph corresponding to the oxide annealed at 650°C during 24 h is depicted in Fig. 3a. It shows sphere-shaped grains with a narrow particle size distribution around 0.5 μm. Grains, having similar shape but slightly larger, were obtained for the samples annealed at higher temperatures. However, the samples annealed for shorter periods (6 h) showed significantly finer grains (Fig. 3b).

Figure 4 shows the variations of BET surface area of oxide samples annealed at different temperatures and periods. In accordance with their grain size evolution, S_{BET} dropped as the annealing temperature and/or the annealing duration were increased.

3.4. Electrochemical Study

Catalytic electroactivity toward both oxygen evolution and reduction reactions was investigated on $Bi_2Ru_2O_7$-coated graphited isobutylene substrate C. The oxide samples prepared at 650°C during 24 h were selected for these experiments. Figure 5 shows cyclic voltammograms plotted for the C/$Bi_2Ru_2O_7$ and for the bare support. The very small currents, observed for the bare support, are related to the electrode capacitive behavior. Electrode reaction over the surface of the oxide exhibits high currents. The electrode film showed good adherence during cycling. It can also be noticed that subsequent cycling gave rise to two large redox

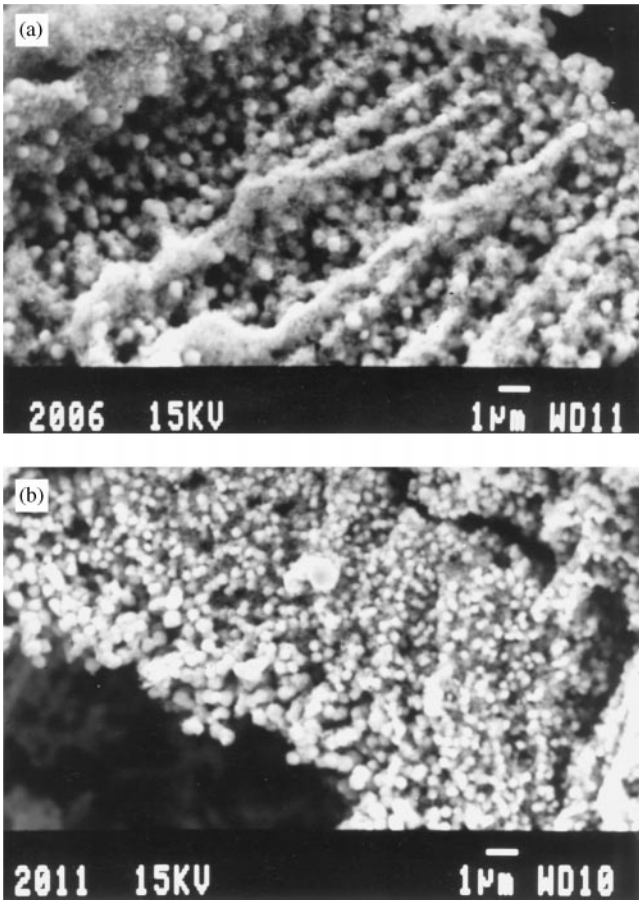


FIG. 3. SEM microphotographs of $Bi_2Ru_2O_7$ powder prepared by the Pechini process, annealed at (a) 650°C/24 h; (b) 650°C/6 h.

peaks which appear at approximately 0.4 and 0.05 V vs Hg/HgO. These peaks can be attributed to the Ru^{4+}/Ru^{5+} couples as reported for the $Bi_2Ru_2O_7$ electrode behavior under similar conditions (4).

To achieve full electrode activity, some 50 cycles in the -0.8 to $+0.8$ V vs Hg/HgO potential range were necessary to be initially applied. No further evolution was observed upon extended cycling. Appreciable enhancement in electroactivity was observed in the anodic and cathodic regions on the electrode materials elaborated following this new synthesis technique. Current densities measured on the $C/Bi_2Ru_2O_7$ electrode and the cycled one, at 0.55 and -0.55 V vs Hg/HgO, are respectively about 5 and 10 times greater than the values recorded on the same compound by Egdell *et al.* (9).

Because the working film-like electrode was immersed systematically in the electrolyte solution overnight before the experiment was started, this electrochemical activation, in contrast to published results (24), does not mean an additional impregnation of the electrode pores. Rather it may be related to the participation of higher valence of Ru species that cause modification of electron transfer rates in the oxygen electrode reaction (25).

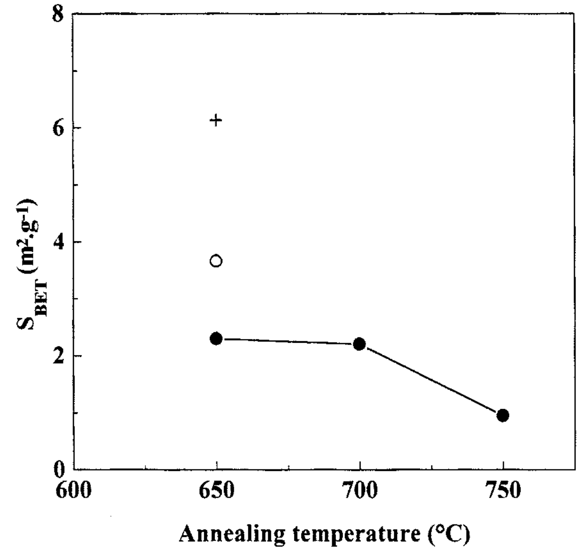


FIG. 4. Calcination temperature and duration dependence of specific surface areas of $Bi_2Ru_2O_7$ prepared by the Pechini process. (●) Annealed at different temperatures, during 24 h. (○) Annealed at 650°C during 12 h and (+) 6 h.

4. CONCLUSION

Using a sol–gel route, we have adapted the Pechini process to develop a new method providing access to $Bi_2Ru_2O_7$ pyrochlore oxide. The XRD patterns of the oxide samples

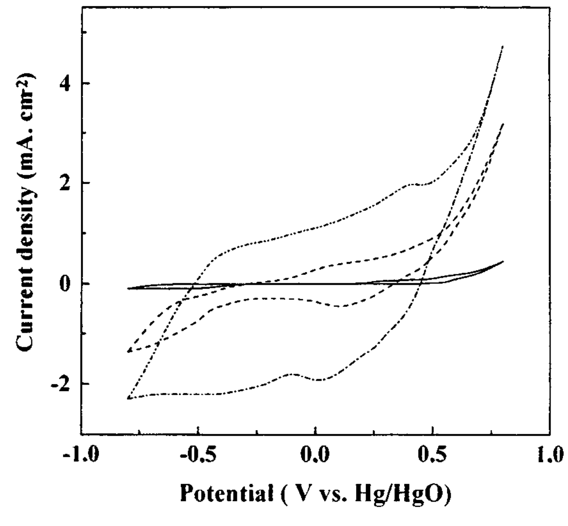


FIG. 5. Cyclic voltammograms plotted at 50 mV.s^{-1} for $Bi_2Ru_2O_7$ oxide-based oxygen electrode in 1 M KOH at 23°C: (——) graphited isobutylene substrate C, (- - -) first cycle obtained on $C/Bi_2Ru_2O_7$ electrode, and (……) cycled electrode (50th cycle).

showed that the $Bi_2Ru_2O_7$ pure phase could be obtained at a moderate heating temperature ($T = 650°C$) during 24 h. The powders synthesized exhibited a narrow grain size distribution and a BET surface area of nearly $2\,m^2.g^{-1}$. The electrochemical study, performed on the oxide samples prepared at the lowest temperature required, showed a substantial enhancement in the electrode activity, both for oxygen evolution and reduction, compared to those reported in the literature. After some 50 polarization cycles, this electrode material displays a durable electroactivity.

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