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Original Article

Preparation and characterization of bismuth ruthenate pyrochlore via solid state reaction and sol-gel methods

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Abstract:

Bismuth ruthenate pyrochlores, potential cathode materials for intermediate temperature solid oxide fuel cells (ITSOFCs), were prepared via solid-state and sol-gel method. Effects of the preparation routes and conditions on the phase and microstructures of the materials were investigated in this study using XRD and SEM. The study showed that the preparation method and the adding sequence of the starting meterials have a significant effect on the crystal phase and the particle size obtained. Sol-gel synthesis could yield a material with only pyrochlore structure, i.e. $Bi_2Ru_2O_7$, while the solid state method yielded powder with a small amount of the secondary RuO_2 phase. The sol-gel synthesis resulted in materials with a finer particle size (~0.3-1.0 μm) compared to powder synthesized via the solid state reaction method.

Keywords: bismuth ruthenate pyrochlore, sol-gel, cathode material, SOFCs

1. Introduction

A solid oxide fuel cell (SOFC) is an interesting electrochemical device because of it's high efficient energy conversion ability coupled with a low pollution emission. Recent researches have been focusing on decreasing the operating temperature of SOFCs to an intermediate temperature range, between 500-800°C, with the aims to reduce overall costs and to prolong the life of the system (Steele *et al.*, 2000).

Required properties of cathode materials are high electronic conductivity, good thermal and chemical stability, compatibility with the electrolyte, and a high catalytic activity towards oxygen reduction. Traditional cathode materials are in the La-Sr-Mn-O perovskite family. However, their poor activities for the electrochemical reduction of oxygen at low temperatures have limited their usage only for high temperature solid oxide fuel cells (Brandon *et al.*, 2003). Oxides with pyrochlore structures are of interest due to their higher conductivity in the intermediate temperature range compared to the traditional perovskite oxides (Takeda *et al.*, 2000). Ruthenium oxide has been known to be catalytically active towards oxygen reduction and ruthenate pyrochlore compounds have been studied as oxygen reduction catalysts (Horowitz *et al.*, 1983) and they are one of the potential cathode materials (Zhong, 2006). In this study, we focused on the synthesis of a bismuth ruthenate pyrochlore type cathode. Effects of preparation routes, solid state reaction and sol-gel methods, and the synthesis conditions on the properties of synthesized powder were investigated and reported here.

2. Experimental Methods

Bismuth ruthenate pyrochlore was prepared via solid state and sol-gel methods. Bi_2O_3 (99.99%, Aldrich) and $RuO_2{\cdot}nH_2O$ (99.99%, Aldrich) were used as the starting materials for the solid-state reaction synthesis. The starting metal compounds were mixed in stoichiometric amounts and the mixture was ball milled for 8 hrs. The mixed powder was then calcined at 900°C for 10 hrs in air. The sol-gel method

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followed the experimental procedure similar to what was reported by Kahoul *et al.* (2001), where Bi_2O_3 and $RuCl_3 \cdot nH_2O$ (~41 Ru%, Alfa Aesar) were used as the starting materials. A mixture of citric acid and ethyleen glycol with a mole ratio of 1:4 was added to the metal oxide compounds, and the solution was stirred for 2 hrs at 140°C until dark colored, almost black, gel was formed. The adding sequence of each of the starting metal compounds was varied to investigate it's effect on phase formation by adding the metal compounds at the same time (Sol-gel A), adding Bi_2O_3 before $RuCl_3 \cdot nH_2O$ (Sol-gel B), and adding $RuCl_3 \cdot nH_2O$ before Bi_2O_3 (Sol-gel C). The gels were then heated to 200°C to remove excess ethylene glycol followed by a calcination at 800°C for 20-40 hrs to obtain the oxide powders.

Thermogravimetric analysis (TGA, NETZSCS 449C) was done on the gel obtained after the 200°C heat treatment. The analysis was performed from room temperature to 900°C in air with a heating rate of 10°C/min. X-ray diffration analysis (XRD, Cu Kα, JEOL JDX-3530) was performed to study the crystal structures of the prepared samples. The powders were analyzed at room temperature using a step scan procedure with a 2θ range between 10-70° and 0.02°/step. The morphology, particle size, and elemental composition of the obtained powders were investigated using scanning electron microscopy (SEM, JEOL JSM-6310F) and energy dispersive spectrometry (EDS, Oxford 5401).

3. Results and Discussion

Figure 1 shows the TGA result of the polymer precursor synthesized by the sol-gel method. It was found that a decomposition of the sample occurred in three stages. The first stage occurred between 170-375°C with 59% weight loss. This first stage of weight loss is likely caused by the loss of water and organic solvent. The second stage of decomposition was found in the temperature range between 375-470°C (27% wt loss). This stage of weight loss is likely caused by the decomposition of ethylene glycol and other residual organics. At higher temperature, in the range between 470-740°C, the final decomposition was likely due to the decomposition of the citric complex (12% wt loss). The first two stages of the decomposition were found to be consistent with what has been reported by Kahoul *et al.* (2001). However, in their experiment, the decomposition was found to be completed at a temperature above 600°C, while a temperature higher than 740°C was needed for the complete decomposition in this study.

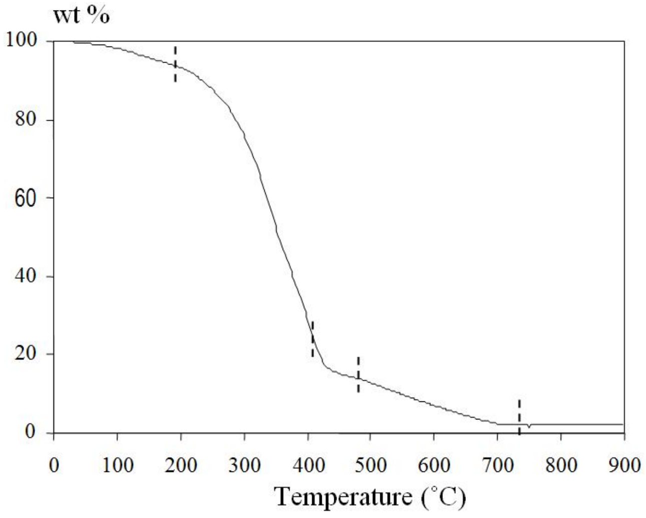

Figure 1. TGA analysis of the polymer precursor synthesized by sol-gel method (Sol-gel A).

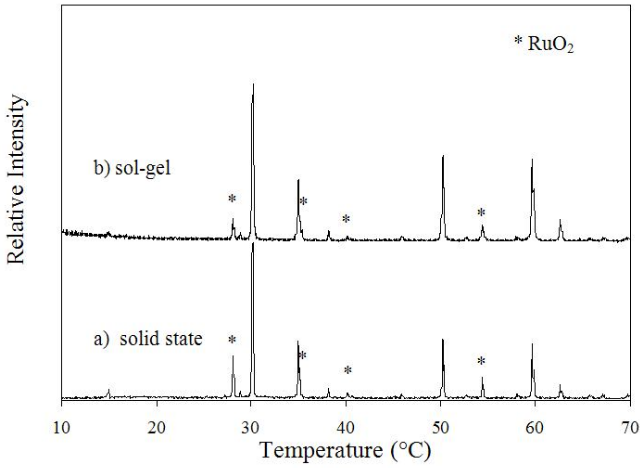

Figure 2. XRD patterns of the powders a) prepared by solid state method b) prepared by sol-gel method (Sol-gel A). Unmarked peaks are corresponding to $Bi_2Ru_2O_7$.

Figure 2 shows the XRD patterns of the powders synthesized by solid state reaction and sol-gel method heat treated at 900°C for 10 hrs and at 800°C for 20 hrs, respectively. Both XRD patterns of the powders prepared by solid state and sol-gel method show X-ray peaks corresponding to $Bi_2Ru_2O_7$ pyrochlore. However, small peaks corresponding to RuO_2 were also found along with the desired $Bi_2Ru_2O_7$. The observation of small peaks of a Ru-based secondary phase has also been reported by Takeda *et al.* (2000) on $Bi_2Ru_2O_7$ synthesized using the solid state reaction method. In an attempt to eliminate the secondary phase of RuO_2, a longer heating time was used in order to promote a better reaction. For comparison Figure 3 shows the XRD results of the powder prepared by the sol-gel method that was also heated at 900°C but for a longer time, here 40 hrs. It was found that the RuO_2 phase was still present. The existence of the unreacted RuO_2 phase without the remaining unreacted Bi_2O_3 in the XRD pattern might indicate a Bi loss during the synthesis. Excess Bi might be needed for the formation of a single phase $Bi_2Ru_2O_7$, comparable to what has been reported in the synthesis of the compound via the co-precipitation method, where a Bi:Ru ratio as high as 1.5:1 was needed (Bae *et al.*, 1999).

The sol-gel process used above was done by adding the metal complex to a acid/solvent solution at the same time.

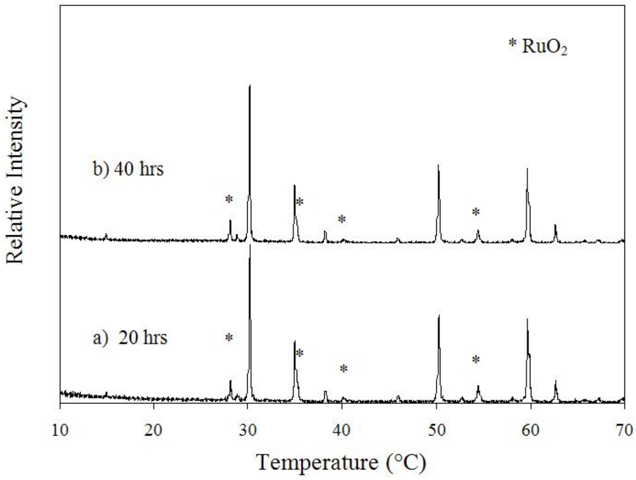

Figure 3. XRD patterns of the powders synthesized by sol-gel method (Sol-gel A) after heat treatment at 800°C for a) 20 hrs b) 40 hrs. Unmarked peaks are corresponding to $Bi_2Ru_2O_7$.

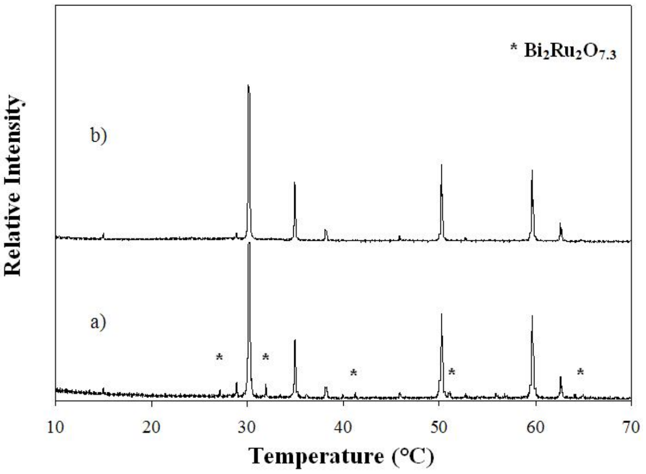

Figure 4. XRD patterns of the powders synthesized by sol-gel method after heat treatment at 800°C, 40 hrs with a) adding Bi_2O_3 first (Sol-gel B) and b) adding $RuCl_3{\cdot}nH_2O$ first (Sol-gel C). Unmarked peaks are corresponding to $Bi_2Ru_2O_7$.

A homogenous mixing of the starting materials and the promotion of the reaction at a lower temperature are important factors in order to obtain a complete reaction between the starting materials. Of further importance is the observation that the different metal compounds might possess different solubility in the mixture of citric acid and ethylene glycol. Therefore, the effect of the adding sequence of the starting metal compound was studied with the aim to resolve the problem of the unreacted RuO_2.

For the first experiment, Bi_2O_3 was dissolved in an organic solution followed by the addition of $RuCl_3{\cdot}nH_2O$ (Sol-gel B). The adding sequence was switched in the second experiment, where $RuCl_3{\cdot}nH_2O$ was added first (Sol-gel C). It was found that $RuCl_3{\cdot}nH_2O$ could dissolve in the citric acid-ethylene glycol solution much more readily compared to Bi_2O_3. This is expected as $RuCl_3$ should have higher a polarisability compared to Bi_2O_3 as the Ru^{3+} cation is smaller in size and contains an unfilled d orbital, while Bi^{3+} is larger with filled d orbitals.

The results on the effect of metallic compound adding sequence on the phase of the resulting powders are shown in Figure 4. From the XRD results, it was found that the powder prepared via sol-gel method with the material adding sequence started with Bi_2O_3 shows no sign of the Ru_2O. A mixture of $Bi_2Ru_2O_7$ and $Bi_2Ru_2O_{7.3}$ was found. The sample in which $RuCl_3{\cdot}nH_2O$ was the first material to be added also showed no RuO_2 peaks that were found earlier in sol-gel A. Only peaks corresponding to a single phase of $Bi_2Ru_2O_7$ were observed.

The morphology and particle size of the powders prepared by the different methods were investigated by SEM. It has been found that the particle size of the powder prepared by the solid state method was larger compared to the powder prepared by the sol-gel method (Figure 5). The particle size of the powder synthesized by sol-gel method was found to be below 1 μm, while the solid state method yielded particle sizes as large as 3 μm. These large particles from the solid sate reaction are similar to what was observed by Wachsman *et al.* (2005). The smaller particle size obtained from the sol-gel method in comparison to that obtained from the solid state reaction method was expected due to significant differences in the reaction conditions. For the sol-gel

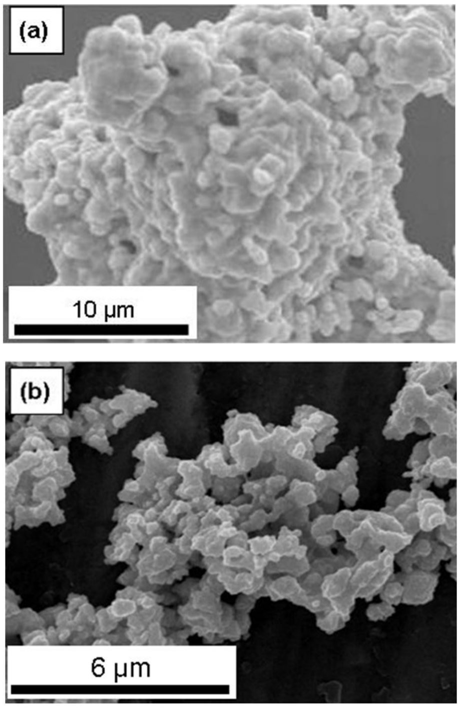

Figure 5. SEM images of the powders after calcination a) prepared by solid state method and b) prepared by sol-gel method.

Table 1. Crystallite size of powders synthesized via solid state and sol-gel methods.

Calcination time	Crystallite Size from XRD (nm)			
	Solid state	Sol-gel A	Sol-gel B Adding Bi_2O_3 first	Sol-gel C Adding $RuCl_3 \cdot nH_2O$ first
20 hrs	>100	70	-	-
40 hrs	-	70	70	90

method, the metal compounds were reacted in the liquid-semi-solid form, where much higher surface reaction sites were available. The result is consistent with the result obtained from the XRD (Table 1). It was found that the crystallite size of the powder synthesized from the solid state reaction was larger than 100 nm after calcination at 900°C for 10 hrs, and the crystallite size of the powder obtained from the sol-gel reactions after calcination was approximately 70-90 nm. Effects of the adding sequence of the starting materials for the sol-gel synthesized powders on the particle morphology were also investigated. As shown in Figure 6, fine particles in the range of 0.3-1.0 µm were found in both samples regardless of the adding sequence. However, for the samples, in which Bi_2O_3 was added prior to the addition of the Ru-compound, particles with a different morphology were also observed (Figure 6a). Facetted particles with much larger size, in the range of 6-10 µm, were found. Elemental analysis of the particles using energy dispersive X-ray spectrometry revealed that the particles are consisted of Bi, Ru, and O, with approximately the same composition as the small particles observed. This result coupled with the XRD results obtained indicated that the large size facetted particles might be the $Bi_2Ru_2O_{7.3}$ phase as found via the XRD analysis.

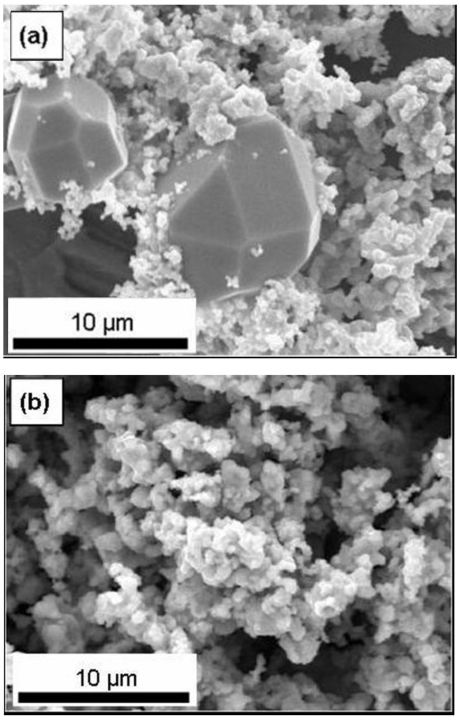

Figure 6. SEM images of the powders synthesized by sol-gel method after heat treatment at 800°C, 40 hrs with a) adding Bi_2O_3 first (Sol-gel B) and b) adding $RuCl_3 \cdot nH_2O$ first (Sol-gel C).

The bimodal particle size distribution, in small sub-micron and micron range, of the Bi-Ru-O compounds observed in the sample where Bi_2O_3 was added first has helped to explain why the more oxygen rich phase, $Bi_2Ru_2O_{7.3}$, was observed in such samples. As mentioned earlier, the large particles observed are likely to be the lower temperature $Bi_2Ru_2O_{7.3}$ phase. This oxygen rich phase, $Bi_2Ru_2O_{7.3}$, was expected to transform to a lower oxygen phase, $Bi_2Ru_2O_7$, when heated to a high temperature starting from 800°C (Linquett-Mailey *et al.*, 1998). However, when the particles are large, the transport of oxygen maybe limited. Therefore, the large $Bi_2Ru_2O_{7.3}$ particles were not easily transformed to $Bi_2Ru_2O_7$ while the smaller size particles did result in a mixture of the two phases. The reason why the different adding sequence of the starting precursors resulted in a different particle size distribution has to be investigated further.

4. Conclusions

A single phase bismuth ruthenate pyrochlore has successfully been synthesized in this study. It was found that the different synthesis methods resulted in different phases of powder being the desired pyrochlore, $Bi_2Ru_2O_7$ and oxygen rich $Bi_2Ru_2O_{7.3}$. RuO_2 was the commonly found secondary phase for some of the preparation routes such as the solid state reaction method. Furthermore, methods of preparation were also found to strongly affect the particle size of the powder obtained. Much finer particles in the range of 0.3-1.0 µm could be prepared via sol-gel method, while the solid state method yielded particles with larger particle size, in the range of 1-3 µm. Homogenous mixing of the starting materials was found to be crucial in obtaining the desired phase. For the sol-gel method, the adding sequence of the starting material was also found to have a strong influence on the phases obtained. Single phase $Bi_2Ru_2O_7$ was found when $RuCl_3 \cdot nH_2O$ was added before Bi_2O_3, while $Bi_2Ru_2O_{7.3}$ was also found along with $Bi_2Ru_2O_7$ when Bi_2O_3 was added prior to the starting Ru compound. $Bi_2Ru_2O_7$ along with RuO_2

were found when the metal compounds were added at the same time, probably due to inhomogeneous mixing causing some Bi loss before the complete reaction could occur. These differences in phase composition are expected to affect the electrical and catalytic properties of the materials when used as cathodes for SOFCs.

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