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 materials 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$_2$Ru$_2$O$_7$, 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 its 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$_2$O$_3$ (99.99%, Aldrich) and RuO$_2$·nH$_2$O (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
followed the experimental procedure similar to what was reported by Kahoul et al. (2001), where Bi₂O₃ and RuCl₃·nH₂O (~41 Ru%, Alfa Aesar) were used as the starting materials. A mixture of citric acid and ethylene 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 its effect on phase formation by adding the metal compounds at the same time (Sol-gel A), adding Bi₂O₃ before RuCl₃·nH₂O (Sol-gel B), and adding RuCl₃·nH₂O before Bi₂O₃ (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, NETZSCHS 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 diffraction 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 20 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 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 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 Bi₂Ru₂O₇ pyrochlore. However, small peaks corresponding to RuO₂ were also found along with the desired Bi₂Ru₂O₇. The observation of small peaks of a Ru-based secondary phase has also been reported by Takeda et al. (2000) on Bi₂Ru₂O₇ synthesized using the solid state reaction method. In an attempt to eliminate the secondary phase of RuO₂, 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 RuO₂ phase was still present. The existence of the unreacted RuO₂ phase without the remaining unreacted Bi₂O₃ in the XRD pattern might indicate a Bi loss during the synthesis. Excess Bi might be needed for the formation of a single phase Bi₂Ru₂O₇, 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 an acid/solvent solution at the same time.
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$_2$O$_3$ was dissolved in an organic solution followed by the addition of RuCl$_3$·nH$_2$O (Sol-gel B). The adding sequence was switched in the second experiment, where RuCl$_3$·nH$_2$O was added first (Sol-gel C).

It was found that RuCl$_3$·nH$_2$O could dissolve in the citric acid-ethylene glycol solution much more readily compared to Bi$_2$O$_3$. This is expected as RuCl$_3$ should have higher a polarisability compared to Bi$_2$O$_3$ 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$_2$O$_3$ shows no sign of the RuO$_2$. A mixture of Bi$_2$Ru$_2$O$_7$ and Bi$_2$Ru$_3$O$_{14}$ was found. The sample in which RuCl$_3$·nH$_2$O 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$_2$Ru$_2$O$_7$ 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 state 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...
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 Bi₂O₃ 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 Bi₄Ru₃O₁₁ phase as found via the XRD analysis.

The bimodal particle size distribution, in small sub-micron and micron range, of the Bi-Ru-O compounds observed in the sample where Bi₂O₃ was added first has helped to explain why the more oxygen rich phase, Bi₄Ru₃O₁₁, was observed in such samples. As mentioned earlier, the large particles observed are likely to be the lower temperature Bi₂RuO₂, phase. This oxygen rich phase, Bi₂RuO₂, was expected to transform to a lower oxygen phase, Bi₄Ru₃O₁₁, 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 Bi₂RuO₂ particles were not easily transformed to Bi₄Ru₃O₁₁ 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, Bi₂RuO₃, and oxygen rich Bi₄Ru₃O₁₁. RuO₂ 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 Bi₂RuO₃ was found when RuCl₃·nH₂O was added before Bi₂O₃, while Bi₄Ru₃O₁₁ was also found along with Bi₄Ru₃O₁₁ when Bi₂O₃ was added prior to the starting Ru compound. Bi₂RuO₃ along with RuO₂

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

<table>
<thead>
<tr>
<th>Calcination time</th>
<th>Crystallite Size from XRD (nm)</th>
<th>Solid state</th>
<th>Sol-gel A</th>
<th>Sol-gel B</th>
<th>Sol-gel C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 hrs</td>
<td></td>
<td>&gt;100</td>
<td>70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40 hrs</td>
<td></td>
<td>-</td>
<td>70</td>
<td>70</td>
<td>90</td>
</tr>
</tbody>
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Figure 6. SEM images of the powders synthesized by sol-gel method after heat treatment at 800°C, 40 hrs with a) adding Bi₂O₃ first (Sol-gel B) and b) adding RuCl₃·nH₂O first (Sol-gel C).
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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References


