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Easy Fabrication of Dense Ceramic Membrane for Oxygen Separation

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Abstract: A combined EDTA-citrate complexing method was developed for the easy preparation of mixed oxygen-ionic and electronic conducting dense ceramic membrane for oxygen separation. The new method takes the advantage of lower calcination temperature for phase formation, lower membrane sintering temperature and higher relative density over the standard ceramic method.

Keywords: Ceramic membrane, oxygen separation, synthesis.

During the past decade, dense-type oxygen-permeable ceramic membranes have received considerable attention both in the fields of scientific research and industrial application[1, 2]. Such membranes have mixed oxygen-ionic and electronic conductivity, and they can permeate oxygen at high temperature under an oxygen gradient without the need of outside connecting line and electrodes. Envisioned applications range from small scale oxygen pumps for medical use to large scale integrated gasification combined cycle plants. Such membranes also find application in the field of chemical processing, such as partial oxidation of hydrocarbons, *e.g.*, natural gas. Successful preparation of dense membranes, *i.e.*, free of cracks and connected-through porosity is a key technology and also a prerequisite for their high oxygen perm-selectivity and concomitant successful application.

The ceramic membranes are usually prepared by powder/pressing method. The powder quality has a significant effect on the properties of the membranes then fabricated. At present, powders of membrane materials are often prepared by standard ceramic method, which is characterized by laborious milling, high temperature treatment and regrinding. The powders thus obtained are often contaminated with one or more of the unreacted reactants and/or abrasives of the grinding media, frequently resulting in inhomogeneities and a bad sintering ability. For this reason, wet-chemical method has acquired its importance recently.

$BaBi_xCo_yFe_{1-x}O_{3-\delta}$ perovskite oxide is a new series of mixed conductors with excellent oxygen permeability[3]. However, due to the easy hydrolyzation of Bi^{3+}, it was somewhat difficult to prepare such materials by wet chemical method. In this letter, we provide a combined EDTA-citrate complexing method for the easy synthesis of the dense membranes. The preparation of $BaBi_{0.2}Co_{0.2}Fe_{0.6}O_{3-\delta}$ oxide, is described as follows. The

necessary amounts of $Ba(NO_3)_2$ and $Bi(NO_3)_2$ were first dissolved in EDTA-NH_3.H_2O solution under heating and stirring, then the calculated amounts of $Co(NO_3)_2$ and $Fe(NO_3)_3$ were added to the solution. After being stirred for a certain time, proper amount of citric acid was introduced, the mole ratio of EDTA: citric acid: total metal ions was controlled to be around 1.1:1.5:1. It was well known that EDTA exhibits strong complexing ability for almost every metal ion. The formation of EDTA complexed bismuth ion can effectively prohibit it hydrolization, furthermore, EDTA-NH_3 and citrate formed a buffering solution, so the pH value of the system was successfully sustained around 6 during the whole process. It was easy for us to obtain a clear gel without the need of adjustment the pH value during evaporating of water. The gel was heated in a hot plate at 120-150 ^oC for several hours to make a primary powder, which was then fired at various temperatures for 2 h to obtain the final product.

Figure 1. XRD diffraction pattern of $BaBi_{0.2}Co_{0.2}Fe_{0.6}O_{3-\delta}$ oxide prepared by calcining the precursor at 700^oC for 2 h.

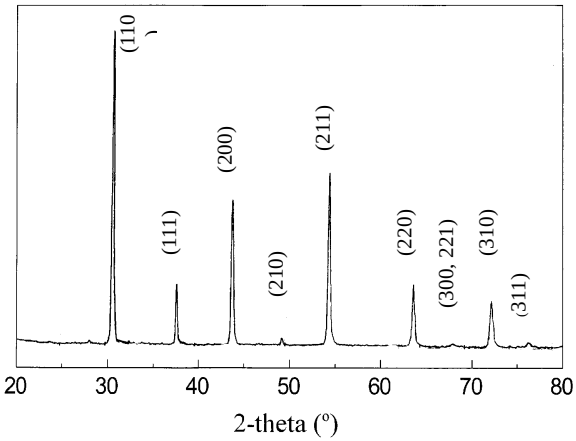
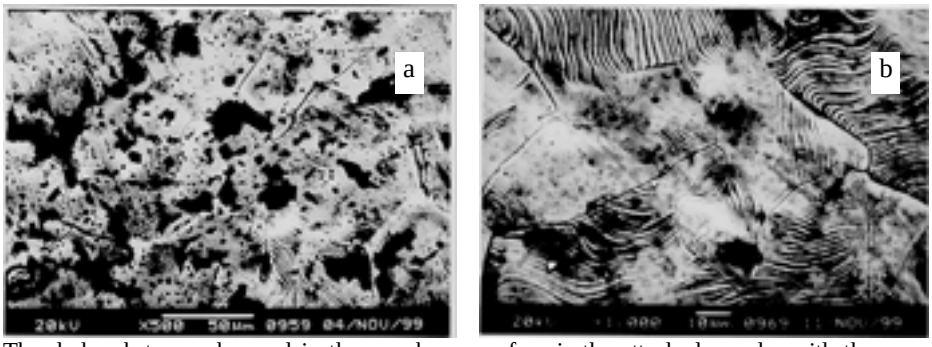


Figure 1 shows the XRD pattern of powder product calcined at 700 ^oC for 2 h. All the diffraction peaks can be indexed on the base of a cubic perovskite well, and no trace of other phases was detected. For comparison, when the standard ceramic method was used, a calcination temperature as high as 1000^oC was needed to acquire the pure phase product. It was well known that Bi_2O_3 has a high volatility, and the formation of a perovskite structure can effectively prohibit the loss of bismuth at high temperature. It seems that the most possible bismuth loss during high temperature calcination was before the formation of a perovskite structure, so low temperature synthesis of Bi-containing perovskite was needed to prohibit the bismuth loss. In this sense, the new preparation method has advantage over the standard ceramic method.

The powder was pressed into disk shape membranes. The green membrane disks were sintered at 1060 ^oC for 5 h. **Figure 2** shows the SEM images of the membrane surface and the cross section. The whole cross section of the membrane was carefully examined by SEM, no pinhole or closed hole was observed. It demonstrated that the

membrane was densified. For green membrane whose material powder was prepared by standard ceramic method, a sintering as high as 1150 ^{o}C was needed. The membrane disks prepared by the new method have much higher strength than that prepared by ceramic method. It was much easier for us to make a gas-tight reactor assembly by using the membrane disks prepared by the new method. Much less leaked nitrogen concentration was detected in the eluted gas during oxygen permeation measurement for the membrane reactor using the new method prepared disks, which demonstrated the membranes prepared by the new method were more dense.

Figure 2. SEM photograph of $BaBi_{0.2}Co_{0.2}Fe_{0.6}O_{3-\delta}$ membrane prepared by the new method sintered at 1060^{o}C for 3h, a: unpolished surface, b: cross section



*: The dark substance observed in the membrane surface is the attached powder with the same composition as the membrane, it is not hole or crack.

Figure 3. Mole ratio of metal ion across the cross-section of a sintered membrane disk (1060 ^{o}C) with a thickness of 1.2 mm measured from EDS

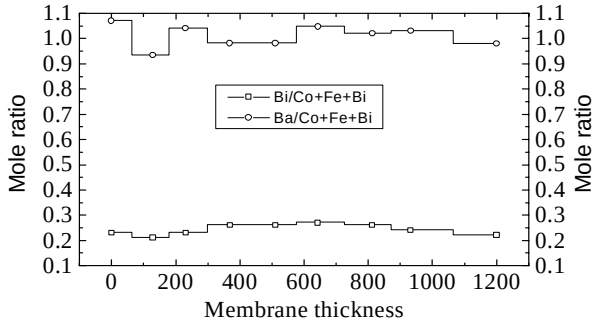
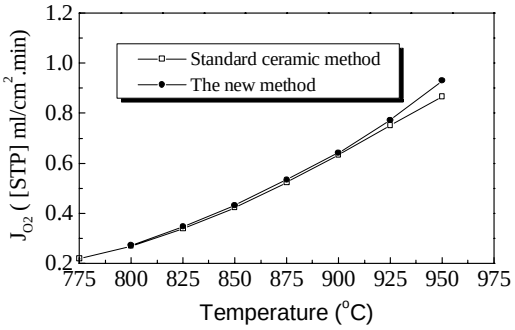


Figure 3 show the Mole ratio of metal ion across the cross-section of a sintered membrane disk with a thickness of 1.2 mm, measured from EDS. Within the error permission, It was reasonably believed that the whole membrane formed a homogeneous $BaBi_{0.2}Co_{0.2}Fe_{0.6}O_{3-\delta}$ solid solution.

The oxygen permeation measurement was made for $BaBi_{0.2}Co_{0.2}Fe_{0.6}O_{3-\delta}$ membranes with a thickness of 1.2 mm prepared by combined EDTA-citrate complexing method and standard ceramic method. The results were shown in **Figure 4**, during the

experiment, ambient air was used at the feed gas and a high-purity helium (O_2/He<4 ppm), at a flow rate of 30 ml/min, as a sweep gas. It showed that the oxygen permeation flux of the membrane prepared by the new method was modestly higher than that prepared by a standard ceramic method, which might be due to the higher relative density of the former than the later.

Figure 4. Oxygen permeation flux through $BaBi_{0.2}Co_{0.2}Fe_{0.6}O_{3-\delta}$ membranes prepared from different methods, d=1.50mm, ambient air versus flowing helium (30ml/min)



The new preparation method was not only suitable for the preparation of Bi-based materials, our results testified that it was also suitable for preparation of Zr-based, Ti-based Ga-based and $Ba_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ mixed conducting oxygen-permeable materials at relatively low temperature. The corresponding sintered membranes then obtained have improved mechanical strengthen and relative density. Further investigation such as the pyrolysis mechanism from precursor to final product is just underway.

Acknowledgments

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