JOURNAL OF MATERIALS SCIENCE **39** (2004) 707–709

Effect of hydrolysis rates on the morphology of sol-gel derived $SrFeCo_{0.5}O_x$ powder

I. R. ABOTHU, W. JIN*
Institute of Materials Research and Engineering, National University of Singapore, 3 Research Link, Singapore 117602, Singapore
E-mail: wanqin.jin@uni-koeln.de

R. WANG
Environmental Technology Institute, 18 Nanyang Drive, Singapore 637723, Singapore

T.-S. CHUNG‡
Department of Chemical & Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore
E-mail: chencts@nus.edu.sg

Mixed-conducting (electronic and ionic) oxides with high oxygen ion conductivity have been investigated extensively for ion transport membranes used in the separation of oxygen from air and the conversion of natural gas to syngas [1]. $SrFeCo_{0.5}O_x$ (SFC) is considered to be a technologically important material due to its high oxygen permeability as well as structural and chemical stability in reducing atmospheres [2–5]. Conventionally, the SFC oxide is synthesized by the solid-state reaction of the constituent metal oxides [2–7], but this method often requires higher sintering temperature and longer heating schedule, and thus leads to poor chemical homogeneity and large particle size. Recent research [8, 9] has shown that the grain microstructure strongly influenced the oxygen permeation flux for mixed-conducting membranes and the oxygen flux increased considerably with decrease in grain size. The microstructure of a sintered material such as grain morphology (size and shape) depends mainly on the synthesis methods and conditions used.

The sol-gel process is a versatile technique for the synthesis of sub-micron sized ceramic powders of high purity and homogeneity [10, 11]. This sol-gel processing involves hydrolysis and condensation of metal alkoxides. By controlling some variables such as precursor, reaction temperature, hydrolysis and condensation, and catalyst, it is possible to change the microstructure of gel and, as a consequence, of the resulting ceramic. In our previous study [12], we have used the sol-gel process to synthesize SCF powders using alkoxide precursors. However, the effect of the preparation conditions on the morphology has not been studied yet. Therefore, this letter deals with the effect of hydrolysis rates on the morphology of the as-prepared powders.

To synthesize SFC powder, strontium granule (99%), iron (III) acetylacetonate $[CH_3COCH{=}C(O{-})CH_3]_3Fe$ (97%), and cobalt (III) acetylacetonate $[CH_3COCH{=}C(O{-})CH_3]_3Co$ (98%) (all Aldrich Company) were used as starting materials. The scheme of preparing SCF powder has been described elsewhere [12]. Initially, a stoichiometric amount of strontium granules was dissolved in 2-methoxy ethanol (2-MOE) as a solvent and refluxed at 125 °C for 8 h in argon atmosphere. This resultant strontium precursor solution was cooled to room temperature and then added with the required amount of iron (III) acetylacetonate and 2-MOE and refluxed again at 125 °C for 8 h in argon atmosphere. The resultant Sr-Fe double alkoxide solution was then cooled to room temperature and added with cobalt acetylacetonate along with 2-MOE and finally refluxed at 125 °C for 12 h in argon atmosphere to obtain a clear Sr-Fe-Co precursor solution. The resultant Sr-Fe-Co complex solution was cooled to room temperature and adjusted the pH value. The solution was hydrolyzed at three different rates by adding different amount of water diluted with 2-MOE (1:4 ratio of water to 2-MOE) to form homogenous SFC gels. The three amounts of water are below: first is 8 times stoichiometric water value, second 6 times stoichiometric water value, and third 4 times stoichiometric water value. These hydrolysis rates are designated as fast hydrolysis (FH), normal hydrolysis (NH) and slow hydrolysis (SH). The obtained gels were dried at 60 °C in air oven. The dried gels were crushed into powders with a mortar and pestle, and then calcined at 850 °C in air for 4 h to produce the final SFC powders.

Fig. 1 shows the X-ray diffraction patterns of the SFC powders synthesized at three different hydrolysis rates, using a Philips X'Pert diffractometer (Cu K_α radiation at a scan rate of $3\,^\circ 2\theta$/min and 45 kV/40 mA). The powders obtained from the three different hydrolysis rates consist of a dominant perovskite phase $SrFe_{1-x}Co_xO_{3-\delta}$, an amount of layer phase $Sr_4Fe_{6-x}Co_xO_{13-\delta}$ and a trace spinel phase $Co_{1-x}Fe_xO_4$, however, the ratios of three crystal phases

---

Present address: Institut für Physikalische Chemie der Universität zu Köln, Luxemburger, str. 116, 50939 Köln, Germany.
‡Author to whom all correspondence should be addressed.

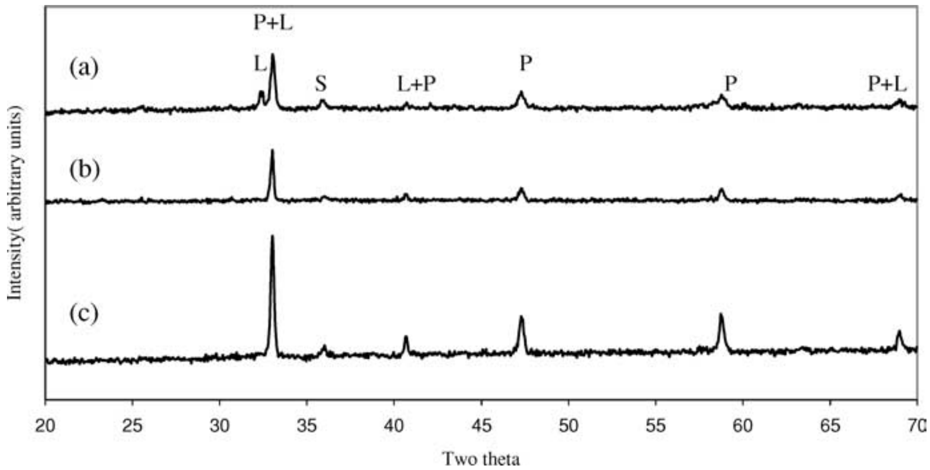

Figure 1 X-ray diffraction patterns of SFC powders synthesized at three hydrolysis rates. P: perovskite phase; L: perovskite-related layered phase; S: spinal phase: (a) FH, (b) NH, and (c) SH.

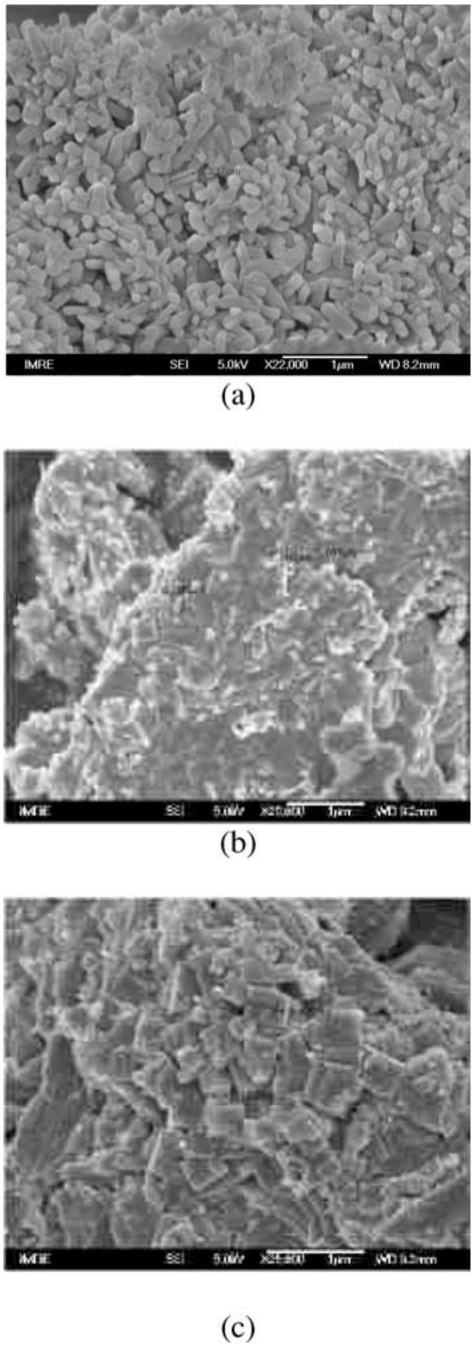

Figure 2 SEM images of the synthesized powders calcined at 850 °C in air: (a) fast hydrolysis, (b) normal hydrolysis, and (c) slow hydrolysis.

are different. This result is in consistent with observation of Kim *et al.* [13], indicating that the amount of the perovskite phase in the composition of SFC depends on the preparation conditions in the sol-gel processing.

The morphologies of three kinds of powders synthesized at three different hydrolysis rates were studied using a scanning electron microscopy (Jeol JSM-6700F SEM, with accelerating voltage 5 KV, emission current 10 μA). As shown in Fig. 2, the powder obtained from fast hydrolysis exhibits rod-shape morphology, the powder from slow hydrolysis cubic morphology, and whereas the powder from normal hydrolysis is of irregular morphology. These results are in agreement with the fact that the hydrolysis rate is very important in determining the particle morphology [11, 14]. The average particle sizes estimated from the SEM images in all cases are about 300 nm. The agglomerate size distributions of the synthesized powders were examined on a N4 Plus Submicro Particle Sizer (Coulter). As shown in Fig. 3, the agglomerate size distributions are narrow in all cases, and the maximum size of the agglomerates as seen from the agglomerate size distribution curve was 20 μm in

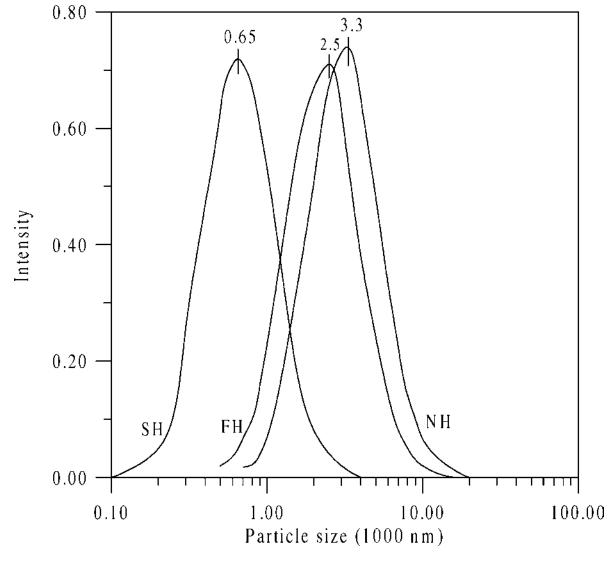

Figure 3 Agglomerate size distribution of the synthesized powders. FH: fast hydrolysis; NH: normal hydrolysis; SH: slow hydrolysis.

the normal hydrolysis case. The average agglomerate particle sizes are 2.5 μm for fast hydrolysis, 3.3 μm for normal hydrolysis and 0.7 μm for slow hydrolysis, respectively. Compared with the conventional solid-state reaction method, which requires the milling, grinding and prolonged calcination at high temperatures [3–5], the sol-gel processing possesses the advantages of low temperature calcinations, sub-micron particle size and a small degree of agglomeration of particles.

In summary, we successfully synthesized sub-micron size SFC powders via a sol-gel processing from metal alkoxides. The hydrolysis rates influenced significantly the morphology of the SFC powders. The results indicated that the slow or fast hydrolysis fast rate is beneficial to form SFC powders of 300 nm average particle size with different regular morphology.

References

1. P. N. DYER, R. E. RECHARDS, S. L. RUSSEK and D. M. TAYLOR, *Solid State Ionics* **134** (2000) 21.
2. W. LIU, G. G. ZHANG, S. XIE, C. S. CHEN, G. Y. MENG and D. K. PENG, *ibid.* **135** (2000) 727.
3. B. MA and U. BALACHANDRAN, *Mater. Reas. Bull.* **33** (1997) 223.
4. U. BALACHANDRAN, J. T. DUSEK, P. S. MAIYA, B. MA, R. L. MIEVILLE, M. S. KLEEFISCH and C. A. UDOVICH, *Catalysis Today* **36** (1997) 265.
5. U. BALACHANDRAN, J. T. DUSEK, R. L. MIEVILLE, R. B. POEPPEL, M. S. KLEEFISCH, S. PEI, T. P. KOBYLINSKI, C. A. UDOVICH and A. C. BOSE, *Appl. Catal., A: Gen.* **133** (1995) 19.
6. B. J. MITCHELL, J. W. RICHARDSON, C. D. MURPHY, B. MA, U. BALACHANDRAN, J. P. HODGES and J. D. JORGENSEN, *Mater. Res. Bull.* **35** (2000) 491.
7. B. MA, U. BALACHANDRAN, J.-H. PARK and C. U. SEGRE, *J. Electrochem. Soc.* **143** (1996) 1736.
8. X. QI, Y. S. LIN and S. L. SWARTZ, *Ind. Eng. Chem. Res.* **39** (2000) 646.
9. K. ZHANG, Y. L. YANG, D. PONNUSAMY, A. J. JACOBSON and K. SALAMA, *J. Mater. Sci.* **34** (1999) 1367.
10. S. KOMARNENI, I. R. ABOTHU and A. V. PRASADARDO, *J. Sol-Gel Sci. Tech.* **15** (1999) 261.
11. T. FUKUI, C. SAKURAI and M. OKUYAMA, *J. Mater. Sci.* **32** (1997) 189.
12. WANQIN JIN, I. R. ABOTHU, RONG WANG and TAI-SHUNG CHUNG, *Ind. Eng. Chem. Res.* 2002, in press.
13. S. KIM, Y. L. YANG, R. CHRISTOFFERSEN and A. J. JACOBSON, *Solid State Ionics* **109** (1998) 187.
14. M. J. HAMPDEN-SMITH, T. A. WARK, C. J. BRINKER, *Coordin. Chem. Rev.* **112** (1992) 81.

Received 12 September 2002
and accepted 21 August 2003