Continuous Hydrothermal Flow Syntheses of Nanosized Energy Materials Used in Solid Oxide Fuel Cells

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ABSTRACT

Nanosized co-precipitates of lanthanum and nickel hydroxides were prepared inside a continuous hydrothermal flow system (CHFS) that uses a supercritical water feed maintained at 450 °C and 24.1 MPa. Co-crystallite with a 4:3 La/Ni ratio was subsequently given a single heat treatment in air for 6 h at 1075 °C, resulting in the direct synthesis of phase pure La₄Ni₃O₁₀. As La₄Ni₃O₁₀ is normally made using very time consuming muti-step processing routes (over several days), the successful method employed herein, could have significant implications for the more rapid synthesis and isolation of other complex or "difficult to make" materials. Electrical conductivity measurement on this material revealed a significant improvement by comparing to that made via more conventional routes, indicating the advantage of use of nanosized materials. Yttria stabilized zirconia (YSZ) with the particle size 4.97 ± 0.84 nm were also prepared by using the CHFS method.

Keywords: La₄Ni₃O₁₀, supercritical water, hydrothermal, solid oxide fuel cell, yttria stabilized zirconia.

1 INTRODUCTION

The (La-Ni-O) system forms a series of compounds with the general formula Lan+1NinO3n+1, whose structures are described by stacking along the c axis of n finite LaNiO₃ perovskite layers separated by LaO rocksalt-like layers[1] and are similar to the Ruddlesden-Popper series[2]. The higher order phase, $La_4Ni_3O_{10}$ (n=3) presenting high metallic and oxygen ionic conductivity, could be used as cathode in electrochemical devices such as solid oxide fuel cell (SOFC)[3]. The multilayered RP nickelates was first synthesized by Wold and Arnott in 1959[4], when the authors observed an unidentifiable phase with a La/Ni ratio between that of LaNiO₃ and La₂NiO₄. The phase pure La₄Ni₃O₁₀ was first synthesized by Sreedhar et al. in 1993[5] and then followed by Zhang and Greenblatt in 1994.[6] Several modified synthesis methods were carried out by Carvalho et al. in 1997[7], as well as by Amow et al. in 2006.[3] However, these alternative methods all suffer the same limitation, where they all required complicated homogenization procedures with extremely long processing time. For example, the synthesis of $La_4Ni_3O_{10}$ by Zhang and Greenbaltt typically involved heating the component metal oxide powders at 1100 °C for 4-5 days with intermittent regrinding and reheating steps. As the as-prepared powder was subjected to such long time calcined, large particles were obtained as expect, leading to extremely low surface area and comparatively high sintering temperature. This then limits their application in intermediate temperature solid oxide fuel cell (IT-SOFC).

Yttria stabilized zirconia (YSZ) is well known to be the most frequently used electrolyte material in SOFCs. In the literature, several different synthetic methods have been used to make the YSZ compounds, including solid state routes,[8-10] dip coating routes,[11] co-precipitation routes,[12;13] etc. Most of these techniques, however, required multiple and complex steps, lengthy processing times and are energy intensive and uncontrollable. Moreover, the particles manufactured by these methods were normally inhomogeity and with poor reactivity

As such, lower temperature synthesis methods, which can produce small and highly crystalline homogenously doped materials, are of interest. Preferably, these methods should also be faster, utilizing relatively few steps. Continuous hydrothermal flow synthesis (CHFS) methods are increasingly being applied in the direct or more efficient manufacture of important technological nanoceramics or co-crystallites. By variation in the CHFS process conditions, some control over particle properties can be achieved and complex nanomaterials can be manufactured under relatively mild temperatures in a crystalline form.

2 EXPERIMENTAL

2.1 Materials

2.2 General Syntheses

This method, hereby referred to as "Hydrothermal Flow Co-precipitation" (HFC) method (Figure 1) produced a range of YSZ and lanthanum nickel hydroxides cocrystallites. In the case of synthesis of 8YSZ, yttrium nitrate hexahydrate (0.016 M) and zirconyl nitrate hydrate (0.092 M) and in the case of synthesis of La₄Ni₃O₁₀, lanthanum nitrate hexahydrate (0.1M) and nickel nitrate hexahydrate (0.75 M) were both dissolved in 500 ml of DI water. 10 vol% H₂O₂ was added and the solution was then pumped into the CHFS system, premixed with 1 M KOH solution (at point T) and then brought to meet a superheated water feed at 450 °C. Additionally, a small 5 cm 200 W band heater set at 450 °C was used at the reactor (R). The suspension from the hydrothermal flow reactor was then collected, centrifuged (4500 rpm for 3 minutes) and cleaned. The wet solids were freeze dried.



Figure 1 Scheme of the three-pump continuous hydrothermal flow synthesis system used for the syntheses of nanoparticles. Key: P = pump, C = cooling, F = filter, B = backpressure regulator, R = reactor, T = stainless steel "Tee" piece mixer and H = heater.

2.3 Characterizations

10 M Ω deionised (DI) water from a USF Elga water deionizer was used throughout. Ultrasonication was carried out in a VWR USC 100T ultrasonic bath at a power setting of 30 W. Gilson model 305 pumps were used in the continuous hydrothermal flow synthesis system. Freezedrying was performed using a Vitris Advantage Freeze Dryer, Model 2.0 ES, supplied by BioPharma; the solids were frozen in liquid nitrogen and then freeze dried for 22.5 h at 1.33×10^{-4} MPa. BET surface area measurements (multipoint) were performed on a Micromeritics Gemini analyzer. All powders were degassed at 80 °C for 2 h prior to BET analysis. Particle size and morphology were investigated using a JEOL 2010 Transmission Electron Microscope (TEM) (200 kV accelerating voltage) and a Philips XL 20 Scanning Electron Microscope (SEM) (10 -20 kV accelerating voltage). Nicolet Almega Dispersive Raman Spectrometer (532 nm) was used in the wavenumber range 200-700 cm⁻¹ averaging 20 scans for 20 seconds each. The spark plasma sintering (SPS) (HPD 25/1) was performed in vacuum using cylindrical graphite dies. The uniaxial pressure was used at 100 MPa with a heating rate of 100 °C/min between 450 °C and 1100 °C and a cooling rate of 50 °C /min down to 450 °C.

X-ray powder diffraction studies were conducted on a Siemens D5000 X-ray diffractometer using Cu-Ka radiation ($\lambda = 0.15418$ nm). Data were collected over the 20 range 5-110 ° with a step size of 0.02 ° and a count time of 10 s per step. The diffraction patterns were analyzed by Rietveld refinement using GSAS[14]. The electrode performance was measured by a 1260 Solartron impedance spectroscopy. Data were collected from RT to 1000 °C. The amplitude of the applied potential signal was 50 mV.

3 RESULTS AND DISCUSSIONS

3.1 Synthesis of La₄Ni₃O₁₀ Material

The as-crystallite made in the hydrothermal flow synthesis system prior to heat treatment was characterized by XRD, revealing a mixture of lanthanum and nickel hydroxides as expected (good match to JCPDS pattern 36-148 for and pattern 14-0117, respectively]. Particle morphology analysed by transmission electron microscopy (TEM) revealed hexagonal plate like nickel hydroxide particles of *ca.* 40 nm diameter that were intimately mixed (surrounded) with 10 nm thick lanthanum hydroxide needles with the length of *ca.* 40X20 nm (Figure 2).



Figure 2 Transmission electron micrograph of as-crystallite made in the hydrothermal flow system at 450 $^{\circ}$ C and 24.1 MPa (bar = 20 nm).

Past literature [5] suggested that after several days single step heating and regrinding of a 4:3 ratio of lanthanum and nickel oxide powders at temperature of 1075 °C, phase pure La₄Ni₃O₁₀ was obtained. On the basis of this point, our as-prepared co-crystallites were directly subjected to 1 h (figure 3a(i)) heat treatment in air at 1075 °C, yielding a mixture of La₄Ni₃O₁₀ and La₂NiO₄. Further increasing the heating time to 6 h, phase pure La₄Ni₃O₁₀ was obtained (figure 3a(ii)). The result obtained herein is significant, as to our knowledge, this material has never been directly synthesized from any similar mixture in a single heat treatment at such short time (only 6 h) previously. Scanning Electron Microscope analysis on the La₄Ni₃O₁₀ product revealed the agglomerates of rounded particles with the size at *ca.* 300 nm (figure 3b). Peak indexation and unit-cell determination were performed by using Rietveld refinement in GSAS software, leading to the identification of La₄Ni₃O₁₀ as being *Fmmm* with the unit cell parameters calculated at a = 0.541 nm, b = 0.546 nm and c = 2.802 nm.



Figure 3 (a) X-ray diffraction patterns of the products made by heat treatment (1075 °C in air) of metal hydroxide cocrystallized mixture with a 4:3 La:Ni molar ratio, for (i) 1 h and (ii) 6 h and (b) Scanning electron microscope image of La₄Ni₃O₁₀ made by a single heat treatment at 1075 °C for 6 h in air (bar = 1 micrometer).

To verify the suitability of this material for SOFC cathode use, impedance measurement was carried out. The normalized area-specific conductivity was shown in figure 4. Measurements were performed under heating and cooling conditions, which was repeated once herein. The RT conductivity was measured at *ca* 500 S.cm², revealing a remarkable improvement by comparing to conventional synthesized materials (*ca.* 200 S.cm²).[3] Further increasing the testing temperature to 800 °C, the material showed metallic behavior of temperature dependence as expected but the conductivity at high temperature was still comparatively high (*ca.* 250 S.cm² at 800 °C). This is assumed due to the presence of very small grain size after the material was sintered by using spark plasma sintering

(SPS) at 1000 °C for 3 min, resulting in high amounts of grain boundaries, facilitating the electrons conducting. The results obtained herein revealed the advantage of use of nanosized materials as energy materials. It was observed that heating and cooling process did not significantly change the electrical properties, indicating the high durability of this material synthesized by the CHFS method.



Figure 4 Electrical conductivity versus temperature for $La_4Ni_3O_{10}$ material, from RT to 800 °C. (2) = second time heating and cooling.

3.2 Synthesis of 8YSZ

The as-produced co-crystallite of 8YSZ particles characterized by X-ray powder diffraction showed a good match with cubic ZrO_2 phase (JCPDS pattern 30-1468(*)) (Figure 5a), indicating the formation of Y_2O_3 -ZrO₂ solid solution.



Figure 5 (a) X-ray powder diffraction and (b) Raman spectra of 8YSZ made by using continuous hydrothermal flow synthesis method at 450 °C and 24.1 MPa.

XRD data for the as-crystallized sample showed only broad peaks, making phase assignments difficult.

Consequently, Raman spectroscopy appears to be more discriminating as expected and can be considered as an effective method for structure characterization. Figure 5b illustrates the Raman spectra of 8YSZ materials. Only one prominent peak was observed at *ca*. 580 cm⁻¹ for 8YSZ spectra. This peak is quite strong but broad and asymmetrical in nature, which is in agreement with the result obtained by Ghosh et al. [15], indicating that cubic phase was obtained. Humps at *ca*. 343 cm⁻¹ and 251 cm⁻¹ observed herein have also been reported by Phillipi and Mazdiyasni in stabilized cubic zirconia [16].



Figure 6 TEM picture of 8YSZ (bar = 10 nm) made by using continuous hydrothermal flow synthesis method at 450 °C and 24.1 MPa.

Particle morphology was investigated by using TEM (figure 6), revealing the presence of rounded particles with particle size at 4.97 ± 0.84 nm (Range 6.26 - 3.16 nm based on 50 particles). BET surface area was measured at $160.6 \text{ m}^2\text{g}^{-1}$, which is unsurprising giving such small particle size. To verify the suitability of this material as electrolyte for SOFC use, oxygen diffusion conductivity measurement is necessary to be carried out, which will be reported in due course.

4 CONCLUSIONS

We successfully achieved our initial objectives to synthesize the target phases of La₄Ni₃O₁₀ and 8YSZ using a direct and efficient method. Particularly, for the synthesis of La₄Ni₃O₁₀, greater intimacy of the two component metal hydroxides (i.e. in the HFC route) led to a more facile synthesis compared to more conventional synthesis methods. Under the experimental conditions employed, our target material was obtained via single heat treatments in a furnace from "co-crystallized" reagents prepared using the continuous hydrothermal flow synthesis system at 1075 °C for only 6 h. This result is significant, as the higher order RP phase (n = 3) is usually synthesized through several days of multiple regrinding and heating. In this regard, our development of a direct route to heterometallic oxides, some of which are conventionally laborious to make, may allow high throughput approaches to be developed for oxide materials discovery. We are currently investigating this very concept, the results of which will be reported in due course.

5 ACKNOWLEDGEMENT

EPSRC is thanked for funding the "High Throughput Inorganic Nanomaterials Discovery" project [EPSRC Grant Reference: EP/D038499/1] (JAD, SK) and an industrial case award (PB). The School of Engineering and Material Sciences at QMUL is thanked for a scholarship (XW). Johnson Matthey is thanked for supporting the industrial case award (PB). M. Phillips, V. Ford, J. Caulfield, M. Willis and Z. Luklinska are thanked for technical assistance.

REFERENCES

- (1) Lacorre, P. Journal of Solid State Chemistry **1992**, 97, 495-500.
- (2) Ruddlesden, S. N.; Popper, P. Acta crystallographica **1958**, 11, 54.
- (3) Amow, G.; Davidson, I. J.; Skinner, S. J. Solid State Ionics 2006, 177, 1205-1210.
- (4) Wold, A.; Arnott, R. J. Journal of phys.Chem.Solids **1959**, 9, 1959.
- (5) Sreedhar, K.; McElfresh, M.; Perry, D.; Kim, D.; Metcalf, P.; Honig, J. M. Journal of Solid State Chemistry **1994**, 110, 208-215.
- (6) Zhang, Z.; Greenblatt, M. Journal of Solid State Chemistry **1995**, 117, 236-246.
- (7) Carvalho, M. D.; Costa, F. M. A.; Pereira, I. D. S.; Wattiaux, A.; Bassat, J. M.; Grenier, J. C.; Pouchard, M. Journal of Materials Chemistry 1997, 7, 2107-2111.
- (8) Jiang, Y.; Bhide, S. V.; Virkar, A. V. Journal of Solid State Chemistry 2001, 157, 149-159.
- (9) Dodd, A. C.; McCormick, P. G. Journal of the European Ceramic Society **2002**, 22, 1823-1829.
- (10) Dodd, A. C.; McCormick, P. G. Acta Materialia **2001**, 49, 4215-4220.
- (11) Lenormand, P.; Caravaca, D.; Laberty-Robert, C.; Ansart, F. Journal of the European Ceramic Society **2005**, 25, 2643-2646.
- (12) Xin, X.; Lu, Z.; Ding, Z.; Huang, X.; Liu, Z.; Sha, X.; Zhang, Y.; Su, W. Journal of Alloys and Compounds **2006**, 425, 69-75.
- (13) Oliveira, A. P.; Torem, M. L. Powder Technology 2001, 119, 181-193.
- (14) Larson AC; Von Dreele RB Los alamos national laboratory report LAUR **1986**, 8, 748.
- (15) Ghosh, A.; Suri, A. K.; Pandey, M.; Thomas, S.; Rama Mohan, T. R.; Rao, B. T. Materials Letters 2006, 60, 1170-1173.
- (16) Phillipp, C. M.; Mazdiyas, K. S. Journal of the American Ceramic Society **1971**, 54, 254-&.