Synthesis and characterization of bimetallic Ni–Cu particles

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Abstract

Bimetallic Ni–Cu particles were synthesized from either suspensions of nickel carbonate and copper carbonate, and solutions of nickel nitrate and copper nitrate in ethylene glycol which acts both as solvent and reducing agent. The nature and composition of the powders depend on both the reaction temperature and time, and the reactants. Using the carbonates, bimetallic Ni–Cu powders composed of a nickel-rich and a copper-rich solid solution were obtained after 39 h at 140°C. Increasing the reaction temperature to 190°C gives a Ni–Cu powder composed of a copper-rich solid solution and nickel. Particles obtained under these conditions, however, are polydisperse. The nitrate solution gave bimetallic Ni–Cu particles with a narrow size distribution of about 140 nm after 4 h of reaction at 196°C. These particles are made of a copper core and a nickel shell. The mechanism of bimetallic particle formation is controlled by the solubility of the reactants, the formation of intermediate metal glycolates and Cu_2O, and the required reduction temperature.
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1. Introduction

Powders of nickel and copper are widely used in numerous applications because they possess good catalytic, electronic and magnetic properties. Ni powders, for example, have been used in catalysis for the direct cracking of methane [1] whereas CeO_2-supported copper catalysts have been tested for NO reduction [2]. The influence of aggregation on the magnetic properties of Ni nanoparticles synthesized by hydrogen reduction [3] and the magneto-resistance of Ni-based thick films [4] have also been investigated. Nickel [5] and copper [6,7] powders are extensively used as the active anode material in solid oxide fuel cells.

When a metal is associated with another metal in bimetallic or alloy form, the properties of the resulting material can be enhanced with respect to those of the pure metals. This is the case for Ni-based bimetallic particles containing copper, which exhibit better catalytic activity [8] and selectivity [9] than monometallic nickel. To improve the properties of pure Ni and Cu powders, several methods have been proposed for the preparation of bimetallic and alloyed Ni–Cu particles. Reduction of a mixture of nickel and copper compounds under hydrogen has been used to prepare Ni–Cu–Al [10] and Ni–Cu/Al_2O_3 [11] catalysts, and Ni–Cu alloys [12]. Evaporation of a Ni–Cu alloy and co-condensation with organic solvents gives bimetallic Ni–Cu colloids [13]. Mörke et al. [14] synthesized Ni–Cu alloy particles with a nominal ratio of 60:40 on SnO_2 and characterized them by ferromagnetic resonance. Bimetallic and alloy powders containing Ni or Cu have also been synthesized using the polyol process, a well-known and simple method to prepare metal powders of uniform particle size and shape under controlled conditions [15]. Both Co–Ni and Fe–Ni particles have been prepared by Viau et al. [16], while Chow et al. [17] implemented successfully the polyol process to the synthesis of nanocrystalline Co–Cu powders to study their magnetic properties. Also following the polyol principles, Lu et al. [18] synthesized a PVP-protected Cu–Pd alloy with a high copper content and characterized it by surface-enhanced Raman scattering.

The polyol process involves the reduction of a metallic cation by EG leading to the metallic powder. Besides, the oxidation products of EG depend largely on the synthesis conditions, mostly on the temperature.

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Previous works [19] identified diacetyl as the main product when the synthesis is carried out around the boiling point of EG (196°C) for the synthesis of Cobalt or Nickel. At lower temperature synthesis (180°C) for Copper or Silver, a mixture of acetic acid, glycolic acid or glycol aldehyde was detected [20].

In this paper we present results on the synthesis of Ni–Cu bimetallic powders (80:20 molar ratio) using carbonates and nitrates of nickel and copper, and ethylene glycol as solvent and reducing agent exclusively showing the influence of the experimental conditions on the final powders. Bimetallic Ni–Cu powders were characterized by X-ray diffraction, electron diffraction, and scanning and transmission electron microscopy coupled with energy dispersion X-ray for microanalysis.

2. Experimental

2.1. Materials

With the exception of nickel carbonate, all chemicals used in this research work were reagent grade. Copper nitrate ($Cu(NO_3)_2 \cdot 3\ H_2O$, Prolabo), nickel nitrate ($Ni(NO_3)_2 \cdot 6\ H_2O$, Merck), nickel carbonate (Outokumpu), and copper carbonate (Prolabo) were used as source of metal. Ethylene glycol and di-ethylene glycol (Prolabo) served as solvent and reducing agent. Polyvinyl pyrrolidone (PVP) K-15 (Aldrich, MW 10 000) was used as protective agent.

2.2. Methods

The required amount of nickel and copper compounds to produce bimetallic Ni–Cu (80:20 mole ratio) particles was mixed with 75 mL ethylene glycol (Prolabo) at room temperature in a four-neck round flask under magnetic agitation. Then, the system was heated to the required temperature using a heating mantle connected to an Eurotherm regulator. Because carbonate compounds are insoluble in ethylene glycol at room temperature, they were ground in an agate mortar to reduce the particle size and aid the dissolution process. When PVP was used, it was added at room temperature. At the end of the reaction time, the solids obtained were separated from the liquid by centrifugation, washed with acetone, and dried in air.

2.3. Characterization

Bimetallic Ni–Cu powders were characterized by X-ray diffraction with a Philips PW 1710 diffractometer using $CuK\alpha$ radiation ($\lambda = 1.5418$ Å) and a diffracted beam monochromator. Diffraction data were collected at a rate of $2\theta = 0.02°/1.2$ s. Si (NIST, srm 640b) was added to the sample as a reference. Powder X-ray

diffraction patterns were computer processed for peak deconvolution using the Diffrac AT software, and structural parameters were calculated using an in-house made software. The calculated parameters were used to determine the composition of the phase from Vegards's law.

Scanning electron microscopy (SEM) was performed with a Philips XL FEG30 apparatus coupled with an Oxford Link ISIS energy dispersion X-ray (EDX) for microanalysis. Each sample was observed on a carbon tab in order to minimize the EDX Cu contribution of the sample holder. Transmission electron microscopy (TEM) was performed with a JEOL 2010 microscope coupled with an Oxford microanalysis device. The particle sizes were measured from the SEM or TEM micrographs. For EDX microanalysis with TEM, samples were deposited on Al grids covered with carbon, and a beryllium sample holder was used to avoid EDX Cu contribution from other parts of the sample.

3. Results and discussion

3.1. Synthesis from copper and nickel carbonate

The reduction process appears to be sensitive either to the time and temperature, but mostly to the nature of the metallic salt. From the carbonates, the reduction remains quite difficult. The increase in time does not compensate the temperature effect.

After 39 h of reaction at 140°C, a mixture of nickel and copper carbonates (80:20 ratio) dispersed in EG was found to produce either a copper-rich Ni–Cu solid solution and a Ni–Cu nickel-rich solid solution. The X-ray diffraction pattern of this powder is presented in Fig. 1. The copper-rich solid solution is characterized by three well defined reflections whose positions are slightly shifted from those of pure Copper (JCPDS file No. 04-0836) towards the Ni reflections. Its cell parameter was calculated to have a value of 3.602(2) Å, which differs from that of pure copper: $a = 3.6150$ Å (JCPDS file No. 04-0836). According to Vegard's law, the calculated value of the cell parameter would correspond to a $Ni_{16}Cu_{84}$ composition. The cell parameter of two Ni–Cu alloys reported in the JCPDS files are also close to that of the Ni–Cu solid solution obtained in this research work. They are $a = 3.5934$ Å for $Ni_{19}Cu_{81}$ (file 47-1406) and $a = 3.595$ Å for $Ni_{21}Cu_{79}$ (file 09-0205). On the other hand, the other three peaks are slightly shifted with respect to the reflections of pure Ni, then characterizing the nickel-rich solid solution. According to the same calculations, the cell parameter ($a = 3.535(2)$ Å) corresponds to the $Ni_{86}Cu_{14}$ composition. No metallic nickel was observed at all. Fig. 1 still shows a broad band at $2\theta = 36°$ indicating the presence of raw metal carbonates. Also, because the final black
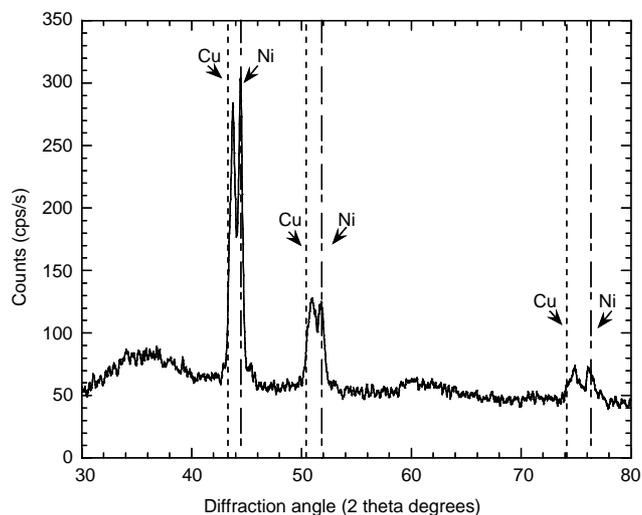
Fig. 1. Powder X-ray diffraction patterns of bimetallic Ni–Cu powders obtained at 140°C from 0.5 g NiCO₃ and 0.25 g CuCO₃ in 75 mL ethylene glycol after 39 h of reaction.

Fig. 2. (a) Powder X-ray diffraction pattern of a bimetallic Ni–Cu powder obtained at 190°C from 0.5 g NiCO₃ and 0.25 g CuCO₃ in 75 mL ethylene glycol. (b) SEM micrograph of the corresponding powder.

powder contains a green solid, it is clear that the reactants do not dissolve completely even after 39 h of reaction at 140°C.

After 6 h of reaction only, the copper-rich solid solution $Ni_{18}Cu_{82}$ which is very close in composition to the one described after 39 h, was formed already whereas the nickel-rich one was not clearly. The diffraction peaks of the former which present high intensities, indicate that dissolved Cu(II) species are easier to reduce than Ni(II) by ethylene glycol, and also that copper carbonate is more soluble than nickel carbonate. Neither single nickel carbonate nor single copper carbonate yields Ni or Cu particles, respectively, in ethylene glycol even after 15 h of reaction at 140°C. In the case of nickel hydroxycarbonate, metallic nickel is obtained only after the temperature of the dispersion reaches 185°C [21]. These findings indicate the synergistic effect that a mixture of Ni(II) and Cu(II) species has on the temperature needed to chemically reduce them to the metallic state by ethylene glycol. A synergistic effect also influences the formation of bimetallic Ni–Cu particles under these conditions. Copper germs may act as nucleating agents inducing the reduction of Ni at this low temperature and formation of a copper–nickel alloy phase with a high copper content first. As the reaction proceeds, the unreacted nickel undergoes reduction, favoring then a high nickel content copper–nickel alloy.

To ensure complete dissolution of nickel carbonate and reduction of Ni(II) species, the temperature was increased to 190°C and the reaction was allowed to proceed for 4 h. Fig. 2a presents the X-ray diffraction pattern of a powder obtained under these conditions. Clearly, there is no indication of carbonate compounds in this sample. In addition, no green particles are
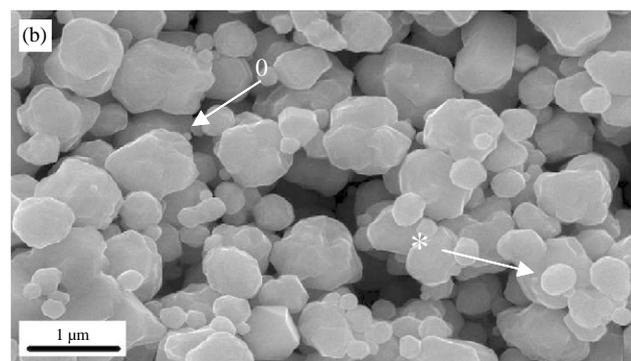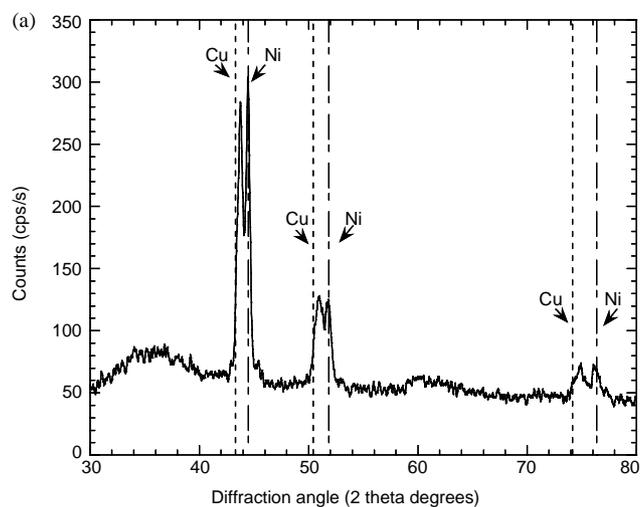
observed in the final product. Similar to the diffraction patterns of the powders obtained at 140°C, Fig. 2a also shows three double peaks: the first one in each doublet corresponds to the reflections of a copper-rich alloy whereas the other peaks are assigned to pure nickel. The cell parameter value was calculated to be 3.591(2) Å for the copper-rich alloy, with a composition of $Ni_{16}Cu_{84}$, and 3.522(2) Å for pure nickel. According to these results, an increase in temperature aids dissolution of the reactants but does not favor the formation of a single solid solution. Cu(II) species reduces to Cu(0) faster than Ni(II) to Ni(0). This seems to be responsible for the formation of a copper-rich Ni–Cu solid solution, which most likely appears first during the course of the reaction, whereas pure nickel forms later. Fig. 2b presents a SEM micrograph showing the features of the bimetallic Ni–Cu particles synthesized at 190°C. Small quasi-spherical particles (*→) and big particles with clear evidence of sintering (0→) whose particle size is in the range of 0.3–1.0 μm are observed. Previous results have shown that spherical nickel particles are synthesized in ethylene glycol [19], whereas copper particles produced in this glycol have a tendency to

sinter [15]. Therefore, the big particles may have the composition $Ni_{16}Cu_{84}$, as established from the X-ray diffraction pattern.

For preventing particle sintering of copper-rich bimetallic Ni–Cu particles at 190°C, a protecting agent, namely PVP, had to be added before heating the dispersion of copper and nickel carbonates. X-ray diffraction patterns of powders synthesized in the presence of different amounts of PVP are similar to that presented in Fig. 3a, which corresponds to a sample prepared with 1.0 g PVP. Again, the X-ray reflections of this sample and the calculations of cell parameters clearly indicate the presence of two distinct phases: a copper-rich Ni–Cu alloy with $a = 3.607(1)$ Å and a composition of $Ni_{10}Cu_{90}$, and metallic nickel with $a = 3.521(4)$ Å. The TEM micrograph presented in Fig. 3b reveals quasi-spherical particles with a size of about 250 nm and polyhedral particles with a size of about 0.4 μm. According to X-ray micro analysis the small particles co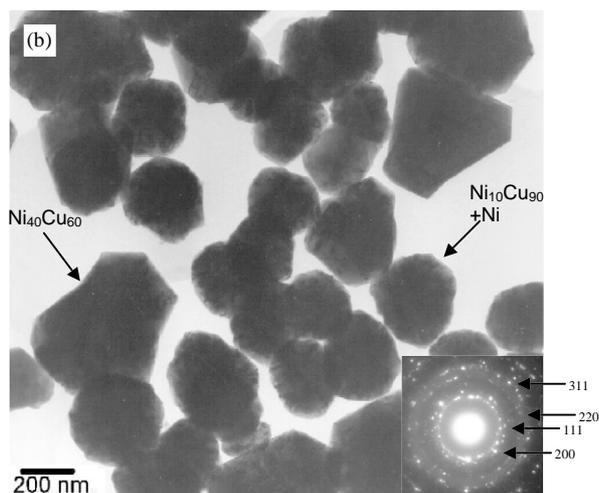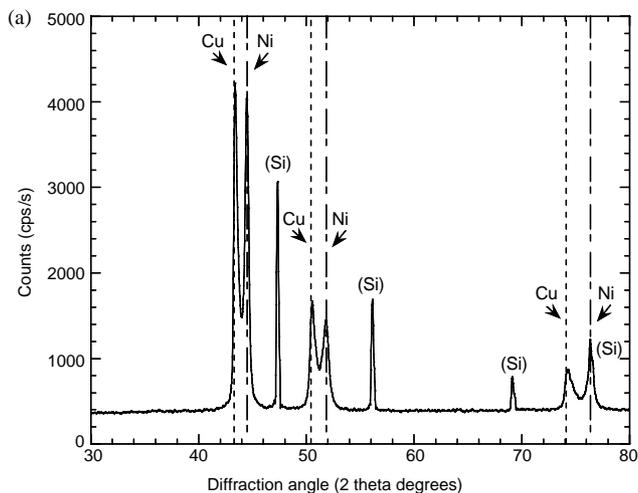ntain a copper-rich core and a nickel shell, whereas polyhedral particles are made of a Ni–Cu solid solution with a composition $Ni_{40}Cu_{60}$. This discrepancy between the composition of the copper-rich solid solution determined from X-ray diffraction data and X-ray micro-analysis could be explained if one considers that the position of the $Ni_{40}Cu_{60}$ alloy reflections are hidden at the center of the peaks that belong to the $Ni_{10}Cu_{90}$ phase, as indicated by the slight shoulder towards larger angles associated with these reflections. The inset in this Fig. 3b is the electron diffraction rings corresponding to an assembly of particles. These rings are wide because the reflections of both Ni–Cu solid solutions and pure nickel must form a continuum due to the close proximity of these phases. As a result, from the electron diffraction pattern one cannot distinguish the $Ni_{40}Cu_{60}$ alloy from the $Ni_{10}Cu_{90}$ one.

3.2. Synthesis from copper and nickel nitrates

Because the reduction kinetics may be driven by the poor solubility behavior of the carbonates, the study was pursued with the nitrate salts whose solubility is higher in glycols. Bimetallic Ni–Cu particles were also obtained when an ethylene glycol solution containing nickel nitrate and copper nitrate was heated up to 196°C and allowed to react for 4 h. Fig. 4 presents a SEM micrograph showing the particles that constitute a typical Ni–Cu powder synthesized under these conditions, and an inset of a TEM micrograph of a single particle. These particles are polyhedral, have an average size of 140 nm and, as opposed to bimetallic Ni–Cu particles synthesized from nickel and copper carbonates, their size distribution is quite narrow and they are free of sintering. X-ray analysis shows that they have a copper core and a nickel shell, which coincides with the structural characteristics deduced from their
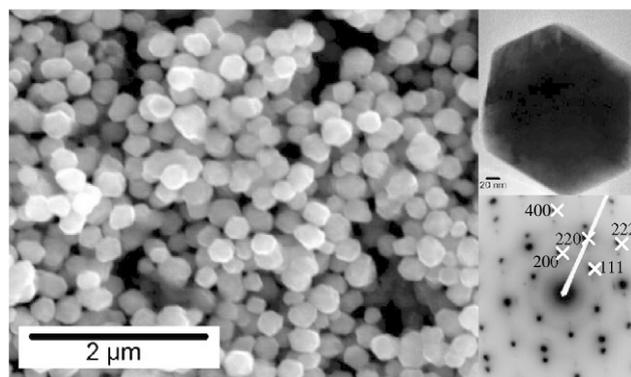

Fig. 3. (a) Powder X-ray diffraction pattern of a bimetallic Ni–Cu powder obtained at 190°C from 0.5 g $NiCO_3$, 0.25 g $CuCO_3$ and 1 g PVP in 75 mL ethylene glycol. (b) TEM micrograph and electron diffraction pattern of the corresponding powder.

Fig. 4. SEM micrograph of a Ni–Cu powder obtained at 196°C from 4.95 g of $Ni(NO_3)_2 \cdot 6\ H_2O$ and 1.02 g of $Cu(NO_3)_2 \cdot 3\ H_2O$ in 75 mL ethylene glycol. The insets show a TEM micrograph of a single particle and the electron diffraction pattern of the powder.

corresponding powder X-ray diffraction pattern ($a_{Ni} = 3.529(2)$ Å and $a_{Cu} = 3.6132(7)$ Å). In addition, this sample was characterized by electron diffraction and its pattern is included as an inset in Fig. 4. This micro-diffraction pattern presents relatively diffuse and large spots, characteristic of the simultaneous diffraction of two metals that have been easily indexed according to the JCPDS files of Ni and Cu. The small spots in the form of discrete marks cannot be indexed according to copper or nickel. These small spots could be due to diffraction of copper and nickel atoms located at the core–shell interface, where structural distortions might occur.

The mechanism of formation of bimetallic Ni–Cu particles with a copper core and a nickel shell may be explained if one considers that Cu(II) species reduces to Cu(0) at a temperature lower than that required to reduce Ni(II) to Ni(0). During heating, intermediate solid phases precipitate before the metal powder is formed. Cu(II) first precipitates as copper glycolate, which then transforms to Cu_2O and then to copper metal. Ni(II) precipitates as nickel glycolate, a rather stable compound that begins to transform to nickel metal only after 2 h of reaction at 196°C. In this system the solubility of the reactants does not affect the mechanism of nucleation and growth because both nickel nitrate and copper nitrate are soluble in ethylene glycol at room temperature.

The increase of temperature emphasizes the stability difference between the two copper and nickel intermediary compounds, and does not prevent, as one may think, the formation of the rather stable glycolate. In fact, at higher temperature, working in DEG at 215°C, metallic copper is synthesized with either a nickel-rich phase $Ni_{57}Cu_{43}$ or several solid solutions in a wide range composition. Each kind of mixture mostly depends on the initial concentration of the raw nitrates, high concentrations in the first case against low ones in the last case. The existence of two phases once the reaction ends suggests that the copper intermediary compound is less stable at this high temperature whereas the nickel one still being more stable.

4. Conclusions

Thermally induced chemical reduction of a mixture of Cu(II) and Ni(II) species in ethylene glycol produce bimetallic Ni–Cu powders. The nature and composition of Ni–Cu particles depend on both the reaction conditions and the chemical reagents used as metal sources. After 39 h of reaction at 140°C, a suspension of nickel carbonate and copper carbonate produces a Ni–Cu powder that contains both nickel-rich and copper-rich Ni–Cu solid solutions. Under these conditions, however, a fraction of the initial carbonates is detected in the final product. Reaction of these carbonates for 4 h at 190°C gives polydisperse Ni–Cu particles composed of a copper-rich Ni–Cu solid solution and nickel, with a size distribution between 0.3 and 1.0 μm. When nickel nitrate and copper nitrate are used as source of metal cations, the bimetallic Ni–Cu powder obtained at 196°C contains particles with a narrow size distribution and an average size of 140 nm. These particles are made of a copper core and a nickel shell.

References

[1] R. Aiello, J.E. Fiscus, H.-C. zur Loye, M.D. Amiridis, Appl. Catal. A: General 192 (2000) 227–234.

[2] P. Bera, S.T. Aruna, K.C. Patil, M.S. Hegde, J. Catal. 186 (1999) 36–44.

[3] T. Ould Ely, C. Amiens, B. Chaudret, E. Snoeck, M. Verelst, Chem. Mater. 11 (1999) 536–539.

[4] B. Morten, M. Prudenziati, F. Sirotti, G. de Cicco, L. Olumekor, J. Mater. Sci.: Mater. Electron. 1 (1990) 118–122.

[5] T. Hibino, A. Hashimoto, T. Inoue, J.-I. Tokuno, S.-I. Yoshida, M. Sano, Science 288 (2000) 2031–2033.

[6] R.J. Gorte, S. Park, J.M. Vohs, C. Wang, Adv. Mater. 12 (2000) 1465.

[7] S. Park, J.M. Vohs, R.J. Gorte, Nature 404 (2000) 265.

[8] Y. Li, J. Chen, L. Chang, Y. Qin, J. Catal. 178 (1998) 76–83.

[9] F.M. Bautista, J.M. Campelo, A. García, R. Guardeño, D. Luna, J.M. Marinas, J. Mol. Catal. A: Chem. 104 (1996) 229–235.

[10] S.K. Shaikhutdinov, L.B. Avdeeva, O.V. Goncharova, D.I. Kochubey, B.N. Novgorodov, L.M. Plyasova, Appl. Catal. A: General 126 (1995) 125–139.

[11] H. Noller, W.M. Lin, J. Catal. 85 (1984) 25–30.

[12] R.G. Samel'yan, E.S. Abovyan, S.G. Agbalyan, N.N. Manukyan, M.S. Sakanyan, Soviet Powder Metall. Met. Ceram. 30 (1991) 606.

[13] G.T. Cardenas, R.C. Oliva, Mater. Res. Bull. 33 (11) (1998) 1599–1608.

[14] W. Mörke, T. Bieruta, J. Jarsetz, C. Görsmann, U. Schubert, Colloids Surf. A: Physicochem. Eng. Aspects 115 (1996) 303–309.

[15] M. Figlarz, C. Ducamp-Sanguesa, F. Fiévet, J.-P. Lagier, Powder Production and Spray Forming—Advances in Powder Metallurgy & Particulate Materials, Metal Powder Industries Federation, Vol. 1, 1992.

[16] G. Viau, F. Fiévet-Vincent, F. Fiévet, Solid States Ionics 84 (1996) 259–270.

[17] G.M. Chow, L.K. Kurihara, K.M. Kemmer, P.E. Schoen, W.T. Elam, A. Ervin, S. Keller, Y.D. Zhang, J. Budnick, T. Ambrose, J. Mater. Res. 10 (1995) 6.

[18] P. Lu, J. Dong, N. Toshima, Langmuir 15 (1999) 7980–7992.

[19] B. Blin, F. Fievet, D. Beaupère, M. Figlarz, New J. Chem 13 (1989) 67–72.

[20] C. Ducamp-Sanguesa, Ph.D. Thesis, University of Picardie Jules Verne, Amiens, France, 1992.

[21] B. Roche, Ph.D. Thesis, University of Picardie Jules Verne, Amiens, France, 1993.