Advanced Powder Technology 25 (2014) 609–614

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Physicochemical properties of cubic Ni complex powders synthesized using urotropine chelating ligand for solid oxide fuel cells

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ARTICLE INFO

Article history:
Received 7 May 2013
Received in revised form 24 July 2013
Accepted 26 September 2013
Available online 9 October 2013

Keywords:
Flower-like stacked sheets
Tetradentate chelating ligand
Urotropine
Cube
Electrical conductivity

ABSTRACT

New nanometer nickel-based solid oxide fuel cell (SOFC) anode material has been synthesized by a hydrothermal reaction with nickel (II) chloride as a metal-containing precursor and a tetra dentate chelating reagent, urotropine. SEM images reveal that the Ni complexes change from two-dimensional flower-like stacked sheets to truncated cubes with increasing mol concentration of urotropine chelating additive. The truncated cubes show sizes of 50.0–200.0 nm. The electrical conductivity of the truncated cubic Ni complex (60.0 wt.%)-loaded commercial YSZ (40.0 wt.%) for an application in SOFC anode is superior compared to that of commercial NiO/YSZ at the same composition. The zeta-potential value in aqueous solution determined by electrophoretic light scattering (ELS) show a positive surface charge in the range of pH 3.0–9.0, related to the surface stability, but it changes to a negative value at above pH > 9. The H_2-temperature-programmed reduction experiments confirm that the truncated cubic Ni complex-loaded commercial YSZ shows a better reducibility than the commercial NiO/YSZ.

1. Introduction

Nickel oxide (NiO) has been the subject of strong research interest due to its unique electrical, optical and magnetic properties. Specifically, the electronic properties of NiO have been widely applicable to anodes for lithium ion batteries [1], solar cells [2], anode material for fuel cells [3], anti-ferromagnetic materials [4], and chemical gas sensors [5]. As an example, NiO/YSZ has been used as an anode material in SOFC having sufficient electronic conductivity and good catalytic reaction for fuel gas at an operating temperature. Generally, anode materials in SOFC should also maintain thermal and chemical compatibility compared with other component materials at an operating temperature or higher temperatures, because SOFC normally operates at high temperatures of 800–1000 °C. However a commercial NiO-loaded YSZ anode material has a serious problem; it is strongly deactivated during the operation of SOFC, mainly because NiO aggregates at high temperatures.

To overcome this problem, NiO nanoparticles showing unique behaviors have been utilized. Various synthetic methods of NiO nanoparticles include sol–gel [6], micro emulsion precipitation [7], chemical vapor deposition [8], and sputtering [9], and the research has increased a lot during the past decade. Recently, hydrothermal method has proven to a good method to synthesize many metal oxide nano-materials, and also employed to different material systems [10]. Hydrothermal treatments has been used to control grain size, particle morphology, crystalline phases, and surface chemistry by modifying sol composition, reaction temperature, pressure, solvent nature, additives, and aging time. Nano-size particles prepared by a hydrothermal method are expected to have a larger surface area, smaller particle size, and higher stability than those obtained by other methods, such as sol–gel method. Recently, the hydrothermal treatment has been modified by employing various polymeric or surfactant additives to synthesize various Ni materials with unique morphologies like spherical [11], porous [12], rod [13], and sheet types [14]. However, no study of synthesizing cubic Ni material using a hydrothermal method has been reported in literatures.

Motivated by this, we have employed a hydrothermal method to synthesize nano-size cubic Ni material by introducing a chelating amine additive of urotropine. The synthesized samples are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), zeta potential, specific surface area, and H_2-temperature-programmed reduction (H_2-TPR).

2. Experimental

Ni samples with morphologies of stacked 2-D sheets, flower-like microspheres, and truncated cubes were synthesized by a

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http://dx.doi.org/10.1016/j.apt.2013.09.013

hydrothermal method. The synthetic procedure is as follows. First, we completely dissolved $NiCl_2{\cdot}H_2O$ (99.95%, Junsei Chemical, Japan) in distilled water, followed by adding urotropine (a tetra dentate chelating reagent, $(CH_2)_6N_4$, Aldrich, USA) and stirring homogeneously. Here, four types of solutions corresponding to urotropine to Ni precursor molar ratios of 0.5, 1.0, 1.5, and 2.0 were prepared. Ni compounds are generally to be stabled when they have six coordinated linkages, and thus urotropine (a tetra dentate chelating reagent) of 1.5 mol is needed to combine completely with 1.0 mol of Ni ions. The other concentrations of urotopine according to little or a lot were selected arbitrarily to be 0.5, 1.0, and 2.0 mol to find a proper concentration for obtaining a perfect cubic Ni material. Next, diluted HCl aqueous solution was slowly dropped into the mixed solution until pH = 1.8. The homogeneously mixed solution was transferred into a Teflon-lined stainless autoclave, and the solution was thermally treated at 130 °C for 20 h. After the treatment, the sample was allowed to cool to room temperature, and then the precipitate was collected via centrifugation. Finally, the collected precipitate was dried at 65 °C for 12 h. To avoid confusion during the discussion, we name Ni-a, Ni-b, Ni-c, and Ni-d for materials which synthesized with four types of molar ratios in urotropine:Ni precursors = 0.5:1.0, 1.0:1.0, 1.5:1.0, and 2.0:1.0, respectively. For an effective comparison in electric conductivity, we used commercially available YSZ powder (Yttria-stabilized zirconia, TZ8Y, 0.3 μm, Tosoh, Japan). The prepared Ni materials (60 wt.%) in this study were physically mixed with YSZ (40 wt.%) powders to test the electric conductivity.

The prepared Ni complexes were identified using powder XRD analysis (X'Pert Pro MPD PANalytical 2-circle diffractometer). We used nickel-filtered Cu Kα radiation (30 kV and 30 mA), 2θ angles of 10–80°, a scan speed of $10°\ min^{-1}$, and a time constant of 1 s. The sizes and shapes of the synthesized materials were analyzed by a FE-SEM (field emission scanning electron microscope, SEM-S-4100, Hitachi) instrument operated at 15.0 kV. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) theory that gives the isotherm equation for multilayer adsorption by generalization of Langmuir's treatment of the unimolecular layer. The BET surface area was measured using a Micrometrics ASAP 2000 instrument. The material was degassed under vacuum at 120 °C for 1 h before the BET surface measurement, and then, it was again thermally treated at 300 °C for 30 min to remove the adsorbed water molecules and impurities. The BET surface area of the material was measured through the nitrogen gas adsorption using a continuous flow method with a mixture of N_2 and He as the carrier gas. The zeta potential of a material was determined by electrophoretic mobility using an electrophoresis measurement apparatus (ELS 8000, Otsuka Electronics, Japan) with a plate sample cell. Electrophoretic light scattering (ELS) determination was performed in reference beam mode with a laser light source of 670 nm, modular frequency of 250 Hz and scattering angle of 15°. The standard error of the zeta potential, converted from the experimentally determined electrophoretic mobility, was typically <1.5% and the percent error of <5%. To measure a zeta potential, 0.1 wt.% of each sample was dispersed in de-ionized water, and the pH of the solution was adjusted with HCl or NaOH solution. The relative molecular diameter size distribution of the various solutions was also measured using this equipment. The zeta potential distribution was obtained by averaging 2 or 3 runs. H_2-temperature-programmed reduction (TPR) was conducted as follows. About 0.3 g of the material was pre-treated under He flow ($30\ mL\ min^{-1}$) at 700 °C for 2 h. and then cooled to room temperature. The analysis was carried out by flowing $30\ mL\ min^{-1}$ of H_2 (10 vol.%)/N_2 and raising the temperature of the materials from room temperature to 700 °C at a ramp rate of $5\ °C\ min^{-1}$. The change in hydrogen concentration was measured using a gas chromatograph (GC series 580, GOW-MAC) equipped with a thermal conductivity detector.

Electric conductivity was tested by a 4-probe DC method using an IV meter (Ecosolution, Hanyoung electronics, Korea). For the preparation of a specimen, first, 0.7 g of the material powder was placed in a 1.5 cm diameter mold, and was pressed under $300\ kg\ cm^{-2}$. The mold sample was transferred into a furnace, and the temperature was raised to 1400 °C at a heating rate of $5\ °C\ min^{-1}$, and then held for 4 h under air condition. The resulting green NiO/YSZ mold was cut into a rectangular pellet with a dimension of 2.0 mm × 4.0 mm × 1.7 mm. The pellet was transferred into a furnace, connected to a platinum wire, and coated at one end with platinum paste. Under a gas flow of 30.0 vol.% diluted H_2 in N_2 valance, the furnace was heated to 900 °C and held for 2 h for reduction, and then the conductivity was measured at each temperature step after 1 h.

3. Results and discussions

Fig. 1 shows the XRD patterns of the synthesized materials prepared with four different concentrations of urotropine. We expect that the condensation reaction involving H_2O elimination generally induces a combination between each Ni hydroxide. During this reaction, the condensation reaction continues in the absence of any blocking molecules of tetra dentate urotropine. The resulting nucleation can grow in all directions without any restrictions, leading naturally to a spherical shape. The presence of urotropine molecules, however, induces a selective and competitive condensation reaction at the terminals of the Ni hydroxide complexes, resulting in a cubic shape. Due to a complexity of the synthesis method, cubic Ni complex has not yet been synthesized for an application to SOFC. Fortunately, we are able to successfully obtain a cubic Ni complex. The Ni materials prepared at urotropine concentrations of 0.5 and 1.0 mol (samples Ni-a and Ni-b) show peaks at $2\theta = 12.5°, 26.2°, 36.0°$, and 59.8°, plausibly assigned to the mixture $Ni_2(OH)_2(NiOOH)$ [15] and $Ni_2(CO_3)(OH)_2$ [16]. For Ni-c and Ni-d samples at urotropine concentrations of 1.5 and 2.0 mol, the XRD peaks are attributed to $Ni(HCO_3)_2$ [17], and three major peaks are assigned to (110), (211), and (410) crystal planes.

The SEM images of the four Ni compounds are shown in Fig. 2. The Ni-a and Ni-b samples exhibit stacked sheets and flower-like microspheres (or 2-dimensional nanosheet structures and multi-webs shapes consisting of the bottom of 1.0 μm and the thickness of 50 nm), respectively with sizes of approximately 5.0 μm. Interestingly at higher concentration of urotropine for Ni-c and Ni-d, SEM images show truncated cubes with sizes of 50–200 nm. The Ni intermediate phase is likely to be reduced by OH groups during

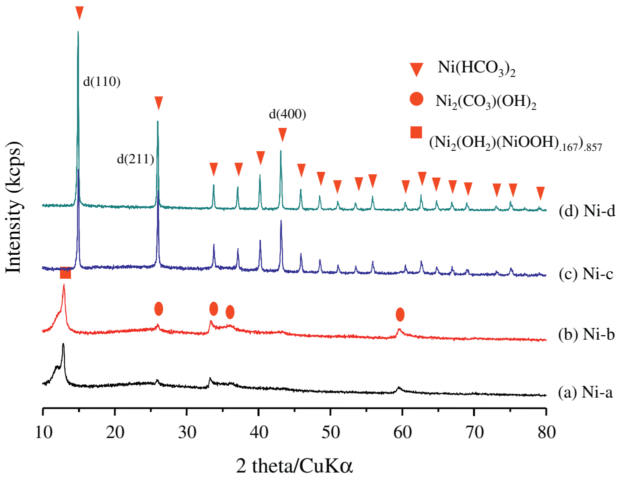

Fig. 1. XRD patterns of the four prepared Ni materials, Ni-a, Ni-b, Ni-c and Ni-d.