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RF plasma synthesis of nickel nanopowders via hydrogen reduction of nickel hydroxide/carbonate

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ABSTRACT

Nickel hydroxide/carbonate was chosen as the precursor to synthesize nickel nanopowders via an RF plasma-assisted hydrogen reduction route. Thermodynamic analysis revealed that the reaction could take place spontaneously. XRD patterns showed that metallic nickel powders could be obtained within the limited residence time. FESEM images indicated that the products consisted of well-dispersed spheres with an average diameter of about 60–100 nm. The obtained nickel powders exhibited high tap density. The use of nickel hydroxide/carbonate as the precursor guaranteed the products of high purity and the processing of environmental safety. The present plasma-assisted hydrogen reduction of nickel hydroxide/carbonate is an ideal route for large-scale synthesis of well-dispersed metallic nickel nanospheres used as electrode materials.

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1. Introduction

Fine nickel powders have great potential technological applications such as conducting paints, rechargeable batteries, chemical catalysts, microwave absorbing materials, and magnetic recording media [1–5]. In addition, they are attracting increasing attention as the substitute for noble metals Pd or Pd/Ag used in the internal electrodes of multilayer ceramic capacitor (MLCC) due to their good electrical conductivity, high melting point, and low cost [6]. Nickel powders as the electrode materials need to be prepared as well-dispersed spheres with a narrow size distribution. Practical application always promotes the synthetic development. A variety of techniques such as chemical reduction, spray pyrolysis, and plasma technique have been employed to produce fine spherical nickel powders [7–14].

Radio-frequency (RF) thermal plasma is an easy way to prepare spherical powders [15–18]. The plasma system has a high temperature flame (up to 10,000 K) with a rapidly cooled tail (10^5-10^6 K/s). The high temperature region can provide enough energy for the melting/evaporation of the raw materials and the rapidly cooled tail could help rapid solidification. Melting–spheroidization and evaporation–condensation often coexist during the formation of spherical powders. Melting–spheroidization results in

micron spheres while evaporation-condensation leads to spherical nanoparticles. When the particle size of the input materials is small enough and the feedrate is proper, all the raw materials would evaporate instantly upon injection into the plasma flame and subsequently condensate into nanoparticles in the quenching region. The plasma gas does not come in contact with electrodes, which can eliminate possible sources of contamination. Furthermore, the operation environment is flexible from oxidizing to reducing atmosphere [18]. So RF thermal plasma is also an effective way to prepare high purity powders. Using the plasma-assisted physical vapor deposition (PVD) method, various nanopowders including metal and ceramic were synthesized [19,20]. RF thermal plasma could also be used in the chemical synthesis due to its chemically active species [18,21]. In this regard, Chau [22] attempted to synthesize Ni and FeNi nanopowders using nickel chloride as precursor in reduction atmosphere provided by hydrogen. But the generated HCl in the exhausting gas would be harmful to the equipments as well as human health and environment. It is also difficult to obtain high purity powders using chloride as precursor for the strong Cl adsorption.

In the present paper, we reported the RF plasma synthesis of spherical nickel nanoparticles via hydrogen reduction of nickel hydroxide/carbonate. Both thermodynamic calculation and experimental results showed that metallic nickel powders could be obtained. Different influencing parameters were examined. The formation process of the nickel particles was discussed based on the experimental results.

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Fig. 1. The schematic illustration of the experimental setup.

2. Experimental

Nickel hydroxide and basic nickel carbonate were used as the precursor. Nickel hydroxide was synthesized using ammonia-precipitation method. Na has low surface energy and is difficult to be removed from the resulting powders. The present ammonia-precipitation method guaranteed the final products of high purity. Basic nickel carbonate was provided by JNMC (Jinchuan Group Ltd., China). Commercial nickel hydroxide microspheres were obtained from WESTAIM.

The experiments were carried out in an RF thermal plasma system under atmospheric pressure. The experimental setup consists of an RF generator (30 kW, 4 MHz), a plasma generator, a reactor, and a powder-collecting filter. The schematic illustration of the setup is shown in Fig. 1 [23]. The screw feeder was homemade and the feedrate could be controlled by setting the screw speed.

In a typical experimental procedure, stable plasma was first generated using argon and nitrogen as the plasma-forming gas and sheath gas, respectively. Nickel hydroxide or basic nickel carbonate was supplied into the plasma flame in a continuous way with the use of hydrogen as carrier gas. Hydrogen also played the role of reducing agent. The precursor underwent vaporization and reduction, and then the resulting metallic nickel species condensed and formed nanoparticles as a result of the high quenching rate. Most of the products were collected from the filters and some were collected from the chamber wall. Detailed processing parameters are given in Table 1.

The crystalline phase of the as-prepared samples was characterized by X-ray diffractometry (XRD, X'pert PRO, Panalytical, Cu K α radiation) in a 2 θ range from 10° to 110°. The purity of the product was demonstrated by energy dispersive X-ray spectrometry (EDX). Their size and morphology were inspected with field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). The thermal stability of the products was recorded using thermal analyzer (Netzsch STA 449 TG–DTA/DSC). The tap density of the nickel powders was examined with the help of a Hall flowmeter.

3. Results and discussion

NiCO₃ (s) decomposes at the temperature of 381 K and Ni(OH)₂ (s) decomposes at the temperature of 600 K. NiO can react with

Table 1

Detailed parameters for plasma processing.

Parameters	Values
Central gas, argon	1.0 m ³ /h
Sheath gas, nitrogen	5.0 m ³ /h
Carrier gas, hydrogen	0.7 m ³ /h
Quenching gas, nitrogen	$0-5.0 m^3/h$
Powder feedrate	2-10 g/min



Fig. 2. ΔG -*T* curves of the possible reduction reactions.

gaseous H_2O and form gaseous $Ni(OH)_2$ [24]. Accordingly, the possible reaction during the plasma processing can be expressed as below:

$$NiCO_3(s) \rightarrow NiO(s) + CO_2(g)$$
 (1)

 $Ni(OH)_2(s) \rightarrow NiO(s) + H_2O(g)$ (2)

$$NiO(s) \rightarrow NiO(g)$$
 (3)

$$NiO(s) + H_2O(g) \rightarrow Ni(OH)_2(g)$$
(4)

$$NiO(s) + H_2(g) \rightarrow Ni(g) + H_2O(g)$$
(5)

$$NiO(g) + H_2(g) \rightarrow Ni(g) + H_2O(g)$$
(6)

$$Ni(OH)_2(g) + H_2(g) \rightarrow Ni(g) + 2H_2O(g)$$

$$(7)$$

The change of the Gibbs free energy ΔG is usually used to judge the spontaneous direction of a reaction. The corresponding ΔG -Tcurves of the reduction are shown in Fig. 2. (The curves were drawn based on the data given in Ref. [24].) The ΔG values for both reactions between NiO and H₂ are below zero and declined as the temperature increased, which means that both of them can take place spontaneously. The ΔG value for Eq. (7) is below zero at the temperature higher than 1550 K, indicating that the reactions can also take place spontaneously at high temperature.

Experimental results showed that metallic nickel powders could be obtained whether nickel hydroxide or basic nickel carbonate was used as precursor. The accomplishment of complete reduction within the limited residence time in plasma flame might be attributed to the unique reaction field provided by the thermal nonequilibrium effects in plasma [25,26]. Fig. 3 shows the typical XRD patterns of the product obtained with proper feeding rate,



Fig. 3. XRD patterns of the product obtained using nickel hydroxide (a) and basic nickel carbonate (b), respectively.



using nickel hydroxide and basic nickel carbonate, respectively. The five diffraction peaks of (111), (200), (220), (311), and (222) of face-centered cubic (fcc) Ni can be easily observed. No peaks of nickel oxide are detected, indicating high purity of the products.

Fig. 4 shows the EDX spectra of the product. Besides that of Ni confirmed by XRD patterns, the peaks associated to O is present. The other peaks originate from the Cu grid and the TEM equipment. The mole content of O was 1.2%. Taking the air adsorbed on the surface of the Ni particles into consideration, the mole content of O in the product was about 1%.

Fig. 5 shows the FESEM images of the homemade nickel hydroxide and commercial basic nickel carbonate, and the products obtained using them as precursors, respectively. The nickel hydroxide particles shown in Fig. 5a are well-dispersed and flake-like in shape, the uniform size and thickness of which is about 500 nm and 50 nm. The basic nickel carbonate particles shown in Fig. 5b are irregular in shape and loosely aggregated. Powders with bigger particle size always have better fluidity, which is helpful for the feedrate control. However, bigger particles are difficult to evaporate and would influence the following reduction. Both the homemade nickel hydroxide and commercial basic nickel carbonate could be used as the raw material, while the commercial nickel hydroxide microspheres are too big and dense for complete evaporation and reduction. Fig. 5c shows the FESEM images of the nickel powders obtained using homemade nickel hydroxide as the precursor with a feeding rate of 2 g/min. The nickel particles are well-dispersed nanospheres and most particles have a diameter in the range of 50-100 nm and only a few coarse particles exist. The products obtained using commercial basic nickel carbonate as the precursor shown in Fig. 5d exhibit similar results.

As mentioned previously, the main products were collected from the filters, and some were collected from the chamber wall. The products collected from the chamber account for about 20%. Fig. 6 shows the FESEM images of the nickel powders collected from the chamber wall using homemade nickel hydroxide as precursor. The powders collected from the high temperature region (shown in Fig. 6a) are more aggregated and have bigger particle size compared to that collected from the low temperature region (shown in Fig. 6b). The reason is that the particles deposited on the wall in high temperature region keep active and can absorb more nickel species and grow. Meanwhile, the active nickel particles have a tendency to aggregate. On the contrary, the particles staying in the low temperature region lose the activity partly.

The cooling rate has great effect on both shape and size of the resulting particles. Rapid cooling is necessary for the formation



Fig. 5. FESEM images of the homemade nickel hydroxide (a) and commercial basic nickel carbonate (b), and the product obtained using them as procedure (c and d).



Fig. 6. FESEM images of the nickel powders collected from the chamber wall: (a) high temperature region and (b) low temperature region.



Fig. 7. FESEM images of the nickel powders obtained with (a) and without (b) quenching gas.

of spherical particles. The plasma system itself has a high cooling rate, so the products exhibited spherical shape whether quenching gas was introduced or not. Fig. 7 shows the FESEM images of the nickel powders obtained in case with (a) and without (b) quenching gas. Both powders consist of spherical nanoparticles. However, the average particle size was reduced from 100 nm to 60 nm when nitrogen was introduced as quenching gas at a rate of $5 \text{ m}^3/\text{h}$.

The effect of feedrate on the resulting powders was also examined. Particle size increased a bit and the aggregation became serious with the feeding rate increased. The concentration of the reactive species would increase when the feedrate was high and the resulting Ni species would increase accordingly, which would lead to the growth and aggregation of the nickel particles. The proper feeding rate was about 10 g/min.

We believe that the reduction and formation of nickel nanoparticles were achieved via vapor instead of liquid phase. In order to verify this process, commercial nickel hydroxide microspheres with the size range of $2-10 \,\mu$ m were used as precursor to synthesize nickel powders. Two separated categories of particles existed in the resulting products. Fine particles similar with that shown in Fig. 5c and d were collected from filters, which were indicated by XRD as pure metallic Ni. Big particles collected from the bottom of the reactor remained the shape and size of the nickel hydroxide precursor as shown in Fig. 8. XRD pattern showed that the main phase of the big particles was hydroxide. It is known that the surface of the particles becomes smooth and the size



Fig. 8. FESEM images of the commercial nickel hydroxide (a) and the product collected from the bottom of the reactor (b).



Fig. 9. TG curve of the obtained Ni powders.

keeps almost constant after plasma melting–spheroidization. If the reduction had been achieved via liquid phase, the obtained nickel particles should be in micron size when commercial nickel hydroxide microspheres were used as precursor. As a matter of fact, nickel nanoparticles were obtained instead, and the newly formed Ni were not on the surface but separated from the precursor. It can be induced that the reduction and formation of nickel nanoparticles were achieved via vapor instead of liquid phase.

Thermal stability and tap density are two important parameters for the electrode materials. The sample obtained with the feedrate of 10 g/min and cooling gas rate of $5 \text{ m}^3/\text{h}$ was examined. The thermal stability of the products was recorded using thermal analyzer. As shown in Fig. 9, obvious weight gain starts at about 250 °C, indicating thermal oxidation of the obtained nickel powders began at about 250 °C. Compared with that reported (300 nm, 340 °C), the obtained nickel nanoparticles are easily oxidized [7]. The low oxidation temperature is related to the small particle size. Most of the electrodes need sintered at relatively high temperature (above 800 °C), so inert/reducing atmosphere is necessary for the materials with poor oxidation resistance.

In order to measure the tap density with the help of a Hall flowmeter, the container was vibrated regularly when the powders were flowing down. The accordingly calculated result was 3.7 g/cm^3 , which was much higher than that reported in the literature (1000 nm, 3.0 g/cm^3) [27]. We also measured the commercial carbonyl nickel powders and the spherical nickel powders synthesized via wet chemical reduction [7], using the same flowmeter-assisted method. Both samples are no more than 2.5 g/cm^3 in tap density. So the present plasma-assisted hydrogen reduction is an effective route to synthesize nickel nanopowders with a high tap density.

4. Conclusions

Spherical nickel nanoparticles with uniform size were synthesized using RF plasma-assisted hydrogen reduction route. Nickel hydroxide/carbonate was chosen as the precursor, which guaranteed the products of high purity and the processing of environmental safety. The product consists of well-dispersed particles in the size range of 60–100 nm and has a tap density as high as 3.7 g/cm³. The present plasma-assisted hydrogen reduction is an ideal route for large-scale synthesis of well-dispersed metallic nickel nanospheres used as electrode materials.

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References

- H. Shoji, Y. Nakano, H. Matsushita, A. Onoe, H. Kanai, Y. Yamashita, J. Mater. Synth. Process. 6 (1998) 415.
- [2] J.Z. Gao, F. Guan, Y.C. Zhao, W. Yang, Y.J. Ma, X.Q. Lu, J.G. Hou, J.W. Kang, Mater. Chem. Phys. 71 (2001) 215.
- [3] H.J. Zhang, H.T. Zhang, X.W. Wu, Z.L. Wang, Q.L. Jia, X.L. Jia, J. Alloys Compd. 419 (2006) 220.
- [4] H. Niu, Q. Chen, M. Ning, Y. Jia, X. Wang, J. Phys. Chem. B 108 (2004) 3996.
- [5] F. Davar, Z. Fereshteh, M. Salavati-Niasari, J. Alloys Compd. 476 (2009) 797.
 [6] K.H. Kim, H.C. Park, S.D. Lee, W.J. Hwa, S.S. Hong, G.D. Lee, S.S. Park, Mater. Chem. Phys. 92 (2005) 234.
- [7] L.Y. Bai, F.L. Yuan, Q. Tang, J.L. Li, H. Ryu, J. Mater. Sci. 43 (2008) 1769.
- [8] J. Park, E. Chae, S. Kim, J. Lee, J. Kim, S. Yoon, J. Choi, Mater. Chem. Phys. 97 (2006) 371.
- [9] Y.Q. He, X.G. Li, M.T. Swihart, Chem. Mater. 17 (2005) 1017.
- [10] B. Xia, I.W. Lenggoro, K. Okuyama, J. Mater. Sci. 36 (2001) 1701.
- [11] Z.Q. Wei, T.D. Xia, L.F. Bai, J. Wang, Z. Wu, P.X. Yan, Mater. Lett. 60 (2006) 766.
- [12] G. Shanmugavelayutham, V. Selvarajan, Bull. Mater. Sci. 27 (2004) 453.
- [13] X.H. Luo, Y.Z. Chen, G.H. Yue, D.L. Peng, X.T. Luo, J. Alloys Compd. 476 (2009) 864.
- [14] L.Y. Bai, F.L. Yuan, Q. Tang, Mater. Lett. 62 (2008) 2267.
- [15] N. Kobayashi, Y. Kawakami, K. Kamada, J.G. Li, R. Ye, T. Watanabe, T. Ishigaki, Thin Solid Films 516 (2008) 4402.
- [16] S. Kumar, V. Selvarajan, P.V. Padmanabhan, K.P. Sreekemar, J. Mater. Process. Technol. 176 (2006) 87.
- [17] X.L. Jiang, M. Boulos, Trans. Nonferrous Met. Soc. China 16 (2006) 13.
- [18] M. Boulos, IIEEE Trans. Plasma Sci. 19 (1991) 1078.
- [19] B.M. Goortani, P. Proulx, S. Xue, N.Y. Mendoza-Gonzalez, Powder Technol. 175 (2007) 22.
- [20] P. Hu, S.K. Yan, F.L. Yuan, L.Y. Bai, J.L. Li, Y.F. Chen, Plasma Sci. Technol. 9 (2007) 611.
- [21] S. Son, M. Taheri, E. Carpenter, V.G. Harris, M.E. McHenry, J. Appl. Phys. 91 (2002) 7589.
- [22] J.L.H. Chau, Mater. Lett. 61 (2007) 2753.
- [23] P. Hu, F.L. Yuan, L.Y. Bai, J.L. Li, Y.F. Chen, J. Phys. Chem. C 111 (2007) 194.
- [24] O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin/New York; Verlag Stahleisen, Dsseldorf, 1991, pp. 309–1458.
- [25] M.I. Boulos, P. Fauchais, E. Pfender, Thermal Plasma: Fundamentals and Applications. vol. 1, Plenum Press. New York, 1994.
- [26] J.G. Li, X.H. Wang, K. Watanabe, T. Ishigaki, J. Phys. Chem. B 110 (2006) 1121.
- [27] R. Liao, D.Z. Zhou, Y. Zhang, G.F. Pan, Chin. J. Electron. Compon. Mater. 22 (2003) 28.