Synthesis and Preparation of Cu-doped amorphous Nano-$Ni(OH)_2$

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Abstract: Cu-doped amorphous nano-$Ni(OH)_2$ powder were prepared by coordination-precipitation method with citrate as the complex agent. The samples were characterized by XRD, TEM, TG-DTG and electrochemical properties testing. The results show that the sample power is amorphous, and the particle size of $Ni(OH)_2$ was about 50 nm. The thermal decomposition temperature of the sample is lower (269.4 ℃) and it contains large amount of crystal water. When the sample was charged at 80 mA/g for 6 h and discharged at 40 mA/g to 1.0 V, it has longer discharge time at 1.260 V, and the discharge specific capacity can be reached as high as 362.976 mA·h/g.

Key words: coordinate precipitation method; Cu-doped; amorphous nano-$Ni(OH)_2$; electrochemical properties
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Now nickel hydroxide material application is limited by several problems such as low capacity and volume expansion of β-$Ni(OH)_2$ and α-$Ni(OH)_2$ is bally unstable in strong alkaline media[1]. For amorphous material and nanomaterial have a lot of unique structure and characteristics that is correlate to electrochemical activity of the electrode material[1][2-4], in this paper, amorphous nano-$Ni(OH)_2$ powder has been produced by coordinate precipitation method and its morphology and electrochemical performance had been studied too. At the present, it has a little report about this.

1 Experimental

Appropriate amounts of 0.5 mol/L $NiSO_4$ solution, $CuSO_4$ solution, alcohol and sodium citrate were mixed uniformly according to the certain proportion, and then 1.0 mol/L NaOH solution was dropped stepwise into this mixed solution at 55 ℃ with constant stirring, pH=12 reacting for 1 h, then quenching in an ice-water bath. The product was filtered, washed and then dried for 10 h at 100 ℃.

The morphology and composition of samples were studied using X-ray diffraction, transmission electron microscopy (TEM) and Thermal analysis (TG-DTG) was carried out with a NETZSCH STA 449C system.

A simulated MH-Ni battery was assembled by the nickel hydroxide positive electrode and then it was charged at 80 mA/g for 6 h and discharged at 40 mA/g to 1.0 V. Electrochemical measurements were performed using a model DC—5C battery-test system.

2 Results and discussion

2.1 Morphology and physical properties of the sample

Fig.1 shows the XRD spectrums of samples, as can be seen, the peak of XRD spectrum is relatively flat. From this result, it can be confirmed that the sample is amorphous and the Cu-doped did not change the structure of sample. TEM image of the sample is shown in Fig.2. The sample particles are similar to spherical, and the grain size is about 50 nm.

TG-DTG curves of the sample are shown in Figure 3. During the process of water loss, the weight loss of the sample is 41.92%, which is more than that of well-crystallized[5] (17.9%), and the thermal decomposition temperatures of the sample is 269.4 ℃. This indicates that the force of intermolecules is weak and the electrochemical activity of the particle is high.

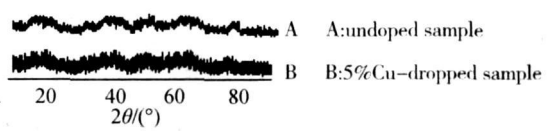

Fig.1 XRD spectrums of $Ni(OH)_2$

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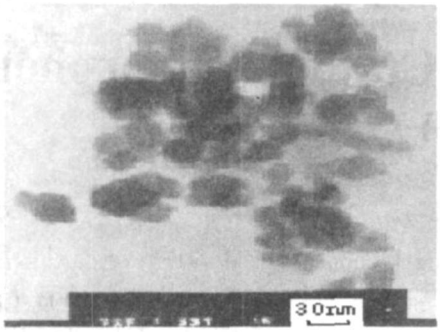

Fig. 2 TEM image of 5% Cu – dropped sample

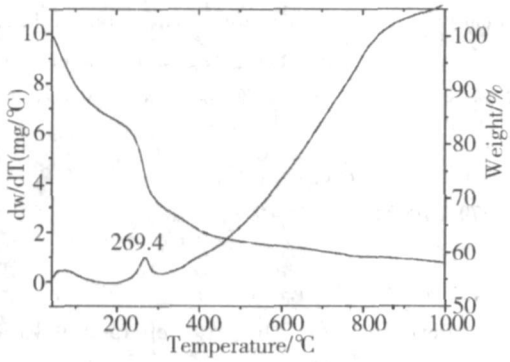

Fig. 3 TG – DTG Curves of 5% Cu – dropped sample

2.2 Electrochemical performance

Fig. 4 are the charge-discharge curves of the samples. The discharge voltages of the dropped sample electrode are higher and it has longer discharge platform in 1.26 V. The discharge specific capacity of the dropped sample can be reached as high as 362.976 mA·h/g which is higher than that of the undoped sample.

3 Conclusion

Cu-doped amorphous nano-$Ni(OH)_2$ powder were prepared by coordination precipitation method. XRD, TEM and TG-DTG analysis of the sample show that it has higher electrochemical activity. A simulated MH-Ni battery composed of Cu-doped amorphous nano-$Ni(OH)_2$ power as positive electrode material has higher charge efficiency and better discharge performance. Its specific capacity reaches as high as 362.976 mA·h/g.

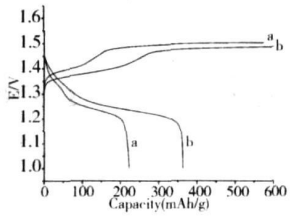

Fig. 4 Charge and discharge curves of 5% Cu – dropped sample

References:

[1] ZHOU Q J, YUAN Q W, WANG L J, et al. The research progress in α-Ni (OH)$_2$ [J]. Battery Bimonthly, 2003, 33 (2): 93—92.

[2] OVSHINSKY S R, FETCENKO M A, FIERRO C. Enhanced Nickel hydroxide positive electrode material for alkaline rechargeable electrochemical cells [P]. US 5523182, 1996-06.

[3] REISNER D E, SALKIND A J, STRUTT P R, et al. J Power Sources, 1997, 65 (1—2): 231—233.

[4] CHU W, WU H, YOU K J, et al. Recent progress of nano scale science and technology in chemical power sources [J]. Chinese Journal of Power Sources, 1998, 22 (6): 256—264.

[5] ZHU W H, ZHANG D J, KE J J. Preliminary research on the reaction mechanism of nickel hydroxide electrode [J]. Journal of Power Sources, 1996, 20 (6): 235—251.

铜掺杂非晶纳米氢氧化镍的制备及性能

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摘 要: 以柠檬酸三钠为络合剂, 采用络合反应快速冷冻沉淀法制备出铜掺杂氢氧化镍超细粉体样品材料, 采用 XRD, TEM和 TG-DSC对其结构进行表征, 并测试其电化学性能。实验结果表明, 样品材料粉体近似为球形, 粒径为 50 nm左右, 热分解反应温度较低 (269.4 ℃) 且含较多的结晶水。充放电结果表明, 当 Cu的掺杂量为 5%时, 样品电极在恒流 80 mA/g下充电 6 h, 40 mA/g放电, 终止电压为 1.0 V时, 放电电压稳定于 1.260 V的时间较长, 开路电位为 1.462 V, 放电比容量可达 362.976 mA·h/g 且循环充放电性能较好。

关键词: 络合反应冷冻共沉淀法; 铜掺杂; 纳米非晶相氢氧化镍; 物理特征; 电化学性能

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