

CHARGE/DISCHARGE PROPERTIES OF MECHANICALLY ALLOYED CATHODE MATERIAL-NiS₂ FOR Na/NiS₂ CELLS

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Abstract. A convenient approach has been proposed to synthesize the cathode material-NiS₂ for Na/NiS₂ cells by mechanically alloying (MA), whereafter the wet milling process was applied with normal hexane as the milling solvent to make the well-distributed powder particles. The cell shows a high initial discharge capacity of 577 mAh/g with the electrolyte of 1 M NaCF₃SO₃ dissolved in TEGDME.

1. INTRODUCTION

Since 80s of the 20th century, with the increasing popularity of portable electronic products as well as the pressing need for high specific energy storages in aviation, aerospace, electric vehicles and other high-tech fields, nickel-hydrogen batteries and lithium-ion batteries as the representatives of the high specific energy rechargeable battery system came into being, and were widely applied in each profession. However, due to the lower capacities of the existing active materials, they still can't meet the general requirements of ideal EVs to the traction battery powers (high energy density of 10 ~100 Wh/kg, high power density of 500~1500 W/kg, low cost of 50 \$/kWh, long cycle life and environmentally friendly, etc.) [1]. Meanwhile, the concerns over the environmental consequences of using fossil fuels and their resource constraints, along with worries over energy security, both have led to growing interest in the research and development of new battery system, such as exploiting new electrode materials and developing better electrolytes.

According to the 3E principle proposed by P. Rüetschi, [1] which contains energy, economics and environment, metal sulfides have been hailed as one

of the most promising cathode materials for it is cheap, non-toxic, available in abundance and meanwhile provide high energy density. Since the electrochemical properties of FeS₂, FeS, Ni₃S₂, and NiS as cathode materials in sodium/metal sulfide cells have been reported many times by different research groups, and all showed the rosy prospects in the application fields of EVs and HEVs even if their cycle properties are still to be improved. Therefore, in this study, we will focus on the discussion of nickel disulfide (NiS₂), including its synthesization, charge/discharge capacities and cycle life in Na/NiS₂ cells to assess whether it owns the specific superiority as a kind of cathode material in comparison with others.

As everyone knows, the 3d transition metal of nickel disulfide processes the cubic pyrite structure and shows interesting photo-electro-magnetic properties, [2] so they are widely used as hydrodesulfurization catalysts, photoactive materials, magnetic materials and solid-state lubricants and so on, and therefore there also exists lots of routes to obtain this production, from the traditional method by reacting stoichiometric amounts of their constituent elements in the evacuated silica tubes

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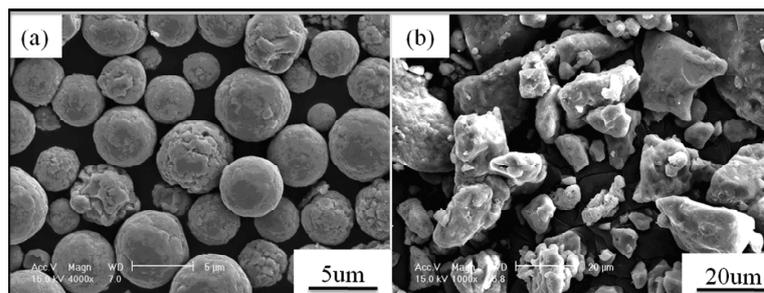


Fig. 1. FE-SEM micrographs of the starting materials of nickel: (a) and sulfur: (b) powders.

at high temperature (1000-1200 °C) [3] to the solid-state reaction between potassium hexafluoronickelate (IV) and sodium pentasulfide hydrate at -65 °C, [4] from the way of precursor-synthesis [5] to the low-temperature solventothermal synthesis. [6,7] However, it is difficult to control the process of manufacture for not only the high temperature or easily to be contaminated, but also the high cost or the complex course. Here, we will report a dry, high-energy ball milling technique employed in the production of a variety of commercially useful and scientifically interesting materials and by which fine final particles can be formed from elemental raw powders through mechanochemical reactions.

2. EXPERIMENTAL

2.1. The synthesis of NiS₂

According to the chemical formulation of NiS₂, raw nickel powders (-325 mesh, 99.9%) and sulfur powders (-100 mesh, 99.5%) along with the grinding mediums (stainless steel balls, 3 mm) were put together into the jar in the argon filled glove box. The atomic ratio of nickel/sulfur is 1:2, and the BPR (ball powder ratio) is 30:1. Meanwhile, in order to prevent the excessive cold welding between the starting elements or the new compounds, about 0.2 g stearic acid (CH₃(CH₂)₁₆CO₂H) as a kind of PCA (process control agent) was added in the beginning, which can be decomposed during high-energy milling process to cover on the surfaces of the powder particles and decrease the level of agglomeration. The total milling time for the complete synthesis of NiS₂ is 4 hrs, and what is said above is called the dry milling process, in which the SPEX miller was used. Actually, in order to improve the particle size distribution and disperse the agglomerated NiS₂ powders to augment the contact areas between the active materials, wet milling process was also applied using the low-energy ball milling machine, the

speed of which was set at 500 rpm. During this course, NiS₂ synthesized in the dry milling process and normal hexane (C₆H₁₄) used as a kind of milling solvent along with the grinding mediums (stainless steel balls, 5 mm) were loaded in the jar under the same atmosphere with the dry milling process, the BPR is 200:1 and total milling time is 30 hrs, then filtered and dried at 60 °C for 24 hrs.

2.2. The preparation of Na/NiS₂ cells

Commonly, the planetary ball mill was applied to prepared the homogeneously suspension which is constituted by 60 wt.% NiS₂ powder particles, 20 wt.% polyethylene oxide (PEO, (-CH₂CH₂O)_n, Aldrich Chem. Co.), and 20 wt.% Super-P (MMM Carbon) together dissolved in acrylonitrile (ACN, Aldrich Chem. Co.) solvent, the speed was set at 300 rpm and the milling time was 3 hrs, then we can get the slurry which was coated upon aluminum foil at normal temperature using the doctor-blade casting method to make the cathode for Na/NiS₂ cells. Finally, the cathode was dried in a vacuum oven for 24 hrs at 80 °C for the evaporation of solvent and then cut into the disk shape stored in the argon-filled glove box. The electrode thickness was about 20 μm and the diameter was about 1.1 cm. Meanwhile, the sodium anode was also prepared by cutting down from the sodium ingot (99.5%, Aldrich Co.) in the same atmosphere. The electrolyte was composed by dissolving 1 M sodium trifluoromethane sulfonate (NaCF₃SO₃) in tetraethylene glycol dimethylether (TEGDME).

2.3. The physical and structural characterization

In this research, the field emission scanning electronic microscope (FE-SEM) was used to investigate the surface morphologies of powder particles, and the X-ray diffraction (XRD) with filtered Cu Kα radiation was to examine the crystal structures and

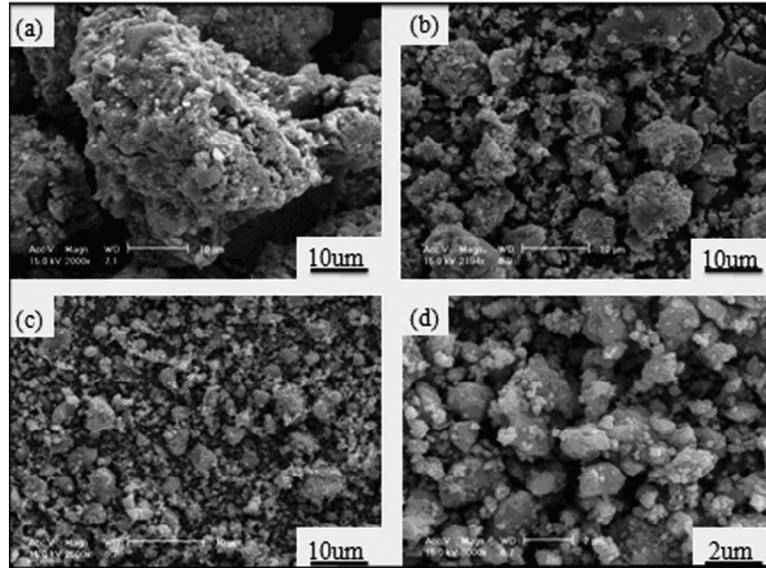


Fig. 2. FE-SEM micrographs of the mechanically alloyed NiS_2 powders in the dry milling process with different milling times: (a) 1 hr, (b) 2 hrs, (c) 3 hrs and (d) 4 hrs.

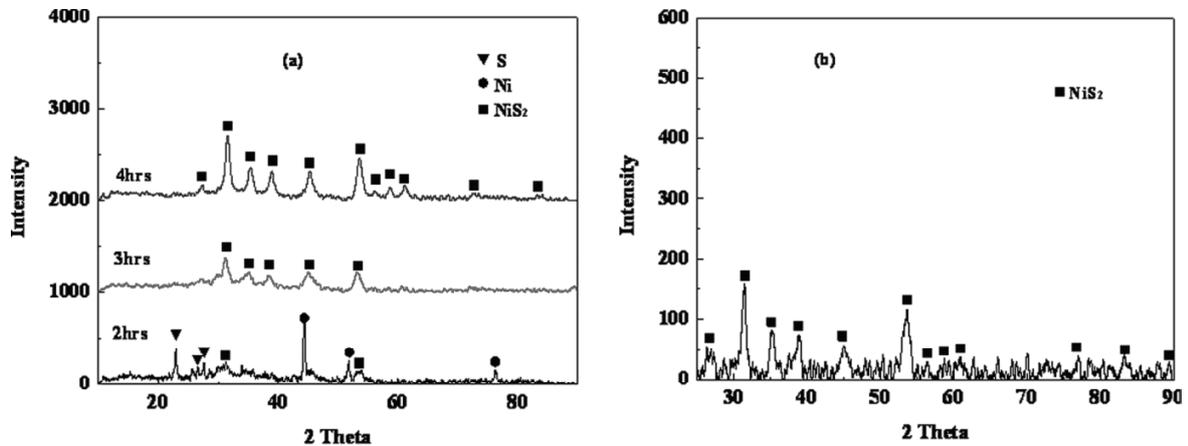


Fig. 3. XRD patterns of alloyed NiS_2 powder particles during (a) the dry milling process and (b) wet milling for 30 hrs.

sample types of the synthesized compounds, the experimental diffraction patterns were collected with a scanning step of 0.02° at the range of $10^\circ < 2\theta < 90^\circ$ using the graphite monochromator. The energy-dispersive X-ray spectrometer (EDS) was also applied to perform a chemical analysis in the FE-SEM to measure the surface image mapping of the alloyed NiS_2 powders. The transmission electron microscopy (TEM) micrographs were taken with an analytical microscope operated at 200 kV to observe the sample structures.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the original surface morphologies of the raw materials of nickel and sulfur used in the

experiment. The spherical shaped nickel powders have a good size distribution, with the mean size of 5 μm shown in Fig. 1a, meanwhile the irregular shape of sulfur particles, which are relatively bigger, were shown in Fig. 1b.

Actually, the dry ball milling process here is the mechanical alloying course what we have mentioned earlier, in which the powder particles were repeatedly flattened, cold welded, fractured, and rewelded, meanwhile results in the generation of a variety of crystal defect, such as the dislocation, stacking faults, vacancies and so on. As the balance between the cold welding and fracturing among the powder particles is responsible for the structural changes and alloying that occurs in them, we have researched the phase transformation (shown in Fig.

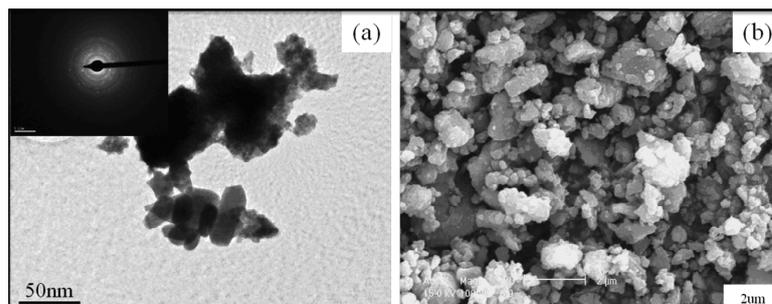


Fig. 4. TEM (a) and FE-SEM (b) micrographs of NiS₂ powder particles after wet ball milling process.

3) and the changes of morphologies between nickel and sulfur elements with different milling times shown in Fig. 2. Clearly we can see, the longer the milling time took, the smaller the powder particles and the better the size distributions could be achieved before the nickel disulfide was formed, which can also indirectly indicates that during the alloying process the rate of fracturing is larger and tends to be balanced with the rate of cold welding. Although the nickel disulfide was synthesized after 4 hrs ball milling and the mean particle size of 3.06 μm can be obtained, the ever-present phenomenon of agglomeration could not be improved greatly, even if the PCA had been added to prevent the excessive cold welding, and that is therefore why we need to conduct the wet milling process next to make the test results better for Na/NiS₂ cells.

The phase transformation during the dry ball milling process was completely recorded and displayed by XRD patterns shown in Fig. 3a, from which we can get the information as followings: after 2 hrs ball milling, NiS₂ was synthesized little by consuming part of the starting materials of nickel and sulfur powders, so we can observed their peaks also. While for 3 hrs most of nickel disulfide peaks replaced the original positions of raw elements, for the long time ball milling can generate high energy in the powder particles and results in the new phase formation. In

order to optimize the particle size distribution, ball milling was unceasingly carried out total for 4 hrs, clearly there are no new phase formed during this period, but the size distribution was greatly improved which can be certified by FE-SEM micrographs shown in Fig. 2 The XRD pattern of wet milled NiS₂ powder particles was shown in Fig. 3b, from which we can know there was no impurity formed by the virtue of the comparison with the represent cubic NiS₂ phase (JCPDS card no.85-1802). Meanwhile, from the broadened diffraction peaks, we can easily get the information that the powder particles were decreased greatly during this process, which can be also demonstrated by its FE-SEM image shown in Fig. 4).

In order to increase the chemical efficiency by cutting down the length of lithium ion intercalation and deintercalation, the wet ball milling process was conducted to decrease the particle size and ensure large areas contact between active materials for Na/NiS₂ cells. Fig. 4a shows the TEM micrograph and SAED patterns of wet milled NiS₂ powders, which indicates the nanocrystalline NiS₂ with an average size of 42 nm could be obtained easily and the calculation results of the ring patterns are also good agree with the represent cubic (NiS₂) phase (JCPDS card no.85-1802). However, for the features of nanopowders, the phenomenon of agglomeration

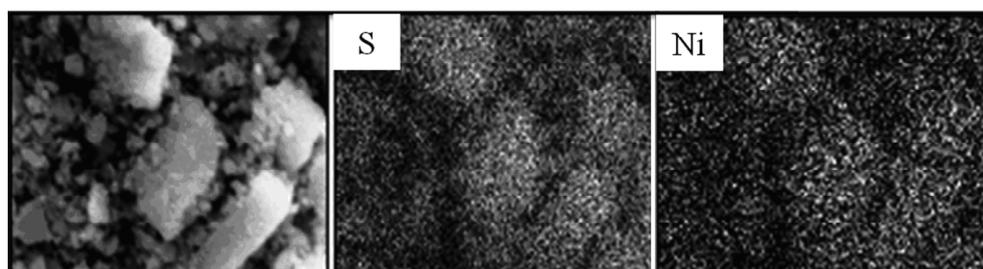


Fig. 5. FE-SEM and EDS mapping results of wet milled NiS₂ powders.

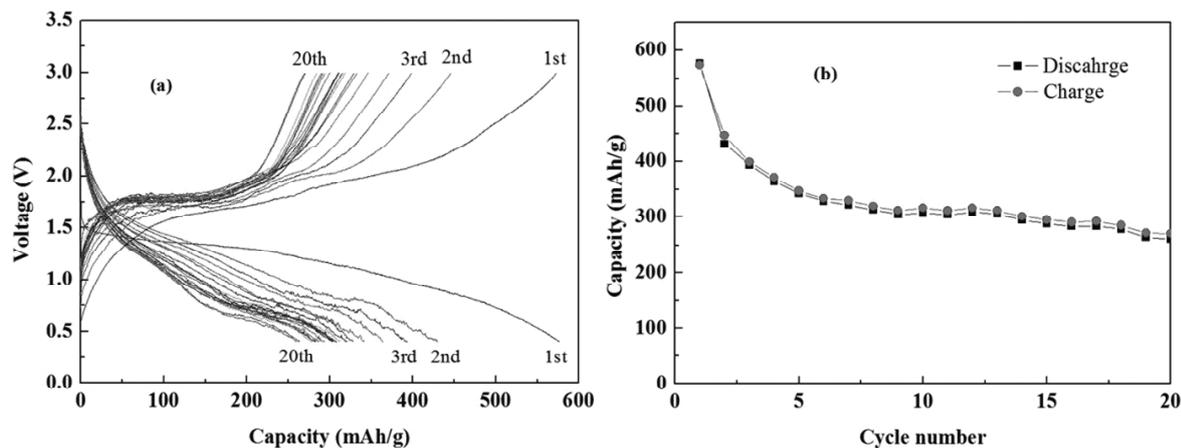


Fig. 6. Charge/discharge curves (a) and cycling performance (b) of Na/NiS₂ cells for wet milled NiS₂ powders.

can't be inevitable, and this would be definitely certified by Fig. 4b, even though the wet milling process was applied to disperse and separate the powder particles for 30 hrs. But compared with the dry production, the particle size distribution has been ameliorated greatly, and which can contribute to the thermal stability of Na/NiS₂ cells.

Fig. 5 shows the FE-SEM morphologies and the EDS mapping results of the wet milled NiS₂ powder particles. Clearly, the elements of nickel and sulfur can have a good distribution on the surface of nickel disulfide powders for its mechanochemical reaction during the dry milling process.

Fig. 6 shows the charge/discharge curves and cycling performance of Na/NiS₂ cells at room temperature using the wet milled nickel disulfide as the cathode materials. The cell was kept to equilibrate electrochemically for 1 hr and then a galvanostatic test was carried out between 0.3 and 3.0 V versus Na/Na⁺ with a current density of 87.4 mA/g. The first discharge/charge capacity was 577 and 573.5 mAh/g-NiS₂ respectively, and which shows the high coulombic efficiency of 99.4%. Meanwhile, the cell shows a plateau at about 1.3 V during the first discharge and then disappeared with the cycle numbers which may indicates that the complex chemical reactions occurred simultaneously. For all the testing process, the charge/discharge capacities faded with cycle numbers almost in the same pattern, which shows the good coulombic efficiency, and even after 20 cycles it still remains almost half of the initial discharge capacity about 270 mAh/g-NiS₂ which show that nickel disulfide synthesized by MA can provide high energy density and own good electrochemical property in Na/NiS₂ cells.

4. CONCLUSIONS

Nickel disulfides were synthesized by a high-energy dry milling process for 4 hrs and a wet milling process for 30 hrs, which can provide a high initial charge/discharge capacity of 573.5 and 577 mAh/g respectively and also show a high coulombic efficiency of 99.4% with sodium as the anode material. Meanwhile, after 20 cycles, it still remains almost half of the initial discharge capacity-about 270 mAh/g-NiS₂. So the rechargeable Na/NiS₂ batteries have a potential to be commercialized when the techniques are matured in the future.

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