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Hydroxylamine hydrochloride: A novel anode material for high capacity lithium-ion batteries
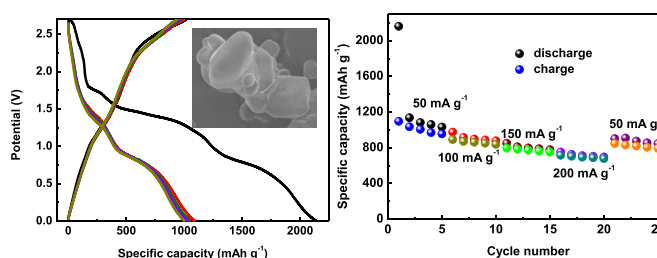
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HIGHLIGHTS

- H_3NOHCl is used as lithium storage material for the first time.
- H_3NOHCl exhibits high reversible capacity and outstanding rate property.
- H_3NOHCl delivers a charge capacity of 1018.6 mAh g^{-1} at 50 mA g^{-1}.
- H_3NOHCl delivers a charge capacity of 715.7 mAh g^{-1} at 200 mA g^{-1}.

GRAPHICAL ABSTRACT

ABSTRACT

H_3NOHCl is used for the first time as anode material for lithium-ion batteries. Electrochemical results show that H_3NOHCl with particle size of 4–12 μm can deliver an initial charge capacity of 1018.6 mAh g^{-1}, which is much higher than commercial graphite. After 30 cycles, the reversible capacity can be kept at 676.1 mAh g^{-1} at 50 mA g^{-1}. Up to 50 cycles, H_3NOHCl still maintains a lithium storage capacity of 368.9 mAh g^{-1}. Even cycled at 200 mA g^{-1}, H_3NOHCl can deliver a charge capacity of 715.7 mAh g^{-1}. It suggests that H_3NOHCl has high lithium storage capacity, excellent cycling stability and outstanding rate performance. Besides, the electrochemical reaction between H_3NOHCl and Li is also investigated by various ex-situ techniques. It can be found that H_3NOHCl irreversibly decomposes into Li_3N and LiCl during the initial discharge process and $LiNO_2$ can be formed after a reverse charge process.

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1. Introduction

Lithium-ion battery is considered as the most promising technology among the energy storage systems for cell phones, laptops, and other portable devices due to its high energy density and outstanding cyclability. At the same time, graphite has been used as an anode material in commercialized lithium-ion batteries for decades due to its low cost and high coulombic efficiency [1–3].

However, its low theoretical capacity (372 mAh g^{-1}) restrains further energy applications in high capacity storage field. Therefore, an enormous amount of attention has been focused on developing new anode materials with high lithium storage capacity, as well as acceptable rate performance and long cycling life for lithium-ion batteries.

In recent years, lithium transition metal nitrides, such as $Li_{3-x}Cu_xN$ [4], $Li_{2.6}Co_{0.4}N$ [5] and $Li_{2.6}Co_{0.2}M_xN$ (M: Cu, Fe, Ni) [6] have caught much attention as a result of their high capacity with good cycle performance in lithium deintercalation and intercalation. In addition, metal nitrides (such as Mn_3N_2 [7], VN [8], TiN [9], RuN [10], Sb_3N [11], CoN [12], CrN [13] and $Si_{0.76}N_{0.24}$ [14]) have been considered as attractive anode materials owing to the low and flat

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working potential, high reversibility and large reversible capacities. Recently, transition metal chlorides, such as CoCl₂ [15], AgCl and CuCl₂ [16], have also been used as lithium storage materials for lithium-ion batteries with good cyclic performance and good rate capability. Consequently, it can be expected that nitriding chlorides may deliver excellent electrochemical properties due to their composite structures, which probably combine the merits of metal nitrides and transition metal chlorides as high performance lithium storage materials.

In this work, we investigate the electrochemical performances of hydroxylamine hydrochloride (H₃NOHCl) as a novel lithium storage material by cyclic voltammetry (CV) and galvanostatic charge–discharge techniques. Besides, we utilize the ex-situ X-ray photoelectron spectroscopy (XPS) and ex-situ high resolution transmission electron microscopy (HRTEM) techniques to clarify the lithium storage mechanism. The electrochemical results show that H₃NOHCl is a potential high capacity anode material candidate for lithium-ion batteries.

2. Experimental

2.1. Material characterization

H₃NOHCl was commercial sample bought from Shantou Xilong Chemical Co. Ltd. and used as received without any purification. The structure, morphology and thermal stability of H₃NOHCl sample were characterized by means of X-ray diffraction (XRD, Bruker AXS D8 Focus diffractometer with Cu Kα radiation, $\lambda = 0.15406$ nm, a scan angle range of 10–80°, a step size of 0.1°, and a count time of 1 s), scanning electron microscopy (SEM, JEOL S3400), thermogravimetric (TG) and differential thermal analysis (DTA, Seiko TG/DTA 7300, a heating rate of 10 °C min⁻¹, argon atmosphere).

The electrodes in Swagelok cells for high-resolution transmission electron microscopy (HRTEM, TECNAI G2 F20) and selected area electron diffraction (SAED) and X-ray photoelectron

spectroscopy (XPS, Kratos Axis Ultra Spectrometer with Al Kα radiation) measurements were disassembled in an argon-filled glove box. The lithiated and delithiated samples for HRTEM and SAED observations were scraped from the electrodes in argon-filled glove box and ultrasonically dispersed in dimethyl carbonate in sealed bottles and dropped on to a carbon-coated TEM grid, then vacuumed for 5 h. The TEM grid covered with sample was transferred into TEM chamber within twenty seconds under continuous argon-blowing. The lithiated and delithiated electrodes for XPS measurement were washed by dimethyl carbonate and then vacuumed for 5 h before investigation. The as-prepared samples were also transferred into XPS chamber within twenty seconds under continuous argon-blowing.

2.2. Electrochemical characterization

The working electrodes were consisted of active material (H₃NOHCl), carbon black and polyvinylidene fluoride at the weigh ratio of 8:1:1 in N-methylpyrodine and then pasted on a Cu foil. The electrodes were dried at 100 °C under vacuum condition for 12 h and then cut into discs with a diameter of 15 mm. The samples were put into Swagelok cells for electrochemical cycling. The Swagelok cells were assembled in an argon-filled glove box using Whatman glass fiber as separator, a pure lithium metal foil as counter electrode, and 1 M LiPF₆ in a mixture of dimethyl carbonate and ethylene carbonate (1:1, v/v) as electrolyte. Firstly, working electrode was put into the Swagelok cell, and then separator, lithium metal, electrolyte were placed/dropped one by one in the chamber. Finally, the Swagelok cell was ready for electrochemical cycles after screwing the screw-cap on the cell body tightly. The structure of Swagelok cell can be found elsewhere [17–19].

Galvanostatic charge–discharge cycles for Swagelok cells were recorded on multichannel Land battery test system at different charge–discharge rates between 0.0 and 2.7 V. CV tests were carried out on Bio-Logic VSP EC-Lab electrochemical workstation with a potential range from 0.0 to 2.7 V at a scanning rate of 0.1 mV s⁻¹.
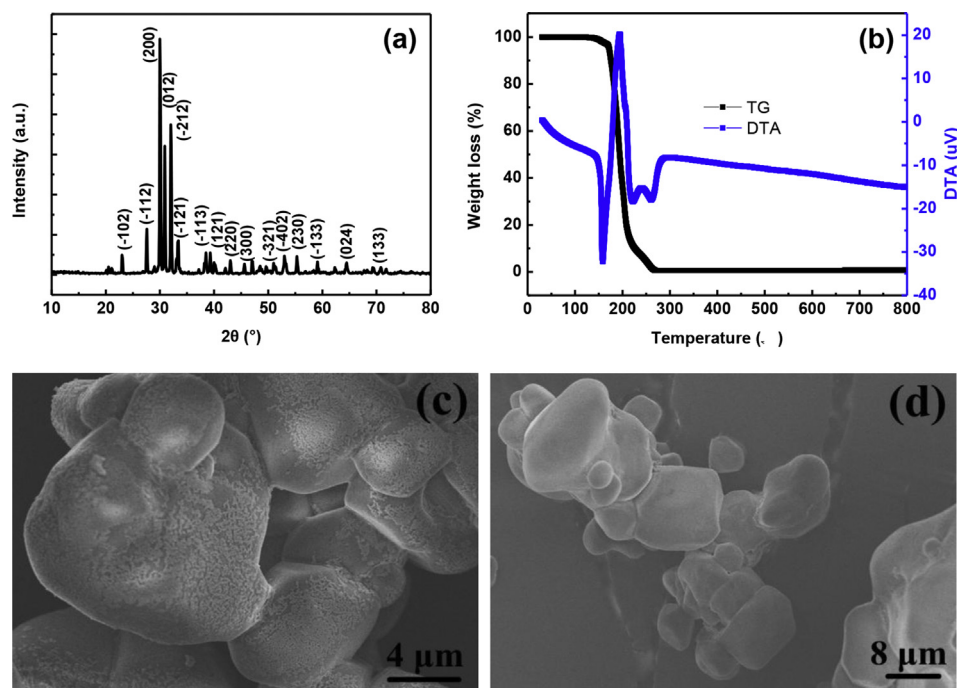

Fig. 1. (a) XRD patterns of H₃NOHCl, (b) TG–DTA curves of H₃NOHCl, (c, d) SEM images of H₃NOHCl.