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Enhanced stability performance of nickel nanowire with 3D conducting network for planar sodium-nickel chloride batteries

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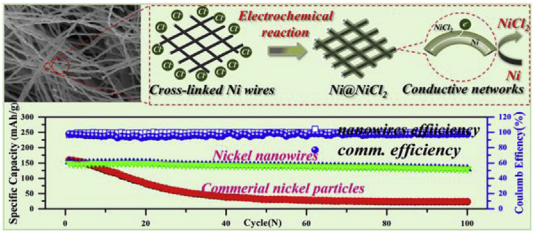
HIGHLIGHTS

- A new cathode composed of Ni nanowires is proposed for planar Na−$NiCl_2$ batteries.
- A high Na-storage capacity of 130 mA h g^{-1} (~14 mA h cm^{-2}) is achieved.
- A high cut-off energy density of 360 W h kg^{-1} is achieved at 0.05 C.
- The nanowire morphology can buffer the aggregation during charge-discharge process.

GRAPHICAL ABSTRACT



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ABSTRACT

High temperature sodium batteries with inorganic electrolytes are attracting increasing attention due to their high thermal stability, reliability, long-cycle life and safety. Despite the intensive investigation of Na-$NiCl_2$ batteries during last decades, designing a stable conducting network in the cathode is still challenging but desirable. In this work, a new cathode structure composed of Ni nanowires with an effective electron conducting network is proposed for planar sodium−nickel chloride batteries. During the first stage of charge, Ni nanowires reacted with Cl ion to form $NiCl_2$ on the surface and the excessive Ni nanowires inside can serve as conducting framework to facilitate the fast electron transport. As expected, the metal nanowires show a high specific capacity of 130 mA h g^{-1} (~14 mAh cm^{-2}) at 0.05 C after 100 cycles. Meanwhile, the batteries show stable cycling performance at 0.05 C with a high cut-off energy density of 360 W h kg^{-1}, much higher than the traditional tubular sodium-nickel chloride batteries (~100 Wh kg^{-1}). Scanning electron microscope (SEM) images of the cathode after long cycling reveal the ultra-slow growth of Ni particles, confirming the excellent stability of the prepared nanowires cathode.

1. Introduction

Sodium secondary batteries with a high energy density, acceptable cycle life, low cost, and high safety that goes beyond the security limitations of sodium-sulfur batteries are required for the increasing demands of energy storage applications, such as the growth of renewable electricity generation from wind, solar power resources, the electric power grid and transportation applications [1–4]. Among these sodium-based batteries, ZEBRA batteries are extremely attractive due to their high theoretical specific energy density, high energy efficiency and good cycle life [5–9]. As shown in Fig. 1, the Na-$NiCl_2$ battery is usually operated under high temperature (280 °C) by using a thick β″-Al_2O_3 solid electrolyte (BASE) to separate the Ni/NaCl cathode and the sodium anode [5,10]. At

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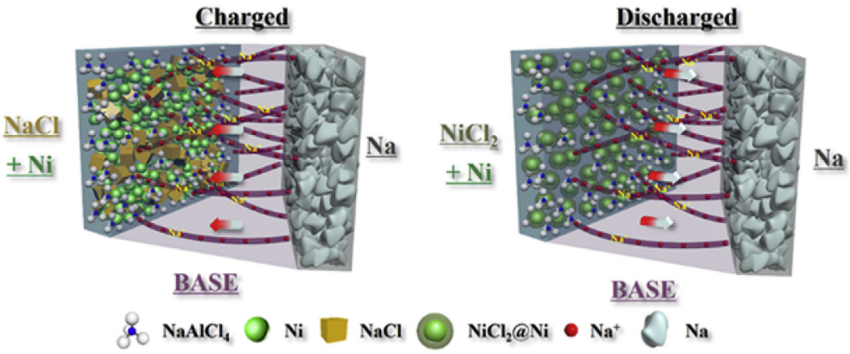

Fig. 1. Scheme of the electrochemical process of the Na–$NiCl_2$ battery.

such high operating temperature, the formation of low-conducting $NiCl_2$ and the rapid growth of Ni particles are extremely prone to trigger over-aggregation of active materials during the electrochemical reaction. Consequently, the accumulated $NiCl_2$ and Ni particles would reduce the effective contact areas between active materials and electrolyte. As illustrated in Fig. 2a, the closely packed Ni particles in traditional Ni cathode don't have enough electrical paths between the active particles. During cycling, the electrical pathway limitation and the volume expansion can gradually destroy the conducting network in the cathode, and resulting in performance degradation [11,12]. To improve the electronic conductivity of the electrode, the conventional tubular Na–$NiCl_2$ batteries are usually loaded with excessive Ni content in the cathode. However, overall energy density obtained from a conventional tubular Na–$NiCl_2$ battery is only about 120–130 W h kg^{-1} [2,13]. Based by the Faraday's laws, the theoretical specific energy density of Na–$NiCl_2$ batteries decreases with the increase of excess Ni content as Fig. S1 indicates. Therefore, a more effective method is required to solve the problem faced by ZEBRA batteries.

General strategies on improving the electrochemical performance of sodium nickel chloride are as follows: (a) Increasing the mass ratio of electron-conductive materials by changing the Ni/NaCl molar ratio or applying electron-conductive additives (include Fe, Al, graphite) [14–16] to ensure the fast ion and electron transportation during the discharge-charge process. (b) Decreasing the temperature [17] or use additives such as S [12], FeS [18], Ni_3S_2 [19] to reduce the growth of Ni grain. (c) Providing the overcharge protection for the cathode by introducing additives, such as NaF and other sodium halides (NaI and NaBr). Up to now, structure design of the cathode that can improve the performance of ZEBRA batteries hasn't been reported. According to previous reports on lithium ion batteries, one-dimensional nanostructured materials such as nanotubes [20], nanowires [21] and nanorods [22], etc., can buffer self-aggregation and keep effective contact areas large by offering clean surface. Therefore, ultra-long nanowires can be one of the promising structures for cathode materials of ZEBRA batteries.

In this work, a magnetic field assisted hydrothermal method was developed to synthesize the magnetic nickel (or Fe, Co) nanowires. As shown in Fig. 2b, the electrode constructed by as-prepared Ni nanowires provided a large surface area and defect sites to form $NiCl_2$ on the metal surface, which could effectively reduce the ion diffusion length and increase electrolyte ion accessibility. During the cell tests, the conducting metal nanowires show a high specific capacity of 130 mA h g^{-1} at a rate of 0.05 C. Even at a high rate of 1 C, the batteries based on the conducting metal nanowires could still deliver a high discharge capacity of 65 mA h g^{-1} after 100 cycles, displaying good rate performance. Moreover, the batteries showed stable cycling performance at 0.05 C with a high cut-off energy density of 360 W h kg^{-1}. SEM images of the cathode after different cycles were also investigated to reveal the advantages of the designed cathode structure during the discharge/charge process. The promising performance makes them strong candidates for the industrial application of Na/β″-Al_2O_3-based rechargeable batteries.

2. Experimental section

2.1. Cathode materials and electrolyte preparation

All chemical reagents in this work were analytical grade and used without further purification. Nickel powder (Type 255, Novamet), sodium chloride powder (British Salt), aluminum powder (granular, 99.7%, Sigma-Aldrich), ferrous sulfide (Fe, 60%–70%,

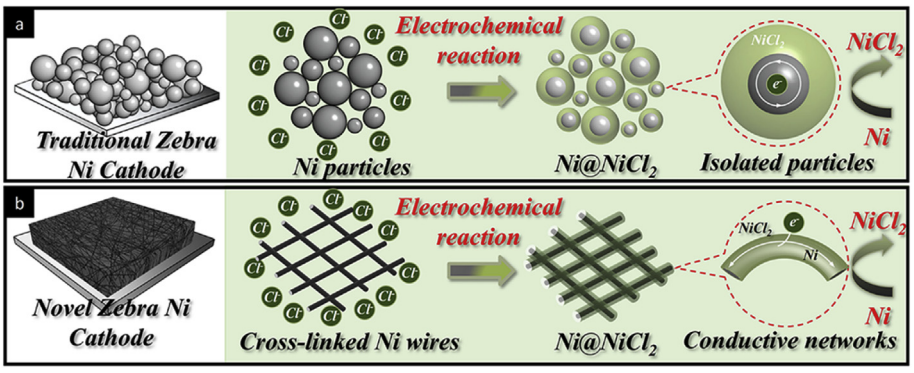

Fig. 2. Schematic illustration of the comparison between (a) the traditional cathodes composed of isolated nickel particles and (b) the designed one-dimensional architecture constructed by the Ni nanowires.