Journal of Power Sources 396 (2018) 379–385

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Self-supported $Na_{0.7}CoO_2$ nanosheet arrays as cathodes for high performance sodium ion batteries

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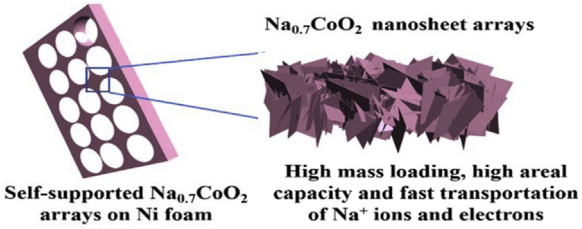
HIGHLIGHTS

- $Na_{0.7}CoO_2$ nanosheet arrays as cathode for NIBs have been fabricated.
- A mass loading of 8 mg cm^{-2} have been achieved for the $Na_{0.7}CoO_2$ electrode.
- An initial capacity of 145.2 mAh g^{-1} at 1 C is derived for the $Na_{0.7}CoO_2$ electrode.
- The areal capacity of the $Na_{0.7}CoO_2$ electrode is calculated to be 1.16 mAh cm^{-2}.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
$Na_{0.7}CoO_2$ nanosheet arrays
Cathode materials
Areal capacity
Mass loading

ABSTRACT

For the first time, we successfully synthesize a self-supported $Na_{0.7}CoO_2$ nanosheet arrays via the facile "sodiation and post-calcination" method. Different from the traditional high temperature solid-state technique, this facile strategy can easily maintain the novel construction of the precursor. A mass loading as high as 8 mg cm^{-2} is achieved for the $Na_{0.7}CoO_2$ electrode with an initial capacity of 145.2 mAh g^{-1} at 1 C. Most importantly, the corresponding areal capacity for the $Na_{0.7}CoO_2$ electrode is calculated to be 1.16 mAh cm^{-2}. This superb areal capacity is higher than that of the previously reported cathode materials. This special "sodiation and post-calcination" protocol mentioned in this article guarantees the high mass loading of $Na_{0.7}CoO_2$ on Ni foam, providing a straightforward direction for engineering high-areal-capacity cathode materials.

1. Introduction

The energy crisis provoked by the shortage of fossil materials is stimulating people to develop an efficient technology to solve the energy storage issues of the renewable energy resources [1–4]. Since lithium ion batteries (LIBs) were first commercialized by Sony company in 1991, tremendous efforts have been devoted to exploring the optimal electrode materials with high energy and power for LIBs [5]. Unfortunately, the limited lithium resources severely impede the large-scale implementation of LIBs. On account of the large storage of sodium resources and the similar properties with lithium element, much attention has been shifted to sodium ion batteries (NIBs) [6–8]. Especially, cathode materials are always considered to be an significantly important component in NIBs, substantially influencing the electrochemical performance of the full NIBs [9–11]. Among of them, layered metal oxides P2-Na_xCoO_2 occupy the advantages of simple structure, high capacity and ease of synthesis, are generally believed to be one of the potential cathode materials for NIBs [12–17]. Most importantly, It has been reported that the Na^+ ion diffusion coefficients of Na_xCoO_2 ($0.5–1.5 \times 10^{-11}$ cm^{-2} s^{-1}) is higher than that of the commercialized $LiCoO_2$ (1×10^{-11} cm^{-2} s^{-1}), giving the hope for probing this kind of cathode materials on behalf of their further applications [4]. However,

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https://doi.org/10.1016/j.jpowsour.2018.06.047
Received 12 April 2018; Received in revised form 21 May 2018; Accepted 10 June 2018
0378-7753/

the poor cycling performance of the Na_xCoO_2 electrode extremely impedes the following development. As all we know, there exists intricate phase transitions for the P2—$Na_{0.7}CoO_2$ electrode in the charge-discharge process. These phase transitions are generally related to the Na^+/vacancy ordering patterns probably caused by the cation interactions of Na^+-Na^+, Na^+-$Co^{3+/4+}$ and $Co^{3+/4+}$-$Co^{3+/4+}$ [12]. It is believed that this phase transitions lead to an affiliated activation energy barrier for Na^+ storage, bringing out the serious capacity loss in the repeated charge-discharge process. In this regard, a myriad of trials have been done to suppress the Na^+/vacancy ordering condition. Recently, it has been reported that the cationic substitution (Ti^{4+}, Cu^{2+} et al.) method can effectively alleviate the Na^+/vacancy ordering condition existed in $Na_{0.7}CoO_2$ and guarantee the cycling longevity of the electrode [12]. However, up to now, the main concerns around the Na_xCoO_2 cathode materials are still centered on reaction mechanisms and structural analysis, few investigations are focused on the morphological control and thereafter the effect on the electrochemical performance [13–18].

In light of the larger radius and heaver mass of Na^+ ions, the dramatic construction collapse combined with embrittlement and detachment of the active materials is more severe especially for the powdered electrode materials. In view of this, engineering arrays directly on conductive substrates have been proved to be an efficient protocol to solve abovementioned issues [19–29]. This open arrayed framework without isolated polymeric binders possesses desired electronic conductivity, sufficient volume change accommodation and strong architecture, can allow the Na^+ ions diffusion more efficiently without destroying the uniform construction and pledges the stable cycling performance. For example, self-supported $LiCoO_2$ nanosheet arrays, $LiMn_2O_4$ nanowall arrays and $Na_{0.44}MnO_2$ arrays have been obtained and applied in LIBs and supercapacitors (SCs) with impressive electrochemical performance [30–32]. The $LiCoO_2$ nanosheet array electrode can deliver a reversible capacity of 104.6 mA h g^{-1} at 10 C rate and sustain a capacity retention of 81.8% at 0.1 C rate undergoing 1000 cycles. The $LiMn_2O_4$ nanowall array electrode exhibits high specific capacity up to 131 mA h g^{-1} (or 0.29 mA h cm^{-2}) with outstanding cycling stability and rate capability. Nevertheless, to the best of our knowledge, there is still no reports about arrayed cathode materials for NIBs. Simultaneously, the derived arrays always demonstrate limited mass loading (< 2 mg), leading to the unsatisfied areal capacity which is far from the implementation.

Based on previous studies [24–26], for the first time, we have successfully synthesized $Na_{0.7}CoO_2$ nanosheet arrays via the facile "sodiation and post-calcination" protocol. The relatively low temperature (~600 °C) synthesized strategy pledges the construction stability of the $Na_{0.7}CoO_2$ arrays. Simultaneously, the high mass loading of $Na_{0.7}CoO_2$ (~8 mg) on the Ni substrate enables the high areal capacity of 1.16 mAh cm^{-2}.

2. Experimental section

2.1. Synthesis of $Na_{0.7}CoO_2$ nanosheet arrays and characterization

The $Na_{0.7}CoO_2$ nanosheet arrays were prepared on the basis of the previous reports [33]. Firstly, 0.58 g $Co(NO_3)_2{\cdot}6H_2O$ was homogeneously dissolved in 40 mL distilled water, then 0.3 g NH_4F and 0.6 g urea were added to the aforementioned solution. Ni foams (2 × 4 cm^2) were treated with 3 M HCl for 15 min followed by the rinsed processes with water and ethanol for several times. Then the pretreated Ni foam and the solution were transformed to a 50 mL Teflon-lined stainless-steel autoclave and were held at 120 °C for 9 h. After drying at 80 °C for 12 h, the obtained arrays were immersed in NaOH solution (2 M) at 80 °C for 8 h followed by the calcination at 600 °C for 3 h in air. Ultimately, the $Na_{0.7}CoO_2$ nanosheet arrays were successfully obtained. On the other hand, the irregular $Na_{0.7}CoO_2$ (*i*-$Na_{0.7}CoO_2$) were prepared by thoroughly mixing commercial Co_3O_4 and Na_2CO_3 powders with a certain proportion followed by calcination at 850 °C for 8 h in air. The structure, chemical composition, and morphology of $Na_{0.7}CoO_2$ were characterized by X-ray diffraction (XRD, Rigaku D/max X-ray diffractometer, Cu Ka radiation), X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600 W), field emission scanning electron microscopy (FESEM, JSM-6330F), energy-dispersive spectroscopy (EDS, X-Max 50), transmission electron microscopy (TEM, JSM-2100), and high-resolution TEM (HRTEM). The weight of the active materials on the Ni substrate (~8 mg cm^{-2}) was determined by a micro balance (METTLER TOLEDO, XS3DU, Switzerland, d = 0.001 mg). It is noted that the reaction of Ni foam can be significantly avoided because of the protection of compact arrayed materials on the Ni foam. So the quality of Ni foam approximately has no change during the reaction. It is also proved that the Ni foam has no chage during the reaction according to the following XRD patterns of $Na_{0.7}CoO_2$ arrays. This is consistent with the result of the previous report [33]. The generation of NiO can be nearly ignored on $Na_{0.7}CoO_2$ arrays especially compared with the high mass loading of $Na_{0.7}CoO_2$. The mass of Ni foam (m_1) and $Na_{0.7}CoO_2$ film (m_2) was carefully calculated by a high precision microbalance. The difference value is the mass loading of $Na_{0.7}CoO_2$. The mass loading of $Na_{0.7}CoO_2$ films was calculated based on the average mass of 10 samples.

2.2. Electrochemical measurements

The electrochemical performance of the $Na_{0.7}CoO_2$ array and *i*-$Na_{0.7}CoO_2$ electrodes were investigated using the CR2025 coin cells. The coin cells were assembled in argon-filled glove box in which the water and oxygen content were remained less than 1 ppm. The $Na_{0.7}CoO_2$ array electrode were directly used as the working electrodes without binders and conductive additives. The *i*-$Na_{0.7}CoO_2$ powders were mixed thoroughly with polyvinylidene fluoride (PVDF) and carbon black (with the weight ratio of 8:1:1). Then the powders were dissolved into a N-methylpyrrolidone (NMP) solvent and stirred for 12 h at the ambient temperature. The solution was then coated onto an Ni foil and dried at 80 °C for 12 h in a vacuum chamber. The mass loading on Ni foil was controlled around 8 mg cm^{-2}. The $Na_{0.7}CoO_2$ and *i*- $Na_{0.7}CoO_2$ films were cut into the electrode with a diameter of about 12 mm. Na foils were used as the counter electrode, and the electrolyte was 1 M NaPF6 in EC/DMC with a volume ratio of 1:1. Cyclic voltammograms (CVs) were obtained using a CHI760E electrochemical workstation between 2 and 3.8 V at a scan rate of 0.5 mV s^{-1}. Charge-discharge measurements were carried out at various current rates with voltage range from 2 to 3.8 V on a Land battery test system. Electrochemical impedance spectroscopy (EIS) was performed on a CHI760E electrochemical workstation in the frequency range from 0.01 Hz to 100 kHz.

3. Results and discussions

Fig. 1 is the schematic illustration of the synthetic process for the $Na_{0.7}CoO_2$ array. First of all, we utilized the typical hydrothermal reaction to deposit uniform $Co(OH)_2CO_3$ precursor nanosheet arrays on Ni foam [33]. After Na^+ ions exchange procedure via the NaOH solution and the followed calcination treatment in air, we obtained the target $Na_{0.7}CoO_2$ nanosheet arrays. Fig. 2a is the X ray diffraction

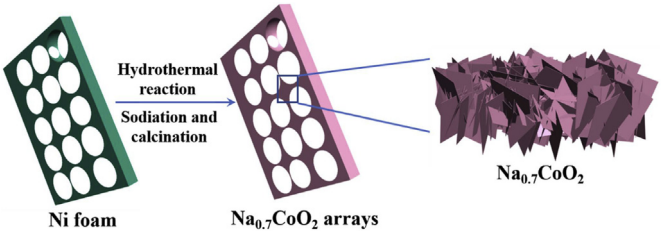

Fig. 1. Schematic illustration of $Na_{0.7}CoO_2$ arrays fabrication process.