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Controlled phase stability of highly Na-active triclinic structure in nanoscale high-voltage $Na_{2-2x}Co_{1+x}P_2O_7$ cathode for Na-ion batteries

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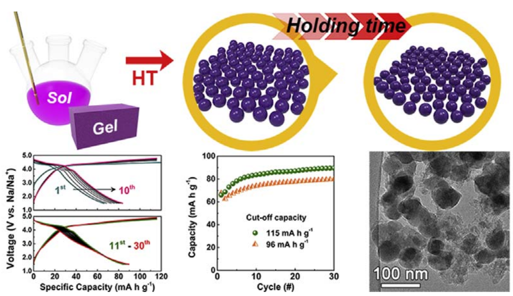
HIGHLIGHTS

- The synthetic condition of metastable $Na_{2-2x}Co_{1+x}P_2O_7$ rose phase is established.
- Rose is synthesized in $Na_{2-2x}Co_{1+x}P_2O_7$/C nanocomposite in the wide Na/Co ranges.
- $Na_{2-2x}Co_{1+x}P_2O_7$/C exhibits a long plateau in high-voltage range with a 90 mA h g^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

With the increasing demand for high energy density in energy-storage systems, a high-voltage cathode is essential in rechargeable Li-ion and Na-ion batteries. The operating voltage of a triclinic-polymorph $Na_2CoP_2O_7$, also known as the rose form, is above 4.0 V (vs. Na/Na^+), which is relatively high compared to that of other cathode materials. Thus, it can be employed as a potential high-voltage cathode material in Na-ion batteries. However, it is difficult to synthesize a pure rose phase because of its low phase stability, thus limiting its use in high-voltage applications. Herein, compositional-engineered, rose-phase $Na_{2-2x}Co_{1+x}P_2O_7$/C (x = 0, 0.1 and 0.2) nanopowder are prepared using a wet-chemical method. The $Na_{2-2x}Co_{1+x}P_2O_7$/C cathode shows high electrochemical reactivity with Na ions at 4.0 V, delivering high capacity and high energy density.

1. Introduction

High-voltage cathodes are being developed for applications in rechargeable Li-ion batteries (LIBs) and Na-ion batteries (NIBs) [1–5]. In NIBs, the net energy density decreases because of the intrinsically low practical capacity due to the higher equivalent weight of Na compared to that of Li and limited Na ion migration due to the larger ionic radius of the Na ion compared to that of the Li ion [5]. Hence, it is essential to use a high-voltage cathode to increase the energy density. However, much effort is required to develop high-voltage cathode materials for potential use in large-scale energy systems such as electric vehicles and energy storage systems [5,6].

Pyrophosphates are among materials that can be used as high-voltage cathodes [7]. Among them, $Na_2FeP_2O_7$ is one of the most investigated materials because of its high rate capabilities and long lifespan performances in the micron- and/or nano-structured form; however, they exhibit a relatively low operating voltage of 3.0 V (vs. Na/Na^+) [8]. In polyanionic materials with the same structure, the operating voltage can be increased if the transition metals (TMs) such as Mn, Co, or Ni are used instead of Fe under electrochemical TM^{2+}/TM^{3+} redox reactions [9,10]. Thus, some studies have been conducted on counterparts using other TMs, particularly on the Co-based

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Table 1
Parameters of phase diagram of $Na_{2\text{-}2x}Co_{1+x}P_2O_7$ prepared by solid-state reaction.

$Na_{2\text{-}2x}Co_{1+x}P_2O_7$ (Holding time: 1 h)			
Temp.	$Na_2CoP_2O_7$	$Na_{1.8}Co_{1.1}P_2O_7$	$Na_{1.6}Co_{1.2}P_2O_7$
Over 650 °C	-	-	rose + impurity
650 °C	blue	rose + blue	rose + impurity
600 °C	blue	rose	rose + impurity
550 °C	blue	rose + impurity	rose + impurity
Below 550 °C	rose + blue	rose + impurity	rose + impurity
$Na_{2\text{-}2x}Co_{1+x}P_2O_7$ (Holding time: 6 h)			
Temp.	$Na_2CoP_2O_7$	$Na_{1.8}Co_{1.1}P_2O_7$	$Na_{1.6}Co_{1.2}P_2O_7$
Over 650 °C	-	-	rose
650 °C	-	-	rose + blue
600 °C	-	rose + blue	-

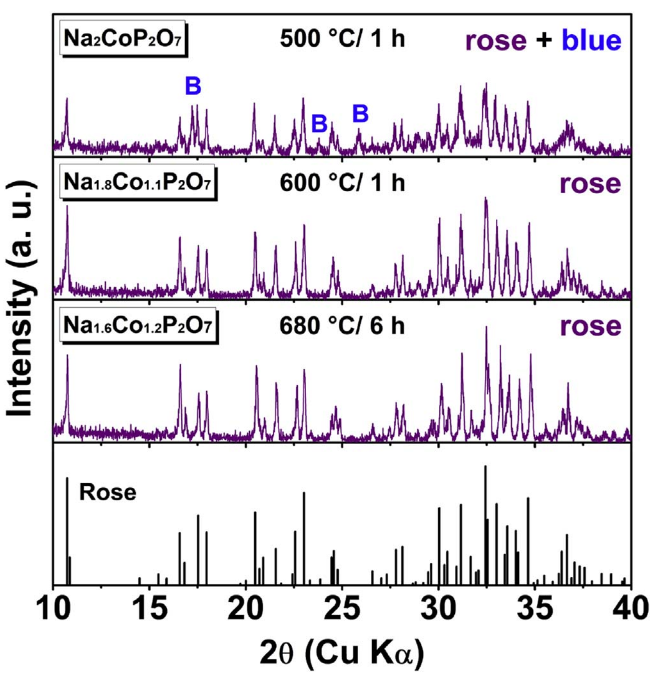

Fig. 1. Representative XRD patterns of rose phase $Na_{2\text{-}2x}Co_{1+x}P_2O_7$ prepared by a solid-state reaction.

pyrophosphate compound $Na_2CoP_2O_7$, which exhibits an average operating voltage of ~4.3 V (vs. Na/Na^+). $Na_2CoP_2O_7$ exhibits a synergistic effect at high operating voltages while maintaining excellent electrochemical performance similar to that of $Na_2FeP_2O_7$.

$Na_2CoP_2O_7$ exists in three different structures: orthorhombic, tetragonal, and triclinic polymorphs [11,12]. Among them, the orthorhombic and triclinic polymorphs are referred to as "blue" and "rose" phases, respectively; the names originated from their color. They are generally synthesized using solid-state or wet-chemical synthetic processes. The orthorhombic polymorph has the most thermodynamically stable phase, whereas the triclinic polymorph exists in a metastable form. Some studies have been conducted on the electrochemical performances of the two phases for NIB electrode. The discharge capacity of the orthorhombic-polymorph $Na_2CoP_2O_7$ (blue phase) is in the range of 75–80 mA h g^{-1} with an average operating voltage of only 3.0 V (vs. Na/Na^+), which is substantially lower than the generally expected Co^{2+}/Co^{3+} redox-reaction voltage observed in polyanionic materials [9,13]. However, the triclinic polymorph (rose phase), which has the same crystal structure as that of $Na_2FeP_2O_7$, exhibits a high average operating voltage of 4.3 V (vs. Na/Na^+), which is one of the NIB cathode materials that electrochemically react with Na ions at high-voltage ranges [14–16]. Hence, it is important to synthesize the rose-phase $Na_2CoP_2O_7$, particularly in the nano-structured rose phase to activate more electrochemical reactions.

Unfortunately, it is difficult to synthesize a pure rose phase in ambient synthetic conditions because of its low stability as mentioned previously. Thus, few studies have been conducted on the synthesis of rose phases. Recently, however, $Na_2CoP_2O_7$ was compositionally engineered, thus demonstrating the potential of synthesizing a pure rose phase. In micron-sized $Na_2CoP_2O_7$ particles synthesized by a conventional solid-state reaction, the metastable rose-phase $Na_2CoP_2O_7$ can be synthesized by controlling the element ratio (Na and/or Co) of its compounds. In other words, the non-stoichiometric factor in $Na_2CoP_2O_7$, *i.e.*, $Na_{2\text{-}2x}Co_{1+x}P_2O_7$ (Na-deficiency/Co-excess for charge balance), affects the phase formation of $Na_2CoP_2O_7$ polymorphs [15].

However, detailed information is required to synthesize rose phase $Na_2CoP_2O_7$ by controlling several variables. In addition, it is important to prepare a highly stable and pure rose phase. Hence, in this study, we analyze an appropriate elemental ratio Na/Co in $Na_{2\text{-}2x}Co_{1+x}P_2O_7$ to prepare a stable rose phase and determine suitable synthetic conditions in each bulk compound. In addition, a new synthetic process is proposed to prepare a highly stable rose-phase nanoscale $Na_{2\text{-}2x}Co_{1+x}P_2O_7/C$ using a wet-chemical method. The electrochemical performance is measured for the high-voltage NIB cathode.

2. Experimental section

2.1. Synthesis of $Na_{2\text{-}2x}Co_{1+x}P_2O_7$

The chemicals used in this study were obtained as reagent grade,