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An investigation of crystallization kinetics of the $Na_3MnCO_3PO_4$ cathode material, synthesized by the hydrothermal method

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HIGHLIGHTS

- Kinetics study of NMCP crystallization was investigated by using XRD analysis.
- Kinetics data of growth period were determined by the Avrami–Erofeev model.
- The apparent E_n and E_g were 29.10 and 73.91 kJ/mol, respectively.
- Formation of NMCP was significantly accelerated via stirring assisted hydrothermal.
- The specific capacity of NMCP was improved by enhancing the degree of crystallinity.

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ABSTRACT

$Na_3MnCO_3PO_4$ (NMCP) is produced by hydrothermal synthesis for rechargeable sodium-ion battery (SIB) cathode. Mechanism of formation of NMCP was investigated by measuring the influence of time and temperature on the rate of production of the NMCP crystallites. X-ray diffraction analysis of the synthesized samples showed that $MnCO_3$ first formed as an intermediate phase. $Na_3MnCO_3PO_4$ was, however, the last phase retained after 24 h of the hydrothermal process at 120 °C. Sigmoidal shape of the crystallization curves followed the Avrami–Erofeev model which described the chemical kinetics of the $Na_3MnCO_3PO_4$ formation. Respective apparent activation energies of 29.10 for nucleation and 73.91 kJ/mol for growth were obtained by application of the Arrhenius law to the experimental data and model calculations. ICP results showed that the Na to Mn ratio in the NMCP got closer to the stoichiometric value by increasing temperature and time of the hydrothermal reaction. Application of the NMCP as a cathode material for sodium ion batteries revealed that the specific capacity was improved by enhancing the degree of crystallinity.

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1. Introduction

Breakthroughs in the cathode materials are needed to reach high specific energy batteries. Rechargeable sodium-ion batteries (SIBs) have attracted considerable interest because of low cost and high abundance of sodium resources on the earth [1,2]. $Na_3MnCO_3PO_4$ (NMCP) is a promising cathode material with a high theoretical capacity of 191 mAh g^{-1} for use in SIBs [3–7].

The hydrothermal method has been recognized as a viable technique for production of purified NMCP phase with fine particles and good crystallinity [4–7]. Its attraction is due to low cost, simplicity, excellent repeatability and mild temperatures needed [8,9]. Among various parameters affecting NMCP phase formation, time and temperature are the most important ones not being investigated. Studying the role of these parameters on morphology and crystallographic texture of the synthesized material helps optimization of the experimental procedure. Results can be helpful at both scientific and industrial scale.

Previous investigations have been on other materials. Hydrothermal temperature effect on $ZnMn_2O_4$, for example, has been studied by Ni et al. [10]. They found progressive morphology change of $ZnMn_2O_4$ from hollow to hierarchical porous microspheres by the temperature rise from 120 to 180 °C. Hierarchical porous microspheres had better overall anodic performance than hollow microspheres. Gao et al. [11] have synthesized various morphologies of $LiMnPO_4$ crystals via the hydrothermal method in

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