

Recent Progress on the Elaboration of Sodium Manganese Phosphate Based Nanostructures as Cathodes for Energy Storage

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Abstract

Successful energy storage technology is one of the key requirements needed for using renewable energies. Over the past decades, the development of lithium-ion batteries (LIBs) has greatly promoted portable electronic equipment and electric vehicles, but there remains a large supply-demand gap, in particular for large scale energy storage. Sodium-ion batteries (NIBs) are considered promising alternatives for LIBs due to the abundance of sodium resources. The phosphate-based polyanion materials have shown significant interest in terms of their stability, high ionic mobility, security, and structural versatility. However, these materials still pose application challenges because of their restricted energy density and low intrinsic electronic conductivity. A lot of work is required prior to their widespread application as commercial NIB cathode materials. In the present paper, the authors have focused on the methods used to elaborate sodium manganese phosphate by discussing the results obtained including the structures and morphology of NaMnPO_4 produced according to the literature.

Keywords

Lithium-ion batteries, Sodium-ion batteries, Nanostructures, Energy storage

Introduction

Nowadays, among the most important concerns of society are energy production, energy storage and global warming. As the global population grows, so does the demand for energy. In response to the energy requirements of the growing global society, our power supply is getting more environmentally friendly and moving towards sustainable energy supplies. Solar, wind, geothermal, tidal, biomass, etc., are renewable energy sources which are inherently irregular and distributed compared to the large-scale confined resources that provide the largest share of electrical energy. In order to utilize the aforementioned energy sources, we need reliable, efficient and economical energy storage devices [1, 2]. Among electrochemical energy storage devices, LIBs, significantly powered the growing population by portable electronic devices and electric vehicles, which considerably reduce the dependency on fossil fuels but raise Li supply requirement [3]. However, their cost has been steadily increasing due to low natural reserves and their unequal geographical dispersion across the terrestrial layer. Consequently, a new battery system with features of low price, large natural occurrence, and environmental friendliness must be designed for replacing LIBs [4]. For this reason, other types of batteries have been widely developed in the last few years, such as NIBs [5, 6], magnesium-ion batteries [7], calcium-ion batteries [8], potassium-ion batteries [9], zinc-ion batteries [10], etc. Based on the earlier investigations, it has been found that Na and Li belong to the identical alkaline

family and to neighboring periods, also SIB and LIB work similarly at room temperature. Furthermore, the availability of Na is unlimited, because this element is the 4th more plentiful element on earth. They are nearly 1000 times greater than Li, and this has attracted the focus of scientists [11]. A number of Na-based materials have been recently published: $\text{Na}_4\text{Ti}_5\text{O}_{12}$, $\text{Na}_2\text{Ti}_3\text{O}_7$, NaTiO_2 , $\text{Na}_4\text{Fe}(\text{CN})_6$, NaVO_2 , etc. [12-14]. Phosphate materials are the best choice for cathode materials in NIBs because of their excellent thermal stability and high voltage due to their powerful inductive properties [15, 16]. They must have a nano-structured matrix to achieve the best electrochemical efficiency. Moreover, a pure cathode material must have the features to provide a good transient response for easy insertion and deinsertion. The employed manganese with Na ions on the conversion reaction basis may supply high capacitance on account of their attractive features of effective storage, good conversion, and several oxidation states, making it accountable for facile access to ions. For such purpose, NaMnPO_4 has been applied as a positive electrode for NIBs [17]. Here, we provide an overview of certain new advances in the elaboration of the positive electrode focusing mainly on sodium manganese batteries similar to LIBs as a starting point of inspiration toward scientists working in the area of battery materials.

Manganese-based Phosphate

Currently, Mn-phosphate materials have attracted much interest in aqueous rechargeable technologies (e.g., IBs and supercapacitors) because of their high discharge voltage plateaus and enhanced ion transport in the open frameworks [18]. NaPO_4 is present in two different phases, olivine and maricite, which are structurally similar to NaFePO_4 . The olivine NaMnPO_4 is also known as natrophilite type due to Na^+ being larger than Mn^{2+} . The results of DFT calculations [19] indicated that the olivine sodium manganese phosphate had lower energy as compared to the maricite phase at low temperatures. The structure of the phosphate group (Figure 1) is identical in both configurations (Pnma space group). The differences comes from the fact that in the olivine structure (Figure 1a), Na^+ and Mn^{2+} ions choose to take up two octahedral positions, while the reverse is true in the maricite-like structure (Figure 1b). The octahedral sites with Na^+ in the olivine

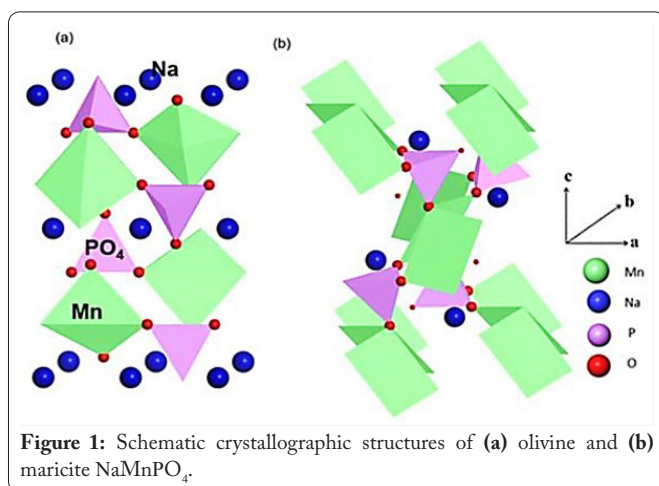
structure share edges and create zig-zag channels the length of the b-axis [6, 20]. The most favorable direction of diffusion of alkali ions within the olivine crystal structure is the preferred way. The maricite phase is electrochemically inactive because the mobility of Na^+ ions is blocked. Nevertheless, the maricite structure is the thermodynamically stable modification of NaMnPO_4 [21].

Elaboration methods

Hydrothermal process

One of the more frequently applied approaches for the synthesis of nanomaterials is hydrothermal process, it refers to the synthesis of materials through chemical reaction conducted in an enclosed container with an aqueous solution of reactants at temperatures over 100 °C and under elevated autogenous pressure, such specialized containers called autoclaves, providing a closed, high-pressure environment to assist in solvation of the reactants and reactions between the liquid precursors. In comparison to various synthesis routes, the hydrothermal method allows the production of highly crystalline nano-sized products under relatively mild operating conditions. It represents a challenging approach that offers easy control of reaction parameters as reaction time and temperature to obtain highly uniform compounds [22, 23].

Many types of nanomaterials have been successfully synthesized using this approach, but we are only focusing on NaMnPO_4 . Jana et al. [24] reported the synthesis of NaMnPO_4 through a hydrothermal reaction of 0.5 g of manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), 15 g of disodium phosphate (Na_2HPO_4), and 0.5 g of hydroxylammonium chloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) in 0.09 L of deionized water at 80 °C during 3 days. The obtained white compound was further rinsed using deionized water, followed by air-drying at 80 °C. The results demonstrate the preparation of N- NaMnPO_4 crystalline monophase compound (Space group: Pnma). A light brown material was formed after warming the N- NaMnPO_4 product to 600 °C in air, which turned out to be another NaMnPO_4 polymorph, commonly referred to as maricite, M- NaMnPO_4 (Space group: Pmnb). Rietveld refinements of the XRD data were performed in order to validate the crystalline compositions of both polymorphic compounds. There is good agreement between the refined cell constants ($a = 10.527 \text{ \AA}$, $b = 6.323 \text{ \AA}$, and $c = 4.984 \text{ \AA}$) determined using the Rietveld refinement investigation and the reported cell constants of orthorhombic N- NaMnPO_4 . Also, the refined cell constants ($a = 6.892 \text{ \AA}$, $b = 9.079 \text{ \AA}$, and $c = 5.108 \text{ \AA}$) for M- NaMnPO_4 were shown to be in accordance with the reported data. Scanning electron microscopy (SEM) images of N- NaMnPO_4 exhibit a cubic shape with facets and clear borders, consistent with the symmetry of the orthorhombic crystal lattice of N- NaMnPO_4 . They are 5 μm to 35 μm in length, whereas the base borders of these crystals are approximately 1 - 2 μm in size. Shi et al. [25] mentioned the elaboration of NaMnPO_4 via hydrothermal reactions using 0.93 g of sodium orthophosphate hydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), 0.40 g of manganese (II) acetate tetrahydrate ($\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$), 0.55 g of diethyl oxalate ($\text{C}_6\text{H}_{10}\text{O}_4$), 0.22 g of sodium hydroxide



(NaOH), and 15 g of H₂O, these reactants were shaken and agitated. Thereafter, the reaction vessels were maintained at 433 K for 6 days, and cooled at room temperature. After filtration, the formed crystals were rinsed with deionized H₂O and then dried under room temperature. XRD and SEM results of the obtained powder show that rod-shaped NaMnPO₄ particles with inner diameters of 10 to 30 μm correspond well to the XRD pattern reported for orthorhombic NaMnPO₄.

Solid-state reaction

A popular route to obtain a polycrystalline material based on solid reactants is the solid-state reaction. Very high temperature is usually required for the reaction to occur. Among the factors influencing the solid-state reaction are the morphological and chemical properties of the reagents, especially the free energy, surface area, and reactivity which vary with the solid-state reaction, as well as other reaction conditions, like pressure, temperature, and the reaction environment. The benefit of this method is its large-scale manufacturing and its simplicity [26]. Wu et al. [27] used solid state reaction to prepare NaMnPO₄ by mixing MnSO₄·H₂O, Na₃PO₄·12H₂O, and polyethylene glycol surfactant-400 in a mortar, thereafter, the mixture was thoroughly ground manually with a mallet during 40 min. Gradually, this reagent mixture turned wet. Afterwards the formed paste was kept at ambient temperature during 3 h, followed by rinsing with deionized water to eliminate soluble inorganic salts. Thereafter, anhydrous ethanol was used to wash the solid and dried at 70 °C for 3 h. The results reveal the compound exhibits a high degree of crystallinity and composed of platelets. No diffraction peaks of the pattern correspond to sodium manganese phosphate of the PDF map, and no diffraction peaks of other impurities like Mn₃(PO₄)₂ or MnO₂, are found, suggesting that the compound is a novel crystalline material with high purity and with crystallite size of 27 nm. Priyanka et al. [28] developed the maricite NaMnPO₄ by employing the anhydrous form of C₂H₃NaO₂, C₄H₆MnO₄, and NH₄H₂PO₄ in the same molar ratio and blended together through a ball mill with 150 rpm during 5 h in a one-way rotating regime. A liquefied material is obtained and warmed under vacuum at 453 K for 5 h to eliminate the by-products. Then it is burned at 973 K in Argon gas to get the M-NaMnPO₄. The XRD pattern affirms that a clearly identified crystalline phase of the compound with a 67% larger crystallinity degree developed as it was heated at 973 K, it matches the orthorhombic framework of maricite having the space group of Pmnb. The network dimensions of the specimen have been computed as a = 6.9113 Å, b = 9.0988 Å, and c = 5.1211 Å. The volume of the single cell has been established as V = 322.03 Å³, in close accordance to JCPDS (84-0852).

Solution combustion synthesis

Among the best way for material synthesis we find Solution Combustion Synthesis (SCS) which is an outstanding process because of its ease of use, economic, and excellent quality of the resulting product. SCS consists of a fast and self-sustaining redox reaction between an organic fuel (Figure 2) [29] and an oxidant (e.g., metal nitrates) in the presence of metal cations. They are mixed as an aqueous (or rarely

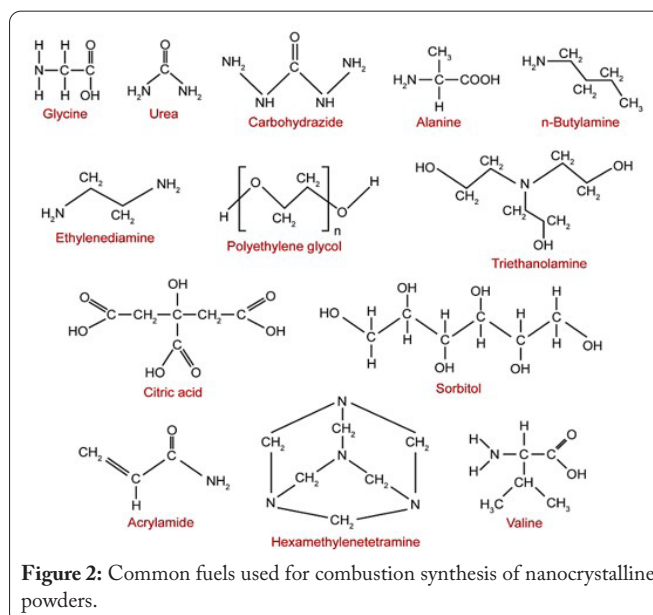


Figure 2: Common fuels used for combustion synthesis of nanocrystalline powders.

non-aqueous) solution and exposed to fairly moderate heating (300 - 500 °C), generally in a preheated muffle furnace. In principle, solution combustion synthesis involves 3 main steps (Figure 3): (1) Combustion mixture generation, (2) Gel generation, and (3) Gel combustion [30]. The resulting product from SCS exhibits high phase purity and better powder characteristics including higher specific surface area, fine particle size distribution, optimal agglomeration, and improved sintering properties. A significant advantage is that it can be used in combination with a variety of precursors, both soluble and insoluble [31].

Several investigations applying this approach to prepare NaMnPO₄ for example Chowdhury et al. [32] describe the formation of this material using a stoichiometric amount of sodium NaNO₃, NH₄H₂PO₄, and MnSO₄ which were diluted in deionized water, afterwards, for 30 min with 600 rpm the resulting mixture was shaken at 353 K. Following, this mixture was supplemented with urea (With the oxidant: fuel ratio = 1:1). pH 8 adjustment was made to the precursor solution using an ammonia solution. Subsequently, for complete dehydration, the obtained solution was shaken and heated to a temperature of 373 K. Thereafter, an oven placed in which the remaining solid material and heated to 383 K for about 12 h. Next, the product was heated in the furnace for calcination

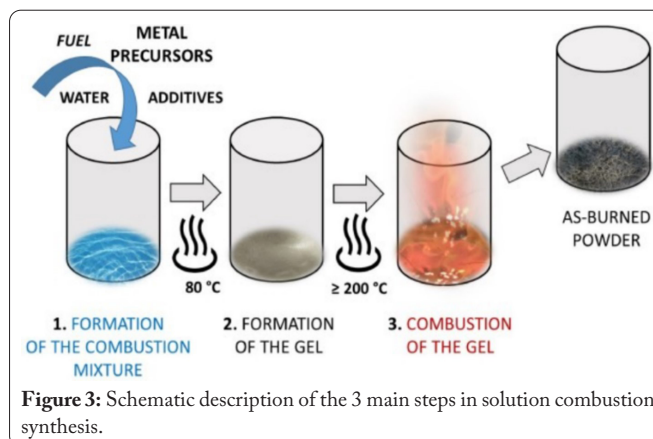


Figure 3: Schematic description of the 3 main steps in solution combustion synthesis.

at 573 K for 8 h and 573 K for 5 h with intermediate grinding. The XRD diagrams of the powder show clear diffraction peaks suggesting the crystalline nature of the synthesized compound. The finding established the maricite phase formation. The matching network dimensions are: $a = 6.7952 \text{ \AA}$, $b = 8.8773 \text{ \AA}$, and $c = 5.0272 \text{ \AA}$. It was found that the crystallites had an approximate average diameter of 38 nm. To synthesize maricite-type NaMnPO_4 according to Senthilkumar et al. [33], a stoichiometric quantity of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, NaNO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$ was dissolved and mixed with distilled water. A glycine amount was diluted with deionized water and mixed into the above solution. The oxidant to fuel ratio of was kept at 1. In addition, an ammonia solution was added to adjust the precursor solution pH of to 7. For dehydration, on a hot plate (473 K), the resulting mixture was transferred. Afterwards, the solid mass remaining was moved to a muffle furnace where an increase in temperature to 573 K was achieved. Following grinding on an agate mortar and pestle, the final foamy product was collected and subsequently processed for further characterization. Thereafter, to obtain a single phase of NaMnPO_4 , the foamed product was burned at about 673 K for 3 h. The XRD pattern of sodium manganese phosphates synthesized by combustion is essentially consistent with the standard diffraction diagram of the maricite-like phase (JCPDS No. 84-0852). The whole profile Rietveld refinement validates the NaMnPO_4 phase constitution and permits us to establish the network dimensions of the orthorhombic NaMnPO_4 ($a = 6.9053 \text{ \AA}$, $b = 9.085 \text{ \AA}$, and $c = 5.1149 \text{ \AA}$). As a result, the calculated lattice parameters appear to be consistent with the reported values.

Polyol process

Polyol approach is a multi-functional liquid phase procedure that uses high-boiling, multivalent alcohols to generate the nanoparticles. It consists of suspending the metal precursor in a glycolic solvent and then heating the solution to a reflux temperature. This technology has been applied to produce oxide, metallic and semiconductor nanoparticles. Polyols have a double function as a diluent and a reducing agent and can regulate particles development. Several types of polyols can be listed, namely ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, triethylene glycol, tetraethylene glycol, etc. Polyols offer significant benefits on several fronts. The elevated boiling point of polyols may support the synthesis in the range of 200 – 320 °C with no high pressure or autoclave. In addition, the strong solubilization capabilities of polyols make it possible to employ inexpensive and simple metal precursors as starting compounds. Furthermore, the chelating property of the polyol is a favorable factor to monitor the key features, like nucleation, growth and agglomeration of the particles [34, 35].

A number of studies are using the polyol method to prepare NaMnPO_4 . For instance, Priyanka et al. [5] describe the formation of NaMnPO_4 by using a precursor such as 0.1 M manganese(II) sulfate MnSO_4 that was taken and left for dissolving in 20 g of polyethylene glycol 6000 and 50 ml of aqueous solution and shaken for 1 h. Then, it was added an equal amount of molar ratio of NaH_2PO_4 dropwise into

the solution at a rate of 1 ml/min. Thereafter, the solution was kept at 373 K constantly for 5 h. The solution was then poured into a crucible and allowed to age for 4 h at room temperature. The sample was later calcined at 873 K for 6 h. From XRD finding, the resulting compound conducts to the crystal structure of $\text{Mn}_2\text{P}_2\text{O}_7$, which is in agreement with JCPDS No: 77-1243. As a consequence, the produced compound has a monoclinic framework with C2/m space group. Network dimensions of $a = 6.632 \text{ \AA}$, $b = 8.589 \text{ \AA}$, and $c = 4.546 \text{ \AA}$ were identified. Although clear crystal texture was obtained, it is not suitable for use as a cathode material because sodium is eliminated with Na_2SO_4 . These researchers used the same procedure for preparing NaMnPO_4 as detailed above but changed the manganese precursor and found decisively that $\text{C}_4\text{H}_6\text{MnO}_4$ was a good precursor. Afterwards they proceeded to a detailed study of the growth of the NaMnPO_4 material but this time with different glycols [36]. They found that extending the length of the diol chain with the use of ethylene glycol, diethylene glycol, and poly(ethylene glycol) (400 and 6000) favors the creation of a pristine product in a single stage. Moreover, the development of the maricite structure is highlighted by the Rietveld refinement method, where the manganese (Mn) atom is located in the 4a position and the sodium (Na) atom is located in the 4c position with the space group of Pmnb . A 1D “rod-like” structure in the material promotes the a ions insertion/de-insertion.

Conclusion

Major focus of current developments in energy storage is the elaboration of electrode materials with high electrochemical efficiency and excellent stability for NIBs. There is no doubt that the volume change caused by the insertion/de-insertion of Na ions will cause a more limited cycle life of NIBs due to their wide ionic radius. Consequently, polyanion compounds like PO_4^{3-} are a good choice for commercial supply batteries in NIB applications thanks to their stable structure. On the other hand, the poor electronic conductivity of polyanionic compounds and the defects of special materials must be addressed. Nevertheless, further efforts are still required in terms of performance improvement and practical application. Regarding efficiency, all methods of NaMnPO_4 preparation are not equipotential. Each approach has different advantages and disadvantages. Most processes use costly raw materials and have difficulties with intermediates, which can be sensitive to moisture. There are sometimes scalability drawbacks and the efficiency can vary depending on the composition and the characteristics of the material to be produced. Briefly, the selection of a durable way to produce materials will be beneficial in terms of: conserving energy; adopting environment-friendly precursors; time and costs; enhancing efficiency; reducing waste generation; generating compounds with advantages for energy, the environment, economy, and the society; developing knowledge regarding the link between synthesis and properties.

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Conflict of Interest

None.

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