



# Optimization of NaFePO<sub>4</sub> nanoparticles act as cathode in Sodium-ion batteries

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Over the next phase of rechargeable batteries, a detailed investigation has gone into creating future cathode materials. The utilisation of phosphate framework materials as electrodes in the next source of energy storage technologies will be a challenging and appealing option and because of its best cycle and cycling rate, as well as its low cost. NaFePO<sub>4</sub> has been regarded a viable electrode material in sodium ion batteries. Microwave, hydrothermal, and solid state procedures were used to synthesize the NaFePO<sub>4</sub> nanoparticles. As per XRD structural studies, the solid state method shows the maximum intensity peaks of NaFePO<sub>4</sub>. Then the FTIR analysis was used to identify the PO<sub>4</sub><sup>3-</sup> groups and the morphology studies were done for the outcome of the solid state method. The findings demonstrated that the solid state produced NaFePO<sub>4</sub> nanoparticles acts as a potential electrode materials for sodium ion batteries.

**Keywords:** NaFePO<sub>4</sub> nano particles; phosphate groups; Optimization; Microwave method; hydrothermal method; Solid state method

## 1 Introduction

Owing of the minimal cost and plentiful supply of sodium, there is considerable attention in the design of Na-based electrodes, particularly ones it that can be synthesised through solid state approach. The fourth most prevalent element in the earth's crust is sodium, which has massive reversal of 23 billion tonnes of soda ash in the United States. Because of its abundance and low cost, sodium is an appealing energy storage technology to replace Lithium-ion batteries<sup>1,2</sup>. Currently, the performance of the cathode materials is driving the Sodium ion batteries technology<sup>3,4</sup>. Many challenges might be overcome by inventive creation of appropriate cathode materials with numerous properties such as high specific capacity, superior cycling stability, and good rate capability<sup>5</sup>. Transition materials, transition-metal fluorides, poly anion compounds and organic materials are four different materials that can be employed as potential cathode materials for sodium ion batteries<sup>6-10</sup>. The poly anions in the above-mentioned cathodes have a greater operating potential, a longer cycling life, strong structural stability, and thermal safety<sup>11-15</sup>. When compared to mono anionic materials, the redox potential of the transition metal in the poly anion compound can be tuned via an inductive effect caused by the ionic-covalent properties of the bonding (e.g., P-O) and the poly anions (e.g., PO<sub>4</sub>) can

switch the metal redox potentials, resulting in an increased operating potential<sup>16-17</sup>.

## 2 Experimental

### 2.1 Characterization

XRD (XPRT-PRO with CuK radiation) was used to investigate the crystalline structure formation. The existence of functional groups of pristine NaFePO<sub>4</sub> was observed using an FT-IR Spectroscopy equipment (Shimadu 8400S). Scanning Electron Microscope was used to determine the morphological feature of nanoparticle surfaces with the highest resolution (SEM: S-800).

### 2.2 Chemicals Used

The standard purification and analytical grade were employed for all compounds used in the synthesis procedure. The samples are made with the following materials: Na<sub>2</sub>CO<sub>3</sub>, FeCO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub> HPO<sub>4</sub> bought from Merk in India.

### 2.3 Methodology

#### (a). Microwave method (SI)

To make NaFePO<sub>4</sub> nanoparticles, Sodium carbonate, ferrous carbonate, and di ammonium hydrogen phosphate were added in a stoichiometric ratio to 50ml of distilled water and was stirred vigorously for 30 minutes. Then, drop by drop, NaOH solution is added until the pH value reaches 9. To ensure homogeneity, the solution is agitated for four hours, then poured into a Teflon tube and

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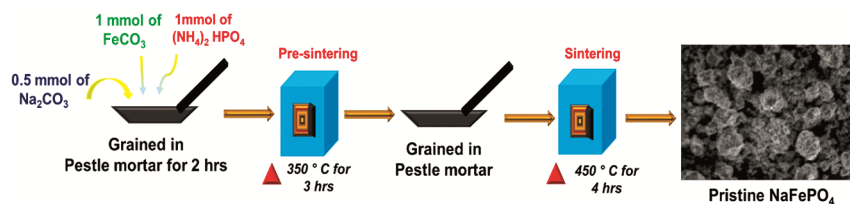


Fig. 1 — Synthesis of NaFePO<sub>4</sub> through Solid state method.

annealed for 16 hours at 140 °C and it is cleaning with distilled water and ethanol, the solution is dried in an oven overnight and ground in a mortar to produce nanoparticles. An ordinary household microwave oven was used for pre-sintering the sample at 150 °C for 20 minutes and for sintering it at 200 °C for 30 minutes.

**(b). Hydrothermal method (S2)**

Using a hydrothermal method, NaFePO<sub>4</sub> nanoparticles were synthesized from Sodium carbonate, Ferrous carbonate and di ammonium hydrogen phosphate in a stoichiometric ratio, then each sample was added one at a time to 50ml of distilled water and stirred vigorously for 30 minutes. In the following step, NaOH solution is added drop by drop to obtain the Ph value of 9. The solution is stirred for four hours to achieve homogeneity, then is poured into a Teflon tube and placed in an oven at 140°C for 16 hours. After cleaning with distilled water and ethanol, the solution is dried in a hot air oven for overnight and then ground by a mortar to make nanoparticles. The sample was then pre-sintered with 750 °C for 12 hours and sintered with 600 °C for 6 hours in an air muffle furnace.

**(c). Solid state method (S3)**

The NaFePO<sub>4</sub> sample was made through solid state process as shown in Fig. 1, using a stoichiometric ratio of sodium carbonate, ferrous carbonate, and di ammonium hydrogen phosphate, which was then ground for 2 hours in a pestle mortar. The as-obtained precursor was then dried in an air muffle furnace, pre-sintered for 3 hours at 350 °C, and then grounded and sintered at 450 °C for 4 hours.

### 3 Results and discussion

#### 3.1 XRD Analysis

Powder X-Ray diffraction was used to acquire data on crystalline structure and phase confirmation of materials for three synthesis process and JCPDS: (89-0816), for orthorhombic structure with Pnma group, matches the phase structure of NaFePO<sub>4</sub> made by solid state method, which clearly specifies the

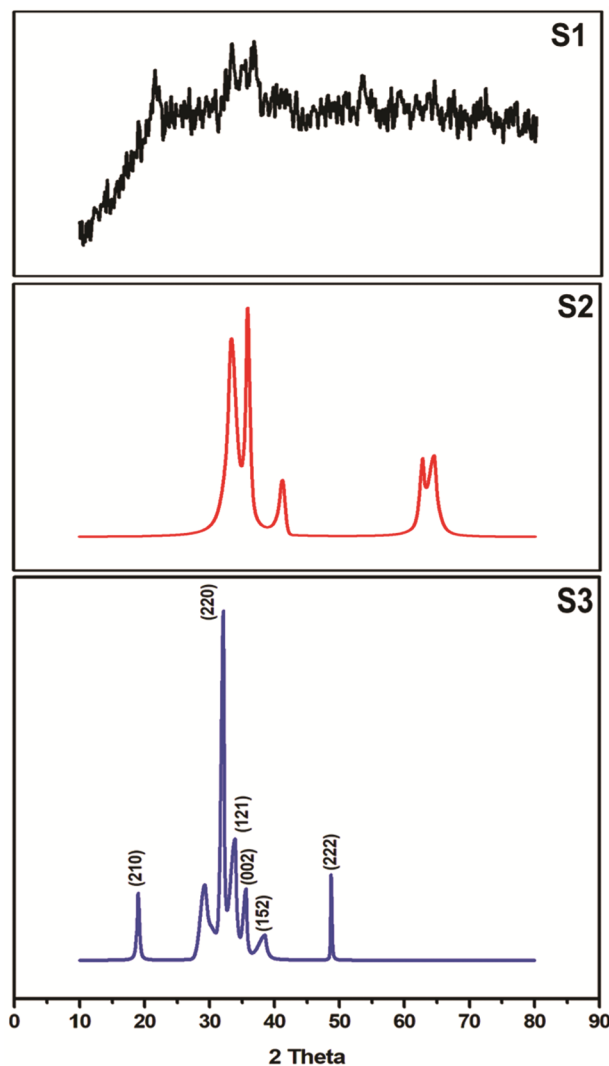
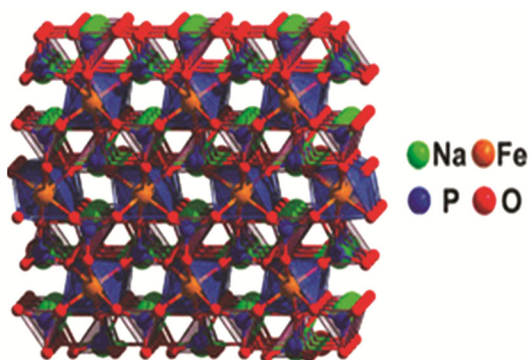
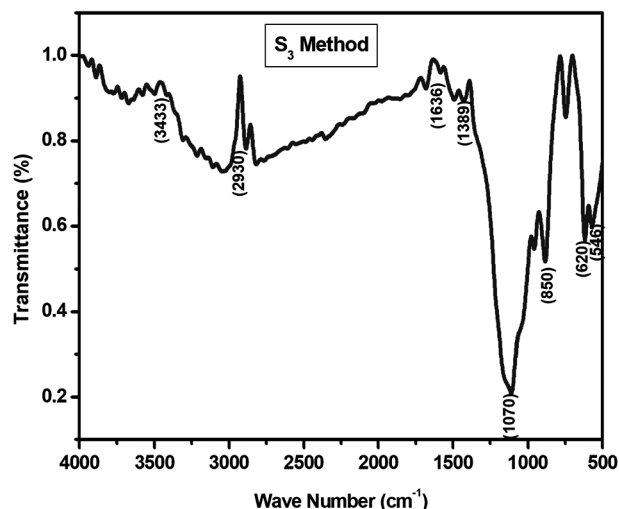


Fig. 2 — XRD pattern of NaFePO<sub>4</sub> through different methods: (S<sub>1</sub>). Microwave method: (S<sub>2</sub>). Hydrothermal method: (S<sub>3</sub>). Solid state method.

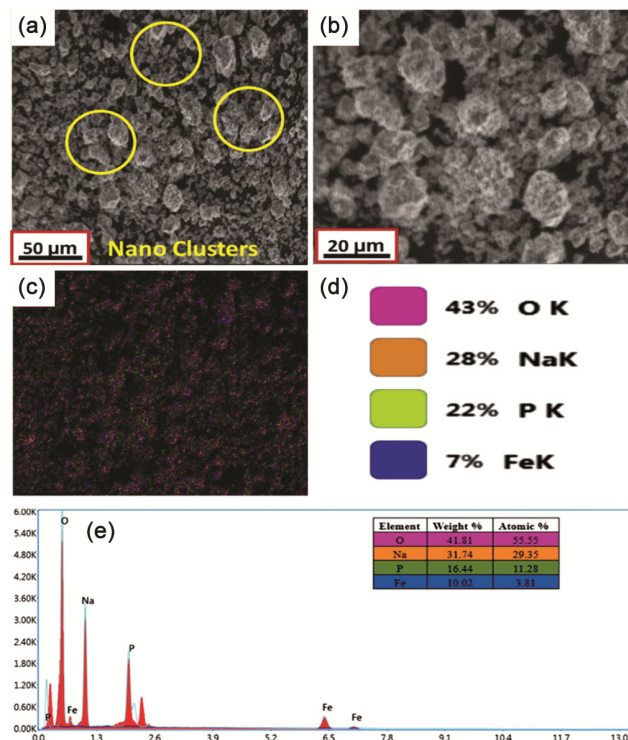
phase formation of NaFePO<sub>4</sub>. Fig. 2 & 3 shows the XRD pattern and crystallographic structure of NaFePO<sub>4</sub> nano materials. The predominate peaks in as-synthesised material are  $2\theta = 32.08, 33.07$  and  $35.56^\circ$ <sup>18</sup>, which correlate to miller indices (220), (121), and (002), respectively. The predicted grain size of pure NaFePO<sub>4</sub> by using the Scherrer equation

Fig. 3 — Structure of NaFePO<sub>4</sub>.Fig. 4 — FTIR pattern of as-prepared NaFePO<sub>4</sub> through Solid state method.

was 15.70 nm. According to XRD data, Micro strain (E) and dislocation density value for pure NaFePO<sub>4</sub> are 0.47 and 4 respectively.

### 3.2 FTIR Analysis

The absorbed peak for solid state synthesis which is illustrated in the Fig. 4, as a result of PO<sub>4</sub><sup>3-</sup> asymmetric stretching is allocated to the board band approximately 1070 cm<sup>-1</sup>. The symmetric stretching vibrations of PO<sub>4</sub><sup>3-</sup> correlate to the weak peak at 620 cm<sup>-1</sup>. The bonds related to PO<sub>4</sub><sup>3-</sup> asymmetric deformation are found in the 540-580 cm<sup>-1</sup> range and Stretching modes of P-O arise in the 1000-850 cm<sup>-1</sup> range, it has been revealed that this substance belongs to the phosphate group<sup>19</sup>. Tertiary alcohol (phenoyl) at 1389 cm<sup>-1</sup> is the location of OH-bend. The quinone or conjugated ketone carboxylic group are attributed at 1636 cm<sup>-1</sup> and dimetric OH-stretching at 3443 cm<sup>-1</sup> and these bands confirmed that the specimen is phosphate group.

Fig. 5 — SEM analysis and element mapping of as-prepared NaFePO<sub>4</sub> through Solid state method.

### 3.3 Morphology Analysis

For a material to improve its electrochemical performance, its morphological characteristics are significant. During combustion, porous particles are formed, and this is one of the unique characteristics of the method, and the number of pores is mainly related to the quantity of gases released during the reaction. As seen in an SEM image of pristine NaFePO<sub>4</sub> nano powder synthesized by solid state process, the sample is composed of huge agglomerated clusters and confirmed in the Fig. 5 (a-c). SEM elemental mapping validates Na, Fe, P, and O with weight percentages of 31.74:10.02:16.44:41.81 as shown in Fig. 5 (d,e).

### 4 Conclusion

Crystalline sodium iron phosphate was synthesized based on three methods. XRD examination revealed that the fine crystalline phase and diffraction peaks of NaFePO<sub>4</sub> which is obtained by solid state method. The functional group vibrations of the produced sample was investigated using FT-IR spectroscopy. Their surface morphology was observed using a scanning electron microscope and the sample is composed of huge agglomerated clusters. The results showed that the NaFePO<sub>4</sub> nanoparticles synthesized

by the solid state could be used as a promising active materials for sodium ion batteries.

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### References

- 1 Ellis B I, Nazar L F, *Curr Opin Solid State Mater Sci*, 16 (2012) 168.
- 2 Goodenough J B, *J Solid State Electrochem*, 16 (2012) 2019.
- 3 Hwang J Y, Myung S T & Sun Y K, *Chem Soc Rev*, 46 (2017) 3529.
- 4 Liu C, Neale Z, Cao G, *Mater Today*, 19 (2016) 109.
- 5 Zhang Q, Uchaker E, Canderaria S L & Cao G, *Chem Soc Rev*, 42 (2013) 3127.
- 6 Zhang X, Zhang Z, Yao S, Chen A, Zhao X & Zhou Z, *Comput Mater*, 4 (2018).
- 7 Moreau P, Guyomard D, Gaubicher J & Boucher F, *Chem Mater*, 22 (2010) 4126.
- 8 Siratsuchi T, Okada S, Yamaki J & Nishida, *J Power Sources*, 159 (2006) 268.
- 9 Junmei Z, Zelang J, Jie M, Fuchun W, Yong-Sheng H, Wen C, Liquan C, Huizhou L & Sheng D, *Chem Sus Chem*, 5 (2012) 1495.
- 10 Liu Y, Xu Y, Han X, Pellegrinelli C, Zhu Y, Zhu H, Wan J, Chung AC, Vaaland O & Wang C, *Nano Lett*, 12 (2012) 5664.
- 11 Bridson J N, Quinlan S & Tremaine P R, *Chem Mater*, 10 (1996) 763.
- 12 Hammond R, Barbier J, *Acta Crystallographica B*, 52 (1996) 440.
- 13 Zaghbi K, Trottier J, Hovington P, Brochu F, Guerfi A, Mauger A & Julien C M, *J Power Sources*, 196 (2011) 9612.
- 14 Lee K T, Ramesh T N, Nan F, Botton G & Nazar L F, *Chem Mater*, 23 (2011) 3593.
- 15 Ranjusha R, Bo C, Zhicheng Z, Xing-Long W, Yonghua D, Ying H, Bing L, Yun Z, Lie W, Gwang-Hyeon N, *Adv Mater*, 29 (2017) 1605694.
- 16 Barpanda P, Liu G, Ling C D, Tamaru M, Avdeev M, Chung S C, Yamada Y & Yamada A, *Chem Mater*, 25 (2013) 3480.
- 17 Kim H, Shakoor R A, Park C, Lim S Y, Kim J S, Jo Y N, Cho W, Miyasaka K, Kahraman R, Jung Y, *Adv Funct Mater*, 23 (2013) 1147.
- 18 Karthick M, Sathishkumar S, Boopathiraja R, Meganathan K L & Sumathi T, *J Mater Sci: Mater Electron*, 31 (2020) 21792.
- 19 Priyanka V, Subadevi R & Sivakumar M, *Int Res J Eng Technol*, 4 (2017) 49.