

Electrochemical Study of NaFePO₄ Cathode Material in Aqueous Sodium-ion Electrolyte

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Abstract: Aqueous rechargeable sodium-ion batteries (ARSIBs) have received more attention because of their low cost, the vast abundance of sodium on the earth, and possible application for smart grid-scale energy storage systems. This work reports the synthesis of NaFePO₄ by a low-temperature ionothermal method using deep eutectic solvent (DES). The physical characterization of the synthesized material is done using X-Ray Diffraction (XRD), Scanning electron microscopy (SEM), Energy Dispersive X-ray analysis (EDAX), thermogravimetry analysis (TGA), and differential scanning calorimetry (DSC) to evaluate its crystal size, structure, composition, and morphology. The electrochemical behavior of NaFePO₄ in 5M NaNO₃ is studied using cyclic voltammetry (CV) and galvanostatic charge-discharge techniques. The electrochemical study revealed that the synthesized cathode material, NaFePO₄ exhibits excellent electrochemical performance at high current rates. The full cell NaTi₂(PO₄)₃/5M NaNO₃/NaFePO₄ delivers a discharge capacity of 96.96 mAh g⁻¹ at C/5 rate and is 62.96% of the theoretical capacity. The cell retains a discharge capacity of 76 mAh g⁻¹ over 50 cycles with good rate capability.

Keywords: ARSBs (aqueous rechargeable sodium-ion batteries); sodium iron phosphate (NaFePO₄); ionothermal method; Cyclic voltammetry (CV); Galvanostatic charge-discharge experiments.

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1. Introduction

Aqueous rechargeable sodium-ion batteries (ARSBs) have attracted extensive attention for the development of high-energy efficient stationary energy storage systems (ESSs) [1-4]. Compared to their lithium counterparts, sodium-ion batteries are heavy. However, lithium-ion batteries (LIBs) have disadvantages like a limited reserve of lithium, high cost, less safety, and reliability. Thus LIBs may not be the best solution for large-scale applications [5-7]. Among the alternatives, ARSBs have certain advantages: an abundance of sodium, a low-cost setup, and safe and environmental friendliness [8-10]. In addition, the electrochemical redox couple of sodium Na⁺/Na is -2.71 v/s SHE (standard hydrogen electrode) closer to the redox couple of Li⁺/Li which is - 3.04 v/s SHE [11]. The aqueous sodium battery system consists of low-cost electrolytes based on salts such as NaNO₃, Na₂SO₄, and NaOH instead of expensive NaPF₆ and has good ionic conductivity [12]. In aqueous batteries, electrode materials must be selected to be water stable because electrode dissolution affects the aqueous battery system's cycling life. The electrode must be inexpensive and easy to synthesize. Also, the electrode

'material's redox potential must be within the stable operating voltage window, which is approximately 1.23V before H₂ or O₂ evolution takes place by decomposition (electrolysis) of water [13-15].

Recent studies have focused on the development of cathode material for Na-ion batteries. Sauvage *et al.* first reported Na⁺ insertion/de-insertion into Na_{0.44}MnO₂ as cathode material in an aqueous electrolyte while studying the material for its sensing properties[16]. Later J.F Whitacre and their team documented a new optimized orthorhombic crystal structured cathode material Na₄Mn₉O₁₈ synthesized by a simple solid-state synthesis route. It shows a specific capacity of 45 mAh g⁻¹, electrochemically tested in 1M Na₂SO₄ with an initial pH of 7-8 against an activated carbon as a negative electrode. The mass ratio is 0.8:1 (negative: positive electrode), resulting in an output voltage of 1.7 V and 1000 deep discharge cycles without loss of capacity with good electrochemical performance. Here similar results are provided for an aqueous and non-aqueous electrolyte [17]. Layered transition metal oxides were initially used as cathode material for Na-ion batteries, exhibiting low performance and poor cyclability. However, their high sensitivity to atmosphere and water lead to the search for new cathode material. The polyanion-based phosphate cathode materials seem to be promising candidates for Na-ion batteries[18]. In our present work, we focused on synthesizing sodium iron phosphate (NaFePO₄) due to the success rate of its lithium counterpart, LiFePO₄(LFP), in vehicles. The main drawback of LFP is low electrical conductivity. Thus LiFePO₄/C was considered LFP/C. Here are the details of iron-based cathode materials which gave a successful result in ARSIB. Na₂FeP₂O₇ (robust crystal structure) reported by Jung *et al.* delivers an initial discharge capacity of 58 mAh g⁻¹ in 1M Na₂SO₄, and the capacity retention after 300 cycles was approximately 86% [4]. Na₂NiFe(CN)₆[15], Na₂CuFe(CN)₆ [19], NaFePO₄/C [20] and NaFePO₄ [21] showed superior performance in aqueous electrolyte achieving 110 mAh g⁻¹ at C/10 and 74 mAh g⁻¹ at 2C, and it has been briefly discussed in the next paragraph. A recent report on olivine NaFePO₄, which delivered a reversible capacity of 111mAh g⁻¹ in the organic electrolyte, obtained in the aqueous electrolyte at the same discharge rate [22]. Among phosphate polyanion cathode materials, olivine structured NaFePO₄ is one of the best promising cathode materials for Na-ion batteries due to its low cost and high theoretical capacity of 154 mAhg⁻¹. Also this combination of materials has been investigated recently as super capacity application [23]. Only a few reports are available in the literature for NaFePO₄ in aqueous electrolytes, which has not been much explored.

MilicaVujkovic[20] reported the electrochemical behavior of olivine structured NaFePO₄/C in saturated NaNO₃ aqueous electrolyte. In this work, the NaFePO₄ cathode material was prepared by the electrochemical method using the cyclic polarization technique where LiFePO₄/C has been transformed to NaFePO₄/C using LiNO₃ and NaNO₃ aqueous electrolyte. The prepared cathode material exhibited a high storage capacity of 118 mAh g⁻¹ at a scan rate of 10 mV s⁻¹ and proved that rate capability is better in aqueous electrolytes compared to organic electrolytes due to weak bonding between Na⁺-PO₄³⁻ in NaFePO₄, which is responsible for faster reaction kinetics in aqueous electrolytes. However, the cathode material undergoes capacity fading because of untransformed FePO₄ present in the electrode material.

A.J. Fernandez-Ropero [21] reported the preparation of NaFePO₄ cathode material by chemical delithiation of commercial material LiFePO₄ followed by chemical sodiation to obtain NaFePO₄. The reported electrochemical studies of cathode material are as follows at room temperature. With a lower voltage window, the aqueous cell delivered a capacity of 70

mAh g⁻¹ at C/5 and 40 mAh g⁻¹ at 2C, but at elevated temperature, i.e., at 55°C, the same cell delivered superior electrode performance and achieved a specific capacity of 110 mAh g⁻¹ at C/10 and 74 mAh g⁻¹ at 2C. The full cell, NaTi₂(PO₄)₃ // NaFePO₄ in 1M Na₂SO₄, delivered an initial capacity of 70 mAhg⁻¹ with an average voltage of 0.6 V and showed capacity retention of 76 % even after 20 cycles. Capacity fading in this work was attributed to the stability of anode material. In both the works reported in the literature for NaFePO₄ in aqueous rechargeable sodium batteries, the synthesis of NaFePO₄ was either chemical delithiation of LiFePO₄ or electrochemical ion-exchange process of LiFePO₄ into NaFePO₄ [24]. One of the drawbacks of the electrochemical method is that LiFePO₄ cannot be completely converted into NaFePO₄ because a part of the electrode remains in the form of FePO₄[20]. Even the synthesis of NaFePO₄ by the conventional solid-state reaction method also had a drawback of an unfavorable phase that limits Na⁺ ion's diffusion [25,26]. These results demand further effort to evaluate the electrochemical performance of NaFePO₄ in aqueous electrolytes and find an optimum solution to reduce capacity fading upon cycling. Thus, an alternative synthesis route had to be used to get better performance.

Deep eutectic solvents (DES) are gaining more attention as solvents alternative to ionic liquids in material synthesis due to their properties close to ionic liquids. DES is a new class of ionic liquids (ILs). They are formed from a eutectic mixture of Lewis or Bronsted acids and bases, containing various anionic/cationic species. The advantages of using DES over ILs are low cost, easy availability, non-toxic, chemical inertness with water, easy preparation, non-flammability, low vapor pressure, and relatively wide liquid-range biodegradable and environmentally friendly benign nature. Abbott *et al.* [27,28] laid the foundation in 2003 by reporting a low melting mixture of urea and choline chloride (ChCl), which produces a liquid at room temperature termed deep eutectic mixture. The physical and chemical properties of this mixture were very close to some of the standard ILs. Choline chloride (ChCl) is the most widely used component for DES formation as it is a non-toxic, low cost, and biodegradable quaternary ammonium salt [27, 29-31]. DES not only acts as solvents but also acts as structure-directing agents in the reaction [29, 32]. Our previous work reported a carbon phosphate-based cathode material synthesized by using DES as a solvent that delivered adequate capacity and better electrochemical properties [33,34].

In this work, we report the synthesis of NaFePO₄ by a low-temperature ionothermal method using DES as a structural directing agent in the reaction medium. According to our knowledge, we are the first to synthesize NaFePO₄ cathode material by the ionothermal method. Electrochemical studies have been done on the synthesized cathode material in an aqueous 5M NaNO₃ solution.

2. Materials and Methods

The chemicals and reagents used in this work for electrode synthesis and electrochemical investigation are purchased from Sigma-Aldrich (98 - 99.79% purity).

2.1. Preparation of DES.

Choline chloride was recrystallized from absolute ethanol, filtered, dried under vacuum, and then used for DES preparation. Ethylene glycol was used as received. In a typical procedure, 200 ml of the solution was obtained by mixing Choline chloride (ChCl) and

Ethylene glycol (EG) in the weight ratio (1:2) and heated to 80 °C with continuous stirrings until a homogeneous colorless liquid was obtained. The chemical structures are already explained in our previous report [33]. Prepared DES was used as a solvent to synthesize NaFePO₄ cathode material by a single-step ionothermal method at low temperatures.

2.2. Synthesis of NaFePO₄.

In a typical procedure, stoichiometric amounts of Na₂SO₄, FeSO₄·7H₂O, and (NH₄)₂HPO₄ are ground in a mortar and taken in a beaker. 10 ml of prepared DES was added, and preheated to 50 °C to ensure the precursor dissolved well. The resulting mixture was stirred vigorously for 30 minutes; the obtained homogeneous mixture was transferred into a 20 ml Teflon-lined stainless steel autoclave. Then the autoclave is placed in the programmable furnace and heated up to 200 °C for 24 hrs. After the completion of heating, the furnace and autoclave are cooled to room temperature. The resulting product was filtered, followed by washing with distilled water and ethanol several times to remove DES. The final product obtained was dried under vacuum at 60 °C overnight.

2.3. Synthesis of NaTi₂(PO₄)₃.

NaTi₂(PO₄)₃ anode material was synthesized using the Reaction Under Autogenic Pressure at Elevated temperature (RAPET) method. In a typical procedure, stoichiometric amounts of Na₂CO₃, TiO₂ (99.95% purity), and (NH₄)₂HPO₄ are taken in a mortar, mixed, and grounded well. The resulting mixture was introduced into a Swagelok cell. It was then heated to 800 °C and held at this temperature for 12 hr in the programmable furnace. It is then cooled to room temperature. The synthesis, root heating, and cooling rates were fixed at 5 °C min⁻¹.

2.4. Physical characterization.

The X-ray diffraction was recorded using a powder X-ray diffractometer (PXRD), the D2 phaser-X-ray powder diffractometer from Bruker using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), LYNXEYE (TM) 1-D solid-state fast detector analytical instrument. The micro and nano-materials of synthesized NMCP were observed on a field-emitting scanning electron microscope (FESEM, Carl Zeiss Microscopy Ltd). The elemental composition was detected with a dispersive energy X-ray (EDX). Thermal analysis was carried out using a thermogravimetric analyzer (TGA) (Model; SDTQ600, TA Instruments, UK). Each film sample (5–7 mg) was subjected to a nitrogen atmosphere with a gas flow rate of 100 mL min⁻¹ and a heating rate of 10 °C min⁻¹ in the temperature range of 25–700 °C.

2.5. Electrochemical test.

The working electrode was prepared by using titanium mesh as a current collector. Ti mesh of 2.25 cm² geometric surface area with a tag for electrical connection was cleaned and washed with doubly distilled water, rinsed with acetone, dried, and weighed before preparing the electrode. Ti was selected as a current collector because of its high potential for O₂ evolution. The mixture of active material (70 wt%), acetylene black (20 wt%), and

polytetrafluoroethylene (PTFE) binder (10 wt%) and were grounded in a mortar, then by adding a few drops of N-methyl-2-pyrrolidone (NMP) to the grounded mixture to get slurry as a coating material. Then the resultant slurry mixture was coated onto a previously cleaned and weighed titanium mesh. The electrode was dried in a vacuum drying oven at 90 °C overnight. Electrochemical measurements were carried out in a glass cell of 25ml capacity using 5M NaNO₃ aqueous solution as an electrolyte, NaFePO₄ as a working electrode, Pt as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. For the galvanostatic charge-discharge experiment, an aqueous sodium-ion battery was assembled using NaTi₂(PO₄)₃ as anode and NaFePO₄ as a cathode. All potential values are reported against SCE. All electrochemical experiments in this work were performed using Biologic's potentiostat-galvanostat instrument, VSP, France.

3. Results and Discussion

3.1. Physical Characterization of NaFePO₄ nanoparticles.

3.1.1. XRD studies.

NaFePO₄ was synthesized by a low-temperature ionothermal method [33]. Figure 1 shows the XRD pattern of the synthesized NaFePO₄, which agrees with the XRD pattern reported in previous works [20, 22]. From Figure 1, we can observe that the intensity of the (110), (200), (211), (220), (202), and (301) diffraction peaks of NaFePO₄ are more robust than those of the other peaks observed approximately at $2\theta = 17.64^\circ$, 25.49° , 29.01° , 31.5° , 32.37° and 35.20° . Diffraction peaks are reduced in intensities and broadened at the base. Besides, it is challenging to distinguish diffraction lines at low XRD resolution attributed to a smaller volume of the elemental cell of NaFePO₄. This indicates a nano-sized crystallite structure of the synthesized material. The XRD pattern of NaTi₂(PO₄)₃ anode material has been reported previously [35], and all the diffraction peaks can be indexed to the NASICON structure in the R3c space group; This suggests the purity of the prepared material [36].

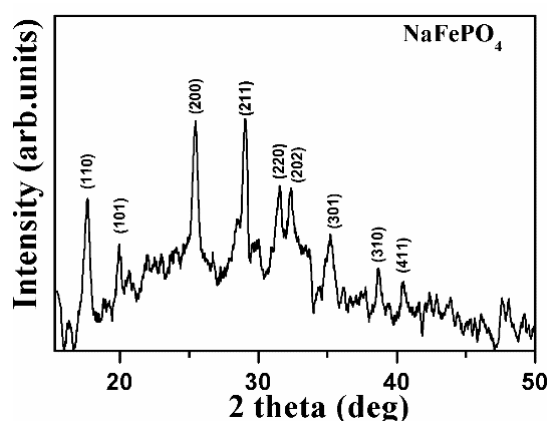


Figure 1. X-ray diffraction pattern of synthesized NaFePO₄.

3.1.2. SEM morphological characterization.

The surface morphology of the material was determined using a scanning electron microscope (SEM). Figures 2A, 2B, 2C and 2D show typical SEM images of NaFePO₄ at 2 μ m, 1 μ m, 200 nm, and 100 nm resolutions respectively. The NaFePO₄ particles are non-spherical in shape and have a flower-like structure, as evidenced by Figures 2B and 2C. In

these flower-like structures, straight bundles of nanobelts are observed in the SEM image. Each bundle consists of hundreds of nano-needles that align in the same direction. From Figures 2C and 2D, it is clear that the synthesized cathode material particle is nano in size and approximately less than 40 nm. Figure 2E shows the EDX spectrum analysis of the NaFePO_4 , where the ratio of Na/Fe/P/O is close to 1:1:1:4. This confirms that Na, Fe, P, and O are well distributed in the sample [22].

3.1.3. Thermogravimetry (TGA) and differential scanning calorimetry (DSC) analysis.

Safety and thermal stability are critical concerns in designing the electrode material for battery application. NaFePO_4 gains much attention among the phosphate polyanion cathode material due to its high operating potentials, safety, and excellent thermal stability [37]. . Figure 3 shows the TG/DSC curves NaFePO_4 , which is useful to determine the decomposition of different moieties at various crystallization temperatures. The first weight loss is about 2.47 wt%, within the temperature range of 32 °C to 350 °C and corresponds to three endothermic peaks at 38.79 °C, 78.92 °C, and 190 °C in the DSC curve (Peak 1, Peak 2 and Peak 3 in Figure 3). The First 2 endothermic peaks, 1 and 2 are below 100°C and can be due to the evaporation of volatile solvents and unbound water. Peak 3 in Figure 3, at 190 °C within the temperature range of 80-316 °C indicates the decomposition of FeC_2O_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ in the temperature zone [38-40]. The last temperature interval with three exothermic peaks (peak 4, peak 5, and peak 6 in Figure 3) within the range of 368 °C to 664 °C can be assigned to the crystallization and grain growth of the synthesized NaFePO_4 .

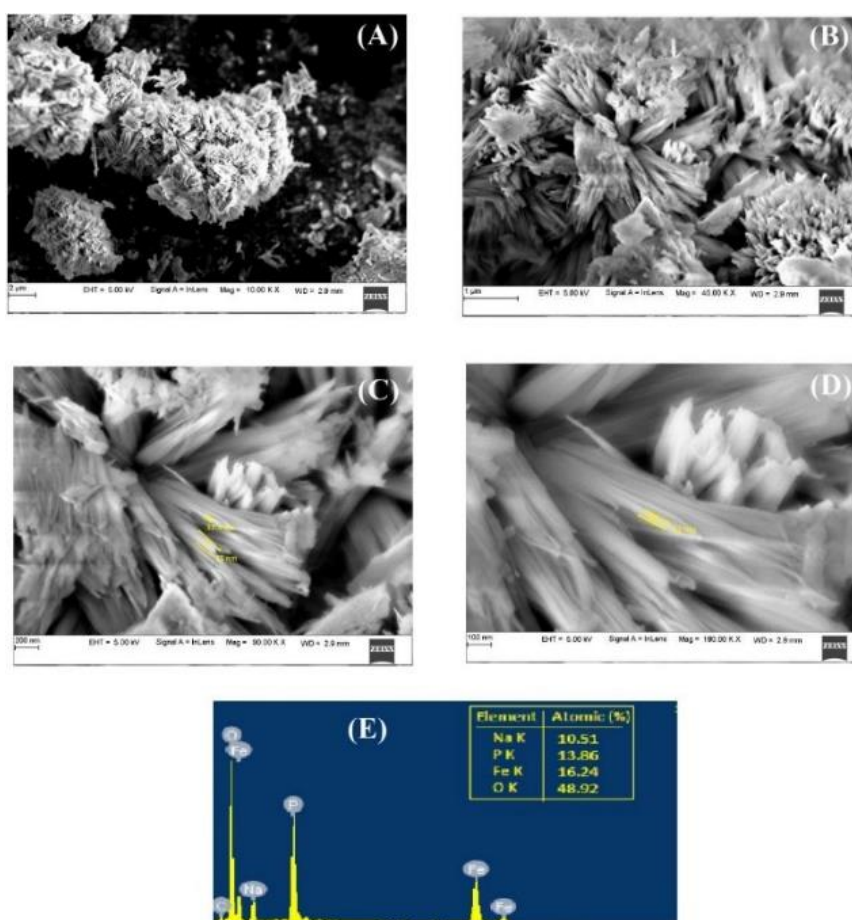


Figure 2. SEM images of the synthesized NaFePO_4 at different magnifications (A) 2 μm , (B) 1 μm (C) 200 nm (D) 100 nm and (E) the EDX spectrum of NaFePO_4 .

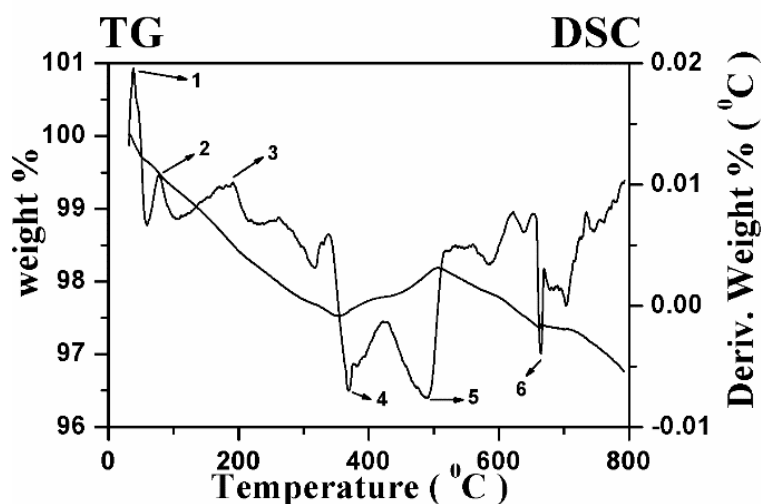


Figure 3. TGA and DSC profile of NaFePO₄ cathode material.

3.2. Electrochemical Characterization of NaFePO₄ nanoparticles.

3.2.1. Cyclic voltammetry study of NaFePO₄ in aqueous solutions.

Electrochemical performances of NaFePO₄ were evaluated using a three-electrode experimental setup, and cyclic voltammetry (CV) is the primary tool to analyze the electrochemical reaction. Figure 4a shows the CV of titanium meshes current collector in 5M NaNO₃ aqueous solution. Between the two peaks, the anodic peak is observed at 1.5 V (vs SCE) (corresponding to O₂ evolution) and a cathode peak at about -1.0V (vs. SCE) (corresponding to H₂ evolution). The stable electrochemical window of water on Ti mesh is about 2.50 V, much larger than the normal 1.23 V due to large overpotential. Figure 4b shows the cyclic voltammograms of NaFePO₄ in 5M NaNO₃ electrolyte at a scan rate of 1.5 mV s⁻¹. However, in previous reports, the cyclic voltammetry of a NaFePO₄ in a charging process showed 2 step phase transformation (i.e., two voltage plateau) where NaFePO₄ would transfer into Na_{2/3}FePO₄ first and then subsequently into FePO₄ [22, 24]. However, in this work, the CV profile of NaFePO₄ in Figure 4B shows only one peak during both the charge and discharge processes. This is because the unit volume expansion of FePO₄ to Na_{2/3}FePO₄ is about 13.5%, which is 3 times larger than that found for (3.6%) of the volume change from Na_{2/3}FePO₄ to NaFePO₄ [25, 41]. Thus, the first transformation should overcome a much higher kinetics barrier than the 2nd one. Therefore Na_{2/3}FePO₄ would transfer into NaFePO₄ immediately [22], thus the apparent reaction in both charging and discharging looks like the direct transformation from NaFePO₄ to FePO₄ and FePO₄ to NaFePO₄ as reflected by a single voltage peak on both charge and discharge profile.

CV profile of NaFePO₄ shows an anode peak at 0.27 V, which corresponds to sodium ion de-insertion, and a cathodic peak at -0.11 V vs. SCE, which corresponds to the sodium ion insertion process. The peak potential difference (ΔE_p) is about 0.38 V, which is too large to compare with a theoretical value of 0.059V for a one-electron transfer system to be reversible. According to theory, we can apply a minimal scan rate to get proper separation between the anodic and cathodic peaks. Practically, we used 1 mV s⁻¹ as the lowest scan rate. The large potential gap of 0.38 V between the anodic and cathodic peaks suggests that the electron transfer process is very slow at NaFePO₄ in an aqueous 5M NaNO₃ solution or may be due to the bigger size of the sodium ion and have some difficulty during the intercalation to the host of FePO₄. Hence this makes the potential gap larger [5-7,42]. The ratio of anodic to cathodic

peak current is 0.97, closer to 1. The results indicate that Na^+ insertion/de-insertion in Na_xFePO_4 matrix is a single-step process like those reported in non-aqueous electrolytes [30].

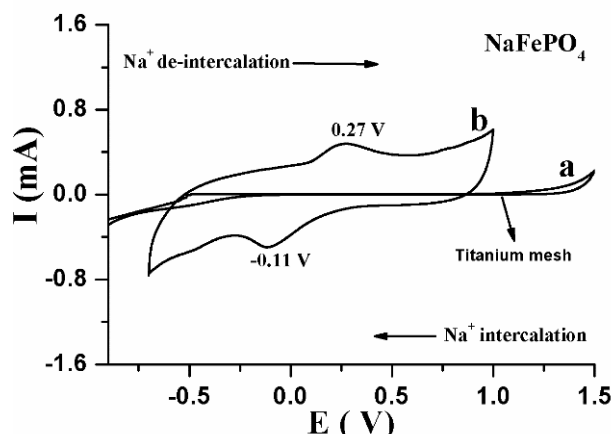


Figure 4. Cyclic voltammogram of, (a) Titanium mesh (Ti) in 5 mol l⁻¹ NaNO₃ aqueous solution (Scanrate; 1.5 mVs⁻¹) and (b) NaFePO₄ electrode in 5 mol l⁻¹ NaNO₃ aqueous solution.

3.2.2. Effect of scan rate.

Reversibility of the cathode material (NaFePO₄) was studied by using CV curves at different scan rates varied between 1 mV s⁻¹ to 10 mV s⁻¹. Figure 5A shows the typical CV curves within a potential range from -0.7 V to 1 V vs. SCE at various scan rates in 5M NaNO₃. The following are the observation made from the CV profiles of different scan rates: a) the peak separation increases with increasing scan rate, (b) a linear dependence during the initial increase in current potential behavior, and (c) all CV profiles overlap regardless of the scan rate at the beginning of charging and discharging [42], most symmetric CV curves in each cycle represent typical battery behaviors; simultaneously, overall CV shape is maintained well as the scan rate increases from 1mV s⁻¹ to 10 mV s⁻¹. The voltage gap between the reduction and oxidation peaks is attributed to the electrode polarization, closely correlating with the active 'material's conductivity [43]. Figure 5B shows the plot of anodic and cathodic peak currents (i_{pa} and i_{pc}) with the square root of scan rate ($v^{1/2}$). The plot shows a linear dependence between i_p and $v^{1/2}$ at almost all scan rates, and the peak currents (i_p) are proportional to the square root of scan rate ($v^{1/2}$), i.e., $i_p \propto v^{1/2}$ at different scan rates. This indicates that the electrode reaction at NaFePO₄ is a diffusion-controlled process [44].

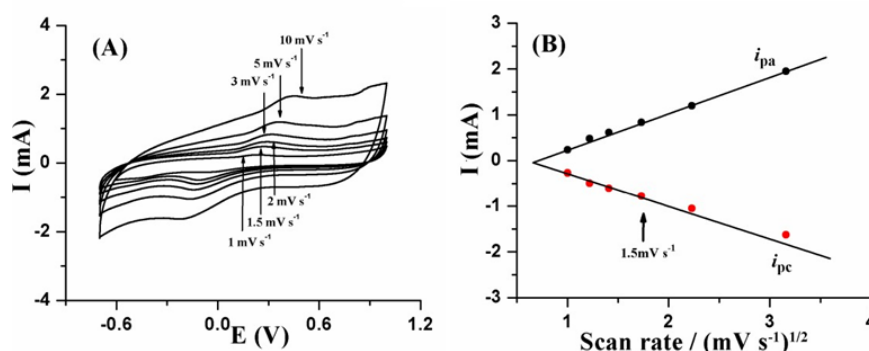


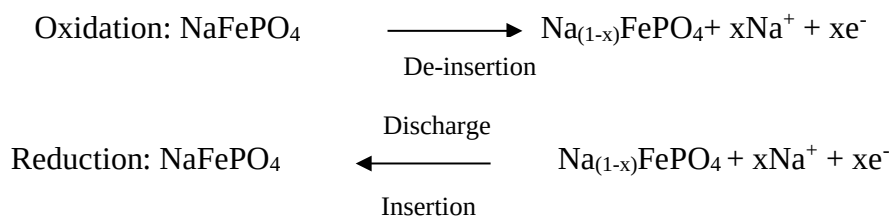
Figure 5. (A) Cyclic voltammograms of NaFePO₄ electrode recorded in 5 M NaNO₃ aqueous electrolyte at various scan rates. (B) The relation between the peak current density and the square root of the scan rate of NaFePO₄ in an aqueous 5 M NaNO₃ solution.

3.2.3. Identification of cation.

Identification of cation intercalated into the electrode is vital in aqueous electrolytes because the interference of proton insertion reaction into the host FePO_4 cannot be ruled out. A set of well-defined redox peaks obtained for the NaFePO_4 electrode can be explained based on the redox activity of iron species in NaFePO_4 , as it is a well-known fact that the center for the primary electron-donating or accepting reaction is iron. NaFePO_4 battery chemistry, Na^+ ions are shuttled between the positive and negative electrodes during charging and discharging, with an electrolyte acting as the transportation media for Na^+ ions [5-7]. Therefore the anodic and cathodic peaks appear probably due to the oxidation of Fe^{2+} to Fe^{3+} and reduction of Fe^{3+} to Fe^{2+} in NaFePO_4 accompanied by the extraction and insertion of the cation. However, from the redox peak potentials, we cannot assume that the cation is Na^+ . Therefore, the identification of cation has to be established. According to Nernst law, the oxidation and reduction reactions should follow the dependence of the redox reaction's formal potential on the sodium ion activity by the following equation [45].

$$E_f = E^0 + 0.059 \log a_{\text{Na}^+}$$

The formal potential $E_f = (E_a + E_c)/2$ (E_a anodic peak potential; E_c cathodic peak potential) of the redox reaction should be directly proportional to the sodium ion's logarithm activity in the NaNO_3 electrolyte. Cyclic voltammetry curves of NaFePO_4 in various concentration of NaNO_3 , 0.05, 0.1, 0.5, 1 and 5 M NaNO_3 are as shown in Figure 6A. We also plotted a graph of formal redox potential (E_f) of NaFePO_4 versus $\log [\text{Na}^+]$, as shown in Figure 6B. A well-fitted straight line with a positive slope was obtained. These results indicate that the redox reaction mechanism of NaFePO_4 in 5M NaNO_3 aqueous electrolyte is similar to that reported for non-aqueous and aqueous electrolytes [46, 47]. The equation for the redox peaks of NaFePO_4 can be written as:



This result indicates the Na^+ alkali metal cation intercalates into NaFePO_4 from 5M NaNO_3 aqueous electrolyte.

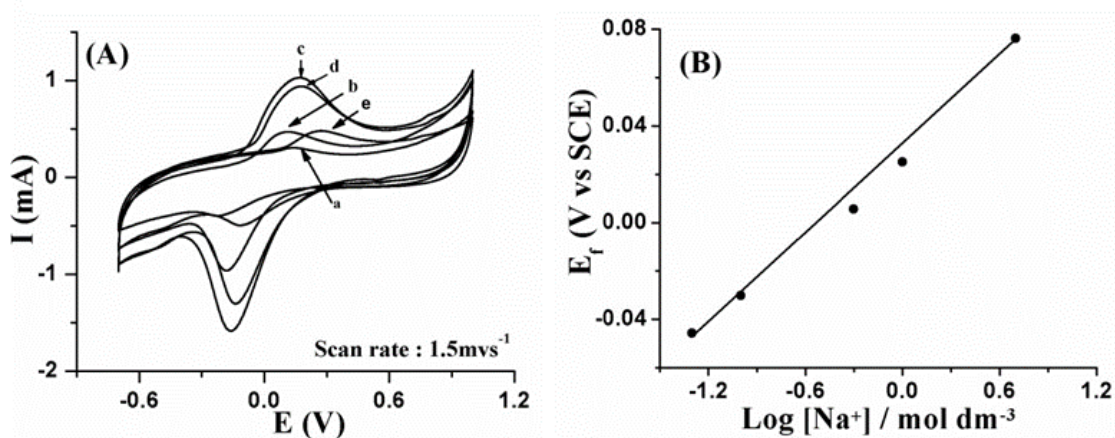


Figure 6. (A) Cyclic voltammograms of NaFePO_4 in different concentration (B) Plot of E_f vs. $\log [\text{Na}^+]$.

3.3. Galvanostatic charge-discharge studies.

To study the charge-discharge cycling behavior of the NaFePO_4 electrode, a full cell was constructed using NaFePO_4 as cathode and $\text{NaTi}_2(\text{PO}_4)_3$ as an anode in 5M NaNO_3 aqueous solution. The voltage profile in Figure 7A shows only one plateau during both charging and discharging. In previous reports, various spectroscopy techniques [48, 49] and composition- temperature phase diagram [26], etc. are used to identify $\text{Na}_{2/3}\text{FePO}_4$ superstructure formation. However, in this work, only a single plateau can be seen in both charging and discharging, which may be attributed to the fact that phase transformation from $\text{Na}_{2/3}\text{FePO}_4$ to NaFePO_4 (3.6% difference in volume) occurs at much lower kinetic barriers compared to that from FePO_4 to $\text{Na}_{2/3}\text{FePO}_4$ (13.5% difference in volume) [25, 40]. Consequently, the unit volume expansion from FePO_4 to $\text{Na}_{2/3}\text{FePO}_4$ is more than 3 times larger than that (3.6%) from $\text{Na}_{2/3}\text{FePO}_4$ to NaFePO_4 .

Similarly, the first phase transformation has to overcome a much higher kinetics barrier than the follow-up one. Therefore $\text{Na}_{2/3}\text{FePO}_4$ formed from the first transformation process would transform into NaFePO_4 immediately. Thus, the apparent reaction is directly transformed from FePO_4 to NaFePO_4 as reflected by a single voltage plateau on the charging and discharging profile. From Figure 7A, we can observe a charge-discharge curve of $\text{NaTi}_2(\text{PO}_4)_3$ / 5M NaNO_3 / NaFePO_4 cell cycled between the voltage range of 0.2 to 1.4 V at C/5 rate delivering a discharge specific capacity of 96.96 mAh g^{-1} , which is 62.96% of the theoretical capacity (154 mAh g^{-1}). This initial discharge capacity is better than most previous reports [21]. The capacity retention of the full cell is 78% over 50 cycles at a C/5 rate. No further optimization is done, and only 20% of carbon black is added to enhance the electrochemical property of cathode material at room temperature. The drawback of capacity fading may be due to anode, as Park *et al.* [36] confirmed that 40% capacity fading is after 30 cycles in NTP cases. Another reason could be the resistance in the aqueous electrolyte. Hence further investigation has to be done to get a better insight into it.

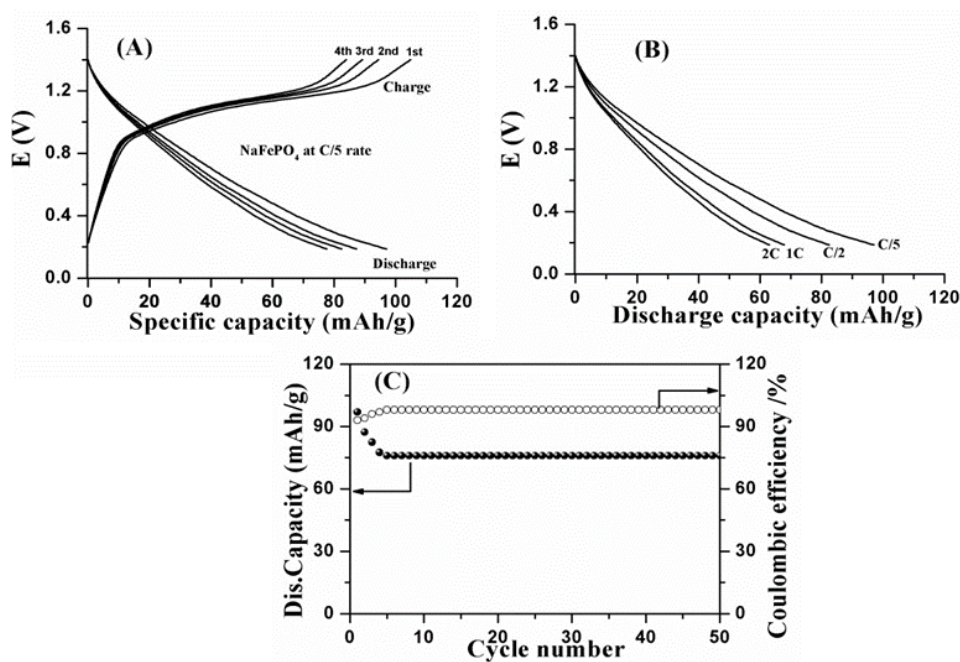


Figure 7. (A) charge-discharge curves (B) Discharge curves at different C rates of NaFePO_4 / $\text{NaTi}_2(\text{PO}_4)_3$ cell in aqueous electrolyte (C) Capacity trend vs. Number of cycles at C/5 rate and coulombic efficiency vs the number of cycles.

The full cell $\text{NaTi}_2(\text{PO}_4)_3$ / 5M $\text{NaNO}_3/\text{NaFePO}_4$ is subjected to a charge-discharge process at various C-rates ($C/5$, $C/2$, $1C$, $2C$), and the voltage profiles are shown in Figure 7B. Discharge capacity gradually decreases from low C-rates to high C-rates, i.e., from $C/5$ rate to $C/2$ rate with an initial discharge capacity of 96.96 mAh g^{-1} to 82.60 mAh g^{-1} with 14% of capacity retained at $C/2$ rate. Surprisingly at a high C-rate, it showed adequate initial discharge capacity, i.e., at $1C$ (68.06 mAh g^{-1}) and at $2C$ (63.2 mAh g^{-1}), which is higher than the previous reports [21]. Figure 7C shows both the coulombic efficiency and discharge capacity of the full cell for each cycle. The results are shown over 50 cycles, in which cycles get stabilized after the first 5 cycles. Discharge capacity dropped by 20% of the initial value in the first few cycles, but it later stabilized. Thus an ARSIB cell $\text{NaTi}_2(\text{PO}_4)_3$ / 5M $\text{NaNO}_3/\text{NaFePO}_4$ has been successfully constructed and studied in an aqueous electrolyte.

4. Conclusions

The NaFePO_4 nanoparticles are synthesized using DES as a solvent medium by a low-temperature one-step ionothermal method. The full cell $\text{NaTi}_2(\text{PO}_4)_3/5\text{M NaNO}_3/\text{NaFePO}_4$ delivered an initial discharge capacity of 96.96 mAh g^{-1} at $C/5$ rate with better capacity retention over 50 cycles. The experimental results of sodium extraction and reversible re-insertion from cathode material like NaFePO_4 in the aqueous electrolyte are also investigated.

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Conflicts of Interest

The authors declare no conflict of interest.

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