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# Synthesis, characterization, and electrochemical studies of chemically synthesized $NaFePO_4$

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ABSTRACT

$NaFePO_4$ is a naturally occurring mineral known as maricite. This compound has not been well characterized or examined for its potential use in battery applications. In the present study, $NaFePO_4$ has been synthesized via the Pechini process with the resulting sample being characterized by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Electrochemical properties have been investigated for possible application as a cathode in sodium-ion batteries. Electrodes of these materials were tested in coin cells using $LiPF_6$ as the electrolyte and lithium metal as the counter electrode. Constant current cycling, cyclic voltammetry, and in situ frequency response analyses were performed. The results obtained demonstrate constant capacity or progressive increase in capacity with the consistently low internal resistance exhibited over consecutive cycles indicating possible application as a lithium analog in Na-ion batteries.

## 1. Introduction

Lithium iron phosphates have been considered as attractive cathode materials in lithium ion batteries due to its flat charge–discharge profile at intermediate voltage, environmental friendliness, reasonable cycling and cycling rate, and the low cost. Presently, the demand for portable, reliable and low cost electronic devices has led to extensive research in lithium-ion batteries. Research in Li-ion batteries has recently been cohesively focused on generating high energy density systems for electric vehicle technology. However, the high cost and limited natural abundance of lithium as well as the potential safety issues still plaguing the system have sparked renewed interest in sodium-ion batteries, particularly for applications with stringent land-based power requirements, such as electrical grid stabilization [1–3]. Current estimates show that, at the present rate of consumption, the world lithium reserve will be depleted in less than 150 years [4–7]. As of now, the dominant use for lithium is in Li-ion batteries. Furthermore, with the increasing demand for Li-ion batteries in electric vehicles and portable consumer electronic devices, this demand can only be expected to further increase. In the coming years, finding a suitable substitute for Li-ion batteries in various targeted applications will become increasingly critical.

A possible natural substitute for lithium in battery applications is sodium; where similar to lithium, sodium is an alkali metal with low ionization potential making it a possible suitable candidate for rechargeable battery electrode materials. Sodium however, is a larger ion than lithium with an ionic radius of 1.2 Å as compared to 0.90 Å for lithium and is also almost three times heavier than lithium, with an atomic weight of 22.99 g $mol^{-1}$, compared to only 6.941 g $mol^{-1}$ for that of Li. As a result, charge transfer will be significantly slower in Na-ion batteries than in Li-ion batteries, due to the increased difficulty of ionic insertion and extraction into the cathode, respectively. This slower charge transfer results in lower capacity of the cell due to the expected transport limitations of $Na^+$ in the electrodes, which correspondingly results in lower energy and lower power densities. Despite these disadvantages, Na-ion batteries appear to be an acceptable replacement for Li-ion batteries in several applications, particularly where weight and size are not important such as stationary land-based power applications or non-portable systems and electrical grid stabilization. Introducing energy storage devices into the electric grid can help store

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electricity when it is being produced in excess of demand and release it during periods of higher demand. This work has been performed with the intention of understanding a non-lithium based cost effective battery cathode with long cycle life for possible land based energy storage system application compared to lead acid batteries. The success of $LiFePO_4$ as a cathode material for Li-ion batteries inspired the present investigation on the analogous $NaFePO_4$ as a cathode material for Na-ion batteries and $Na^+/Li^+$ mixed-ion batteries. This work presents the potential applicability of $NaFePO_4$ related cathodes for possible non-portable electrical storage applications.

$NaFePO_4$ has previously been studied as deposits that result from a process known as phosphate hideout in boilers, which contributes to boiler corrosion [8]; hence some of the material properties of $NaFePO_4$ are known, but there have been no electrochemical tests conducted on the compound so far to the best of our knowledge. To date, $NaFePO_4$ has not been well characterized or examined for battery applications. Ellis et al., have reported a sodium/lithium iron phosphate, $A_2FePO_4F$ (A = Na, Li) system that could serve as a cathode in either Li-ion or Na-ion cells, but indicated that $NaFePO_4$ was not suitable as a cathode material due to the ‘closed’ maricite framework, which results in entrapment of $Na^+$ which prevents reversible redox behavior [9,10]. Contrary to Ellis et al., Moreau et al. have reported the synthesis of $NaFePO_4$ by complete electrochemical sodiation of $FePO_4$ in $NaClO_4$ using a potentiodynamic mode, resulting in electrochemically synthesized $NaFePO_4$ with olivine structure [11]. Shiratsuchi et al., have shown amorphous and crystalline $FePO_4$ could be a better cathode for Li and Na cells by utilizing the Fe(III)/Fe(II) redox reaction. [12]. Trad et al., studied the intercalation–deintercalation process of $Na^+$ ions in $Na_3Fe_3(PO_4)_4$ and showed reversibility during cycling while maintaining the structural framework [13]. In the present study, the electrochemical properties of $NaFePO_4$ are investigated by synthesizing $NaFePO_4$ using the Pechini method and correspondingly, testing the material in coin cells using Li metal as the counter electrode and $LiPF_6$ as the electrolyte salt in ethylene carbonate/diethyl carbonate solvents.

## 2. Experimental

Stoichiometric ratios of $NaNO_3$ and $Fe(NO_3)_2\cdot 9H_2O$ were dissolved in deionized $H_2O$ along with citric acid (CA). $(NH_4)_2HPO_4$ was dissolved in water independently using ultrasound and added into the above solution drop wise. This solution was then heated to 40 °C before adding ethylene glycol (EG) to prevent premature gelling at low temperature. The molar ratio of M:CA:EG used was 1:0.5:0.5, where M is the sum of all metal ions, in this case Na and Fe. The temperature was raised again to 60 °C for 24 h to evaporate $H_2O$. As the water level approached 50 mL, the beaker was transferred into a heating mantle to provide more uniform heating throughout the mixture. The temperature was initially set to 70 °C, but due to the exothermic nature of the ensuing reaction, the temperature quickly increases, releasing $NO_2$ gas. Once the reaction was completed and no further gas release was observed, the resulting compound was placed in an oven at 120 °C for 24 h to complete the drying process. The $NaFePO_4$ precursor was synthesized using this method and then heated to high temperature for 1 h in a number of different environments (nitrogen ($N_2$), argon (Ar), 5 vol.% hydrogen in argon (5% $H_2$/Ar), and air). Annealing in inert environments was done in a Micromeritics AutoChem™ II 2920 Automated Catalyst Characterization System. Annealing in air was performed in a Fisher Scientific Isotemp Programmable Muffle Furnace. Heat treatments were performed at 550 °C and 600 °C in argon (Ar) environment.

### 2.1. Characterization

X-ray diffraction (XRD) was carried out utilizing a PANalytical X’Pert Pro X-ray diffraction system. XRD was used to identify the chemical phase(s) and presence of any crystalline impurities in the sample material. When annealed in an inert or close to inert environment such as $N_2$, Ar, or 5% $H_2$/Ar, some residual carbon is expected to remain in the material due to the presence of ethylene glycol, which could enhance the electronic conductivity of the phosphate depending on the graphitic and non-graphitic nature of the residual carbon. The residual carbon is not considered part of the active material and thermogravimetric analysis (TGA) was conducted on the sample in order to determine how much carbon is contained in the material. For the $NaFePO_4$ sample, the temperature was increased from room temperature to 800 °C at a ramp rate of 5 °C $min^{-1}$ in air.

X-ray photoelectron spectroscopy (XPS) spectra were obtained utilizing a Physical Electronics (PE) SAM-590 UHV system equipped with a PE spherical capacitor type analyzer with an Omni Focus III Lens and a PE 04-303 Argon (Ar) ion Gun. System calibrations were in accordance with PE procedures utilizing the photoemission lines $E_B$ (Cu $2p_{3/2}$) = 932.7 eV, $E_B$ (Au $4f_{7/2}$) = 84 eV and $E_B$ (Ag $3d_{5/2}$) = 368.3 eV [14]. The system had a standing pressure of $10^{-9}$ Torr ($1.3\times10^{-7}$ Pa) and was operated within a pressure range of $10^{-9}$ Torr to $10^{-8}$ Torr ($1.3\times10^{-7}$ Pa to $1.3\times10^{-6}$ Pa). Binding energies (BEs) were referenced to adventitious carbon at 284.8 eV. XPS analysis was also conducted on the $NaFePO_4$ cathodes that underwent multiple cycle tests in order to determine the presence of Li and Na on the cathode surface.

Electrochemical analysis was conducted on the electrodes fabricated as follows. The working electrode (WE) was prepared using 80% of the active material, 10% carbon black (CB), and 10% polyvinylidene fluoride (PVDF) binder. Slurry was made in N-methyl-2-pyrrolidinone (NMP) solvent. This slurry was then uniformly coated onto a aluminum foil current collector using an applicator to generate a coating of 120 μm thickness. After drying in the fume hood for 24 h, the coated foil was cut into 0.5 in. diameter circles, creating the working electrodes. These electrodes were placed in a two-electrode coin cell using lithium foil as the counter electrode (CE) and 1 M $LiPF_6$ salt in ethylene carbonate/diethyl carbonate (1:1 by volume EC:DEC) solution as the electrolyte. A micro-porous separator (Celgard®3501) was placed between the working and counter electrodes. $NaFePO_4$ annealed in Ar at 600 °C have been used to test the electrochemical properties. The battery cycle tests were performed between 2 V and 4 V using the Solartron and Arbin battery test stations. Cyclic voltammetry at a rate of 0.1 mV/s was performed using the Solartron unit. Two separate current rates 5 mA and 20 mA were used to charge/discharge the cells, The electrochemical impedance spectroscopy (EIS) measurements were performed after the electrode reached the end of each charge and discharge states. The measurements were taken over a range of 1000 kHz to 1 MHz with AC amplitude of 10 mV using a Solartron analyzer.

## 3. Results and discussion

The materials synthesized were annealed at different temperatures (550 °C and 600 °C) in different environments ($N_2$, Ar, 5% $H_2$/Ar, etc.) and compared with each other to understand the phase evolution. Fig. 1 shows the XRD patterns collected for $NaFePO_4$ obtained after annealing in three different environments, $N_2$, Ar, and 5% $H_2$/Ar, all at 600 °C for 1 h, along with the standard pattern reported in the literature. In the beginning, some tiny impurity peaks were observed for the $N_2$ annealed samples and further optimization of temperature and annealing time resulted in a single