

Chykyda Tatyana Yuryevna

Krushevskiy Alexander Vladimirovich

Kyiv National University of Technologies and Design

(Kyiv)

Language supervisor: V. A. Velykozhon

SYNTHESIS, CHARACTERIZATION, AND ELECTROCHEMICAL STUDIES OF CHEMICALLY SYNTHESIZED NaFePO₄

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. 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]. 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°A as compared to 0,90°A 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. 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.

The success of LiFePO₄ as a cathode material for Li-ion batteries inspired the present investigation on the analogous NaFePO₄ 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.

Experimental. The NaFePO_4 precursor was synthesized 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). Heat treatments were performed at 550°C and 600°C in argon (Ar) environment.

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 $120\ \mu\text{m}$ 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 1M 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 battery test stations. Two separate current rates 5 mA and 20 mA were used to charge/discharge the cells.

Results and discussion. The materials synthesized were annealed at different temperatures in different environments 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 phase NaFePO_4 . It should be noted that all of the observed XRD patterns for NaFePO_4 synthesized utilizing the Pechini method are being reported for the first time. The XRD pattern reported for standard NaFePO_4 is based on the natural maricite mineral. No

significant difference was observed between the Ar and 5% H₂/Ar annealed samples at either temperature. Samples annealed in Ar at 600°C were used for electrochemical investigation. As stated previously, the XRD pattern for the NaFePO₄ material used in the current experiments matched well to the pattern reported in the literature. Upon heating the sample in air, two small impurity peaks were observed, whose presence is attributed to the formation of iron oxide impurities, as confirmed by TGA (Fig. 2). Electrochemical studies were performed using cyclic voltammetry (CV). CVs for NaFePO₄ cells are presented in Fig. 3. The charge/discharge test for NaFePO₄ cell cycled at a rate of C/10 is shown in Fig. 4. All the electrochemical cycling data has shown low capacity but long cycle life. The insertion of Li into the lattice is proven by the XPS measurements which is discussed in the later section. Electrochemical cycling data for Na⁺/Li⁺ mixed-ion batteries, using both slow and fast cycling rates, are shown in Fig. 5. The charge and discharge capacities for NaFePO₄ over time when cycled at 5 mA g⁻¹ are shown in Fig. 5a. This cell also performed well under fast cycling at 20 mA g⁻¹, as shown in Fig. 5b. Fig. 6 shows the XRD pattern of NaFePO₄ collected separately after 300 cycles at the end of the charge and discharge cycles. The XRD pattern obtained from the electrode in the discharged state indicates that the major crystalline phase corresponds to NaFePO₄. In situ impedance analysis was performed after every 4th charge/discharge cycle for NaFePO₄, with the impedance curves shown in Fig. 7.

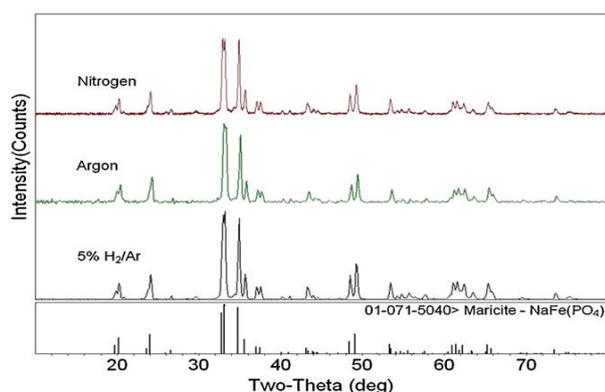


Fig. 1. X-ray diffraction patterns of NaFePO₄ annealed at 600°C for 1 h in three different gases. An accepted pattern reported in the

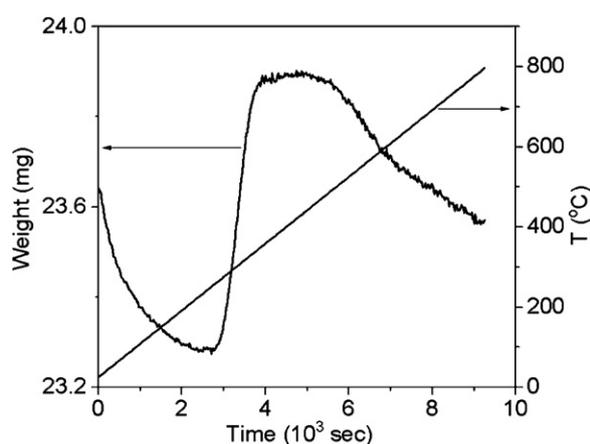


Fig. 2. Thermogravimetric analysis curve for NaFePO₄ sample. Temperature was ramped at 5°C min⁻¹ from room temperature to 800°C.

literature for NaFePO_4 is shown below.

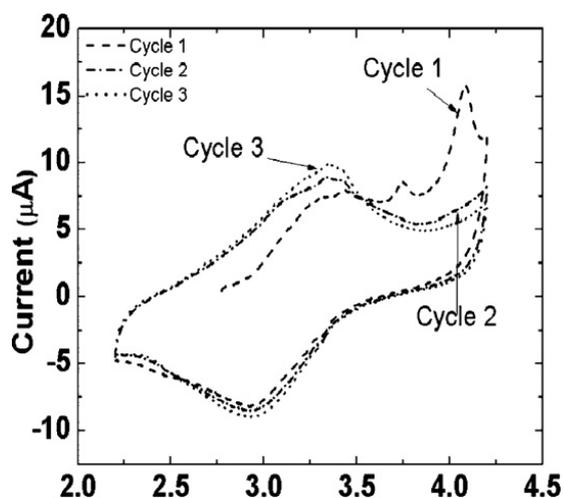


Fig. 3. Cyclic voltammograms of NaFePO_4 . Three cycles were performed at a scan rate of 0,1 mV/s starting from the OCV.

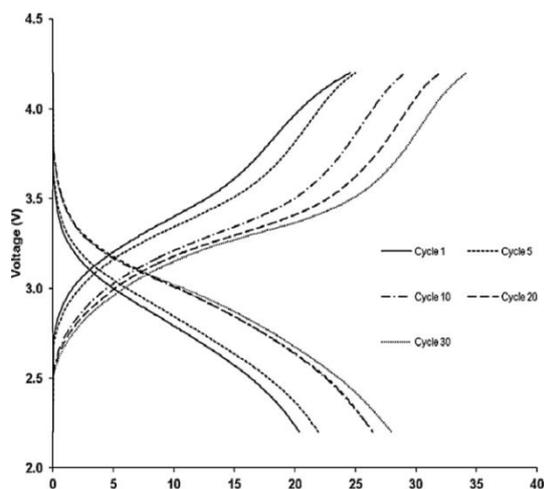


Fig. 4. Charge and discharge voltage curves for the 1st, 5th, 10th, 20th, and 30th cycles for NaFePO_4 at C/10 current rate.

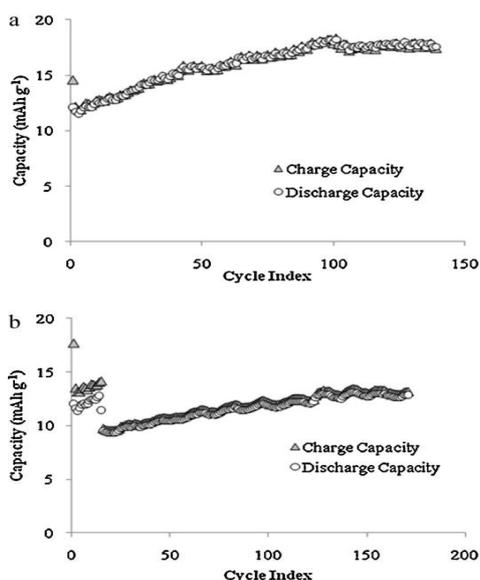


Fig. 5.(a) Charge and discharge capacities of Na^+/Li^+ mixed-ion NaFePO_4 cell cycled at 5 mA g^{-1} for 138 cycles and (b) charge and discharge capacities of Na^+/Li^+ mixed ion NaFePO_4 cell cycled at 20 mA g^{-1} for 171 cycles (initial 15 cycles at 5 mA g^{-1} and the rest at 20 mA g^{-1}).

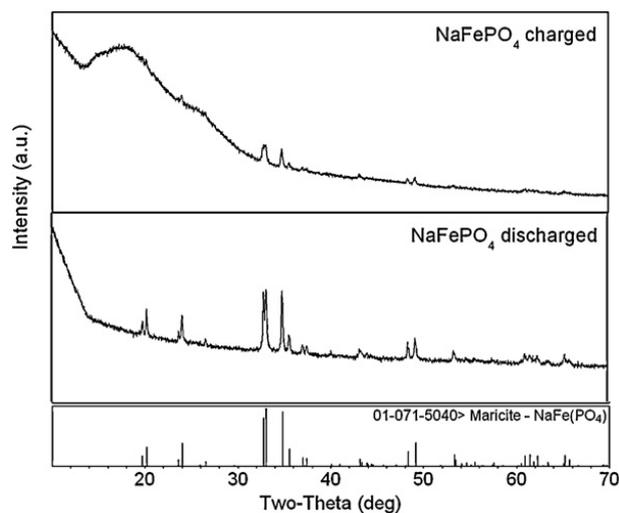


Fig. 6. XRD of NaFePO_4 cathode (top) after completely charged and (bottom) after completely discharged (300 cycles).

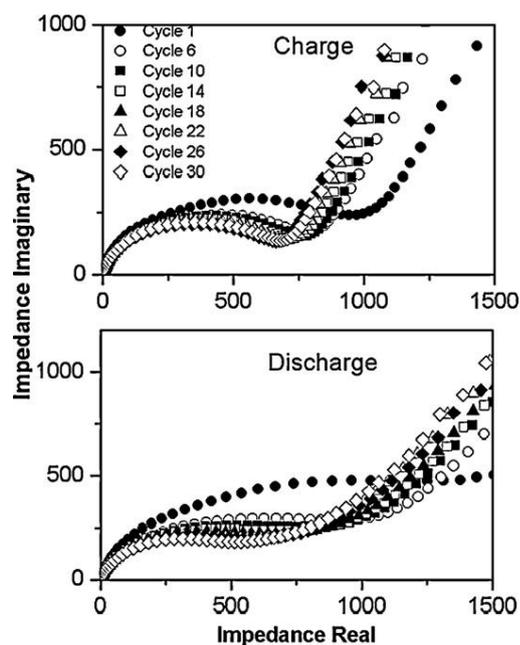


Fig. 7. Impedance curves of the cells at the end of charge and at the end of discharge states for NaFePO₄.

Conclusion. NaFePO₄ was successfully synthesized utilizing the Pechini process. The relative simplicity and versatility of the procedure, as well as the low cost of the materials makes it an attractive approach for preparation of NaFePO₄. As reported above, the synthesis of materials can be controlled by altering the temperature, environment and ratios of starting materials. Despite the relatively low capacities (around 30 mAh g⁻¹), NaFePO₄ and Na_{1-x}Li_xFePO₄ are able to maintain this capacity for a large number of cycles, with the charge discharge capacities continuing to increase after more than 300 cycles.

It is interesting to note whether further charge/discharge cycling will manifest a voltage plateau, although the occurrence of a phase transformation in the material due to replacement of Na-ions by Li has been confirmed. The complex charge transfer impedance mechanics occurring at the different levels of charge and discharge observed in the cells require further study. Although the capacities observed and the corresponding energy densities are lower, the long term stability appears to be good. Even though further study is required, these materials could be of interest for large scale energy storage systems and/or for smart grid applications.

REFERENCES

1. L. Arthouel, F. Moser, R. Dugas, O. Crosnier, D. Belanger, T. Brusse, Journal of the Physical Chemistry C 112 (2008) 7270.

Чуревич Надія Віталіївна

Київський національний університет технологій та дизайну

(м. Київ)

Науковий керівник – Ренська Індіра Іванівна

THE INFLUENCE OF INNOVATIVE TECHNOLOGIES IN THE DESIGN OF CLOTHING

The end of XX beginning of the XXI century in society is characterized by the strongest formation of technologies in absolutely all areas of manufacturing narrowly consumer products. On the one hand, this phenomenon is explained by the distinctive features of the formation of scientific and technological development, and on the other – by the eagerness to the careful use of natural resources. Improving the quality of human existence and the introduction of previously unknown technologies is sometimes ahead of the change in creative currents and the dynamics of artistic preferences. Due to the specificity of work and individual qualities, not all designers are able to master and use the potential of new technologies in the creation of a product in a new way.

Most experts note the rapid changes in technology, worldview, lifestyle, art, environment, clothing, people themselves. The past century was marked by a stormy, if not unique, development of technical thought. Trying to make his life more comfortable, a person changes not only the perception of others about this or that subject, revolutionally modifying it, but also the surrounding reality itself. As you know, any changes affect all aspects of our lives.