
4.1 Introduction

In the past two decades, there has been a surge in average earth temperature, pollution level and disturbance in the weather cycle. To become India a net zero carbon emission country, set year is 2070 (Esha Roy, 2022). Conventional energy sources like Coal and Crude oil majorly fulfill our energy demands. Since we are a net energy importer, India needs energy security at an affordable price in between these transition years (up to 2070). Our energy security has been severely impacted by recent global events like the Russia-Ukraine conflict through supply and artificial price hikes in crude oil prices. So, to tackle an issue like Global warming, unwanted shifting in the weather pattern (Hunt et al., 2020), and energy security, we need to be self-dependent on energy requirements. Renewable like Solar energy system, wind energy, and tidal energy is the nearest and most sustainable solution for our energy need (Daiyan et al., 2020; Evanko et al., 2017; Schmidt, 2016). Solar energy solution is the most viable solution for us due to its availability up to a remote area of our country throughout the year. Solar energy needs to connect to the grid system at a large scale. To get the maximum utilization of our solar energy grid system, we need a grid energy storage system to meet the demand at peak hours (Hussain et al., 2018; Z. Yang et al., 2011). The Discovery of Li-ion batteries revolutionized the portable energy storage system (Manthiram, 2020). The significance of portable energy storage systems is rapidly increasing day by day from consumer electronic devices (Mobile, camera, Laptop), Electric Vehicles (Electric Bikes, Cars, and Trucks) to Grid energy storage systems (Manthiram, 2017). Due to the huge demand for Lithium and its limited reserve (Argentina, Bolivia, Chile, Australia and China) it appears to be future gold. However, as per demand perspective, Lithium is on the verge of scarcity (Nitta et al., 2015); in the view of our renewable energy utilization, Li is our obvious choice, but Sodium is our natural choice because sodium

can be obtained from NaCl by sea (Nurohmah et al., 2022). Sodium-ion batteries can be at least ten times cheaper than Li-ion batteries (Abraham, 2020b). So, the Sodium-ion battery storage system is an economical energy storage system for us. Current Li-ion technology can't be directly implemented into sodium-ion battery technology. So, immediate attention is needed to develop a high-voltage cathode for sodium-ion batteries. In Chapter 1 NASICON structured cathode has been reported as a cathode for sodium-ion battery cathode. Chapter 1 said $\text{Na}_3\text{Fe}_2(\text{SO}_4)_2\text{PO}_4$ operates around 3.2 V, so careful doping with $\text{M}^{2+/3+}$ coupled with Mn, Ni, and Mg are pinned almost 0.5-0.8V above the $\text{Fe}^{2+/3+}$ couple. Also, the recently developed Ni-based layered cathode $\text{Na}_2\text{Ni}_2\text{TeO}_6$ operates between 3.7-4.4V (Gupta et al., 2013b). Hence operating redox voltage can be successfully modified by substituting a suitable quantity of Ni, Mn, and Mg doping on the Fe site to increase the voltage (Rao et al., 2021). I am here trying to improve the material's energy density and power density and expecting a specific capacity of nearly 100 mAh/g at an operating voltage of 3.8-4.0 V and thus expected energy density ~ 400 - 500Wh/Kg similar or closer to Lithium-ion battery.

4.2 Experimental Procedure

A facile low-cost synthesis route has opted to synthesize $\text{Na}_3\text{Fe}_{1.5}\text{Ni}_{0.5}\text{PO}_4(\text{SO}_4)_2$. 0.015 M $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, 0.005M NiSO_4 , 0.01 M NaH_2PO_4 were dissolved in 100 ml of water under continuous stirring at 120 °C on a hot plate. 0.01 M Na_2CO_3 Sodium carbonate was added to the above mixture leading to a spontaneous evolution of CO_2 gas and forming a water-insoluble compound. Water was removed by drying at 100 °C, and light yellowish green-colored powder was obtained. The resulting yellow powder was ground and transferred into an alumina crucible to be sintered at 500 °C

for 12 hours (at a ramp rate of 2 °C per minute). As sulphate ion decomposes to SO₂ gas above 600 °C (Tizzoni et al., 2015), we sintered the sample at 500 °C to avoid any loss of sulphate ions. The sample was cooled naturally till it reached room temperature (25 °C). A similar process has been followed for Na₃Fe_{1.5}Mn_{0.5}(SO₄)₂PO₄ (0.015 M (NH₄)₂Fe(SO₄)₂, 0.005M MnSO₄, 0.01 M NaH₂PO₄ were dissolved in 100 ml of water under continuous stirring at 120 °C on a hot stirring plate. 0.01 M Na₂CO₃) and Na₃Fe_{1.5}Mn_{0.5}(SO₄)₂PO₄ synthesis (0.015 M (NH₄)₂Fe(SO₄)₂, 0.005M MgSO₄, 0.01 M NaH₂PO₄ were dissolved in 100 ml of water under continuous stirring at 120 °C on a hot stirring plate. 0.01 M Na₂CO₃). The phase purity and structure stability of the prepared powders were confirmed by the powder X-ray diffraction (XRD) analysis carried out with a Rigaku Miniflex Diffractometer equipped with a Cu K α source ($\lambda = 1.54056 \text{ \AA}$ (voltage 20 kV, current 20 mA, $2\theta - 10$ to 70°). Structure matched well with Na₃Cr₂(PO₄)₃ having a rhombohedral crystal system and R3⁻c space group.

4.3 Cell Assembling

An electrochemical study of cathode material was carried out by making a homogeneous slurry by mixing active material (NFPS Ni/Mn/Mg), conducting carbon and PVDF in the ratio of 70: 25: 5 weight ratios in NMP. Thus, the resulting cathode was made and used as an electrode in Swagelok-type cells using sodium metal as both counter and reference electrodes. A porous glass microfiber filter paper (GF/D, Whatman Int. Ltd.) was used as a separator, and the electrolyte used was 1.0 M NaPF₆ in ethylene carbonate (EC)/ Propylene carbonate (PC) (1:1 v/v%). Cell assembly was carried out in an argon (99.999%) filled glove box (MBRAUN, Germany) where the H₂O and O₂ concentrations were maintained to ≤ 1 ppm during active mass loading of 4 - 5 mg per

cell. The cells' cyclic voltammetry and galvanostatic charge–discharge cycling tests were carried out at different current rates within the voltage window of 1.5 - 4.2 V. vs. Na^0/Na^+ . All the electrochemical tests were conducted using VMP3Z (Bio-logic) multichannel Potentiostat / Galvanostat workstations under ambient conditions.

4.4 Results and Discussions

4.4.1 Structural Analysis

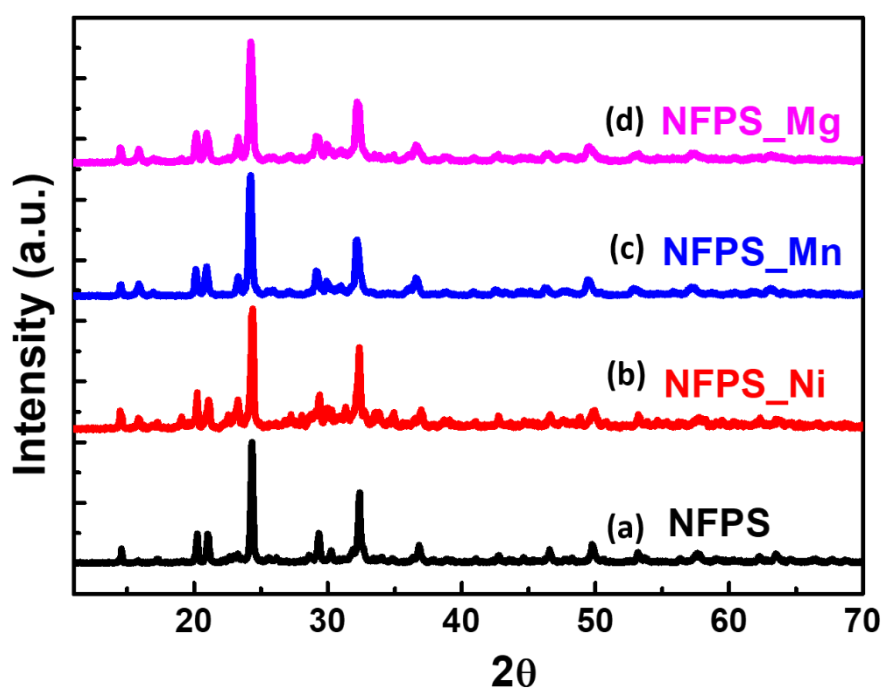


Figure 4.1 Powder XRD Pattern of (a) $\text{Na}_3\text{Fe}_2\text{PO}_4(\text{SO}_4)_2$. NFPS and its doping with (b) Nickel ($\text{Na}_3\text{Fe}_{1.5}\text{Ni}_{0.5}\text{PO}_4(\text{SO}_4)_2$.) (c) Manganese ($\text{Na}_3\text{Fe}_{1.5}\text{Mn}_{0.5}\text{PO}_4(\text{SO}_4)_2$.) (d) Magnesium ($\text{Na}_3\text{Fe}_{1.5}\text{Mg}_{0.5}\text{PO}_4(\text{SO}_4)_2$.)

In Chapter 1 reported material is $\text{Na}_3\text{Fe}_2\text{PO}_4(\text{SO}_4)_2$. In this chapter, Fe is doped with 0.5Ni, 0.5Mn, and 0.5Mg, as shown in Figure 4.1 of a, b, c, and d, respectively. NFPS has a crystal system of Rhombohedral with a space group of R-3c. XRD pattern is matched with X-Pert high score. There is no impurity peak. After doping, the XRD

diffraction pattern verifies the crystal retain structure. Here polyanion (SO_4^{2-} and PO_4^{3-}) goes into the tetrahedra position and link each other by corner sharing and making a network framework structure, whereas Transition metal goes into the octahedra position and bridge oxygen atom, and this way, NASICON makes a tunnel-type structure that helps in better ion movement.

3.3.1 Electrochemical Analysis

3.3.1.1 Galvanostatic Charge-Discharge Analysis

Galvanostatic Charge-discharge studies are carried out for NFPS_Ni/Mn/Mg cathode vs. Na half-cell at C/10 current rate. Our motto in this work was to improve the working potential of the electrode.

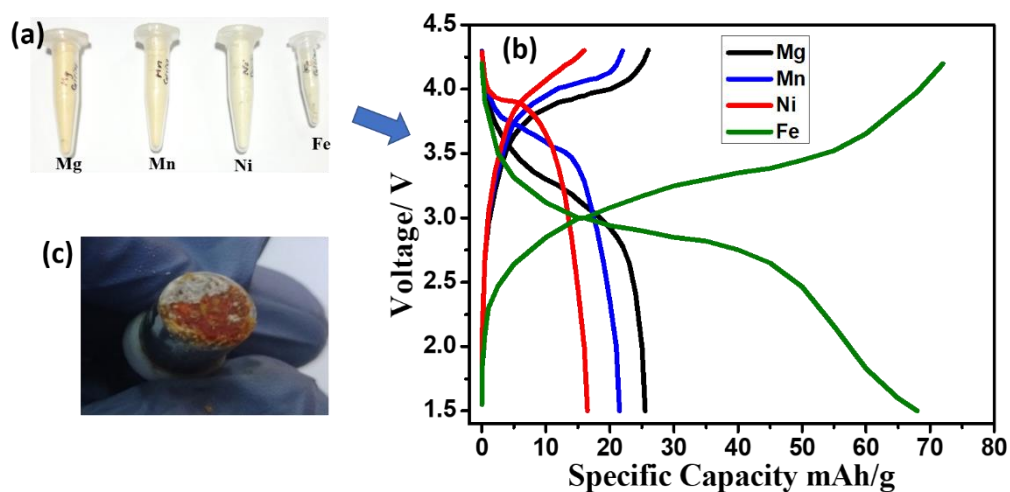


Figure 4.2 Electrochemical analysis of NFPS half cell (a) as prepared electrode powdered material and, doping with (b) $\text{Na}_3\text{Fe}_2\text{PO}_4(\text{SO}_4)_2$ (green), Nickel doping $\text{Na}_3\text{Fe}_{1.5}\text{Ni}_{0.5}\text{PO}_4(\text{SO}_4)_2$. (red), Manganese doping $\text{Na}_3\text{Fe}_{1.5}\text{Mn}_{0.5}\text{PO}_4(\text{SO}_4)_2$. (blue), Magnesium doping $\text{Na}_3\text{Fe}_{1.5}\text{Mg}_{0.5}\text{PO}_4(\text{SO}_4)_2$.(black) (c) electrode degradation

In plot 4.2 (b), it is clearly seen that on doping of iron with active Ni^{2+/3+}, Mn^{2+/3+}, and inactive Mg^{2+/3+} transition metal ions increases the working potential window to 3.9V, 3.8V, and 3.6V vs. Na/Na⁺ but at the same time, a drastic decrease in capacity 16 mAh/g, 22mAh/g, 25.6 mAh/g respectively, as compared to 70 mAh/g Fe^{2+/3+}, is observed. Loss in capacity due to the catalytic activity of Ni and Mn may lead to the degradation of electrolytes at higher voltages. Further high ionic character of SO₄ ligand also results from partial solubility of the electrode in a high dielectric liquid electrolyte. The dielectric constant of EC: DEC electrolyte is close to 55, and water has a dielectric constant close to 80. Thus, a high ionic character responsible for voltage up-gradation resulted in partial solubility of the material into the electrolyte solution. This results in material instability and huge capacity loss. Thus, we cannot go above 3.5V in Na_{1+x}Fe₂(SO₄)₂PO₄ system with doping with Ni, Mn, and Mg.

4.5 Concluding Remark

This work was designed to in the way to increase the energy density of sodium-ion batteries by increasing the working cell potential. High ionic NASICON framework Na₃Fe₂(SO₄)₂PO₄ was doped with active (Ni^{2+/3+}, Mn^{2+/3+}) and in-active (inactive Mg^{2+/3+}) transition metal ions. Synthesis was done by facile low-cost Co-precipitation method. XRD structure reveals no structural changes taking place on doping. There is an increase in cell potential on doping, but at the same time, there is a drastic decrease in the specific capacity due to the catalytic nature of dopant and electrolyte degradation at high potential. In addition to this high ionic nature of ligands like SO₄²⁻ there is partial electrode dissolution taking place. These two factors lead to the heavy capacity ding during charge discharge. Thus, in the coming work, it need to frame our work to change

the transition metal to tackle the heavy capacity fading. So, it is difficult to work with the Sulphate framework in the high-potential cathode.