

# Preface

---

Rising risk of global warming, pollution due to burning of fossil fuel, disturbance of crude oil supply due to rising geopolitical tensions, and becoming a net energy importer. Our country needs an urgent self-reliant and sustainable energy solution. Energy sources like wind and solar seem to be a good solution for our energy needs. However, to utilize the maximum potential of solar energy systems we need a huge energy storage infrastructure. Li-ion battery has revolutionized the portable electronic energy storage market. It is also capturing the electric vehicle segment. However, the huge Li demand in the electric vehicle market and its limited reserve in south American continent countries (Argentina, Bolivia and Chile) raise question on its future supply, and lithium will become a new gold. On the other hand Sodium emerges as a good alternative to Li-ion batteries due to low cost and high abundance. But current Li-ion technology can not be directly applied to sodium-ion battery technology. There is a need of deep research in the cathode material segment. This thesis is focused on the development of a cost-effective electrode with high safety.

**Chapter 1** entitled as "*Introduction and Literature survey*" describe about the significance of Sodium-ion battery storage system in the changing world order in energy consumption. According to McKinsey's global energy perspective 2022, due to growing living standards and electrification needs, power consumption is projected to triple by 2050 (500 million TJ). 3-4% annual growth rate. It is expected to meet 80–90% of the total energy demand from renewable energy sources (RES) by 2050. Global warming is one of the biggest issues of the decade. The average global temperature is rising at a rate of 0.18°C per year. Global warming causes severe climate change seen

in the recent decade, like changes in weather patterns like the drought in the northern part of India (Madhya Pradesh, Jharkhand, and Rajasthan), Severe floods in Kerala. Renewable energy has the opportunity to tackle the issue of energy security and environmental challenges. CO<sub>2</sub> footprint in the environment can be minimized by the use in commercial and passenger vehicle segment, renewable energy storage systems. The lithium-ion battery has dominated the energy storage sector. Detailed electrode material development history has been discussed in the chapter.

**Chapter 2** is entitled as "*Methodology and Instrumentation*". This chapter compose of two segments first is the Materials synthesis and cell fabrication and second is the materials characterisation and cell testing. Coming to the first process, material is synthesized by the facile and low-temperature coprecipitation method, where the nontoxic solvent is used. Cell fabrication needs slurry mixing, slurry coating and a pressing process. The prepared electrode is assembled in a glove box. The second segment is material and cell characterisation which is further subdivided into two sections physical and electrochemical characterization. Physical characterisation process like X-Ray diffraction (XRD), Fourier Transform Infrared Ray Spectroscopy (FTIR), UV-Visible spectroscopy (UV-Vis), X-Ray Photo Electron Microscopy (XPS), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) has been detailed elaborated in the chapter. An electrochemical performance like Cyclic Voltammetry (CV), Galvanostatic Charge Discharge (GCD), Impedance Spectroscopy, Galvanostatic Intermittent Titration Technique (GITT) has been detailed studied in the chapter.

**Chapter 3** is entitled "*NASICON structured Na<sub>3</sub>Fe<sub>2</sub>PO<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub> as a cathode for Rechargeable Sodium-ion battery*". This chapter emerges with new Iron based of NASICON type of material as a cathode for Sodium ion battery, which is cost-

effective, earth-abundant and a great opportunity for a rechargeable Na-ion battery as an ideal replacement for a rechargeable Li-ion battery. However, larger size and strong  $\text{Na}^+\text{-Na}^+$  interaction create multidimensional phase instability and transformation problems, especially in layer-structured  $\text{Na}_x\text{MO}_2$  (Mn, Co, Fe, and Ni) that inhibit the direct transformation of rechargeable Li-ion battery technology to Na-ion battery. However, the framework structure offers superior structural stability due to the interconnection of polyanions or polyhedra forming cation octahedra. Sodium Superionic Conductors (NASICON) type structure is well known for superior  $\text{Na}^+$  ion transport and also identified as an interactive host as an electrode for the rechargeable-Na-ion battery. Here, we report the synthesis of  $\text{Na}_3\text{Fe}_2\text{PO}_4(\text{SO}_4)_2$  in a NASICON framework structure and its investigation as a cathode of  $\text{Na}/\text{Na}_3\text{Fe}_2\text{PO}_4(\text{SO}_4)_2$  cell working on the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple. The cell provides a single-phase reaction having a capacity approaching  $70 \text{ mAh g}^{-1}$  at  $0.1 \text{ C}$  after 50 cycles in the voltage range 2 to 4.2 V with a columbic efficiency approaching 100%. The large availability of Na and Fe with stable redox and charge/discharge performance of NASICON type  $\text{Na}_3\text{Fe}_2\text{PO}_4(\text{SO}_4)_2$  make it a possible cathode for next-generation rechargeable sodium-ion batteries.

**Chapter 4** entitled "Effect of Transition metal ion ( $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ) doping in  $\text{Na}_3\text{Fe}_2\text{PO}_4(\text{SO}_4)_2$  (NFPS). This chapter is dedicated to guiding chapter for sodium ion battery material and cell development. This work was a frame to increase the energy density of sodium-ion battery by increasing the working cell potential. Doping of  $\text{Na}_3\text{Fe}_2(\text{SO}_4)_2\text{PO}_4$  with active ( $\text{Ni}^{2+/3+}$ ,  $\text{Mn}^{2+/3+}$ ) and in-active (inactive  $\text{Mg}^{2+/3+}$ ) transition metal ion to improve the working potential of the cell. Synthesis was done by facile low-cost Coprecipitation method. Very interesting results are found for the Ni, Mn and Mg-doped NFPS. This chapter provides new findings in sodium ion cell

technology. It guides us about the what is limiting factor and what we have to avoid during the designing of new cathode material and what are the other limitation which we have to take care during the cell fabrication. so detailed studied are included in the chapter.

**Chapter 5** is entitled "NaCr(SO<sub>4</sub>)<sub>2</sub> as a Potential Anode for Sodium and lithium-ion Battery". This chapter emerge with the development of new type of Cr transition metal-based layered material as an anode for rechargeable sodium / Lithium-ion battery. We are presenting here, NaCr(SO<sub>4</sub>)<sub>2</sub>, a transition metal-based polyanionic layered material having low cost and high stability during the charge/discharge process vs. Na, operating on Cr<sup>3+/2+</sup> redox couple. Materials are characterized by characterization techniques like XRD, FTIR, SEM, UV, XPS, TGA-DTA, and a detailed electrochemical analysis of the charge/discharge capacity of the materials is presented here. Here findings are enlightening towards achieving Cr<sup>3+/2+</sup> redox couple-based sodium-ion battery with specific capacity of 75mAh /g and 150mAh/g at operating voltages of 0.95V vs. Na and 1.05V Vs. Li respectively and achieving 100% coulombic efficiency. Cr<sup>2+</sup> is a very special oxidation of Cr that cannot be obtained easily and CrTa<sub>2</sub>O<sub>6</sub> is the only known oxide where Cr exists in 2+ state. Here the shift in redox energy of Cr<sup>3+/2+</sup> couple is obtained due to its bonding with (SO<sub>4</sub>)<sup>2-</sup> polyanions in eldfellite that made accessibility of Cr<sup>3+/2+</sup> possible, resulting in superior intercalation/deintercalation of Na and Li and superior energy storage capacity of the NaCr(SO<sub>4</sub>)<sub>2</sub> vs. Na/Li cell.

**Chapter 6** is entitled "(MoO<sub>2</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> as a Potential Cathode for Rechargeable Sodium-ion Battery". This chapter emerges with the new flake type of Mo<sub>2</sub>P<sub>2</sub>O<sub>11</sub> cathode with enhance capacity for sodium ion battery. Iron, Nickel,

and Co-based NASICON structured materials give the stable capacity with reversible intercalation of almost one sodium in the host lattice. In the current work, we suggest a cathode material made of 3D framework-structured molybdenum polyanionic phosphate ( $\text{Mo}_2\text{P}_2\text{O}_{11}$ ) for a reversible sodium-ion battery.  $\text{Mo}_2\text{P}_2\text{O}_{11}$  was synthesized using the heat treatment of  $\text{MoO}_2\text{HPO}_4\cdot\text{H}_2\text{O}$  precursor at  $560\text{ }^\circ\text{C}$ , having the morphology of stacked flakes. Characterization techniques like XRD, FTIR, TGA, XPS, and SEM, EDS were utilized to confirm the structure and morphology of the materials. For electrochemical performance CV, charge-discharge, and stability tests have been performed.  $\text{Mo}_2\text{P}_2\text{O}_{11}$  work on active participation  $\text{Mo}^{6+/4+}$  redox couple with reversible intercalation of  $\text{Na}^+$  ions. The electrode exhibit a reversible intercalation at  $3.0\text{ V Vs. Na}$  and a steady capacity of  $\sim 90\text{mAh/g}$  ie  $\sim 1.4\text{ Na}$  per formula achieving a coulombic efficiency of nearly 100%. The current finding opens up a new route for using transition-metal phosphates as efficient and stable charge storage cathode material for sodium-ion batteries.

**Chapter 7** is entitled as "Conclusion and suggestion for future work". It comprises a brief summary of the entire Ph.D. work and future suggestions.