NOVEL P2-TYPE $Na_{0.6}Fe_{0.5-2x}Mn_{0.5}Ti_xV_xO_2$ CATHODE FOR HIGH-CAPACITY AND STABLE SODIUM-ION BATTERIES

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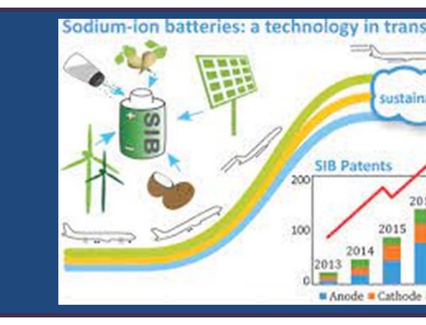

OBJECTIVES

- Doping of Vanadium and Titanium in NaFeMnO2 cathode by sol-gel method for getting higher energy density Na-ion battery and suppressing the undesired phase transition.
- Verification of stability and cyclic performance by various morphological and structural characterizations helping to compare between materials with different doping percentage.

INTRODUCTION AND MOTIVATION

- With the surge of global energy issue, a compatible alternative to Li-ion battery is a dire necessity.
- Sodium-ion battery technology is the most attractive option to replace Li-ion battery as Na is the 6th most earth-abundant material along with similar chemical characteristics as Li.
- Solid solution layered transition metal-oxide materials with ordered structure, namely, 'Cation-ordered Rock-Salt Superstructure' is the most promising electrodes due to:
  - high reversible capacity,
  - less voltage plateaus, and
  - higher cycle stability [2].

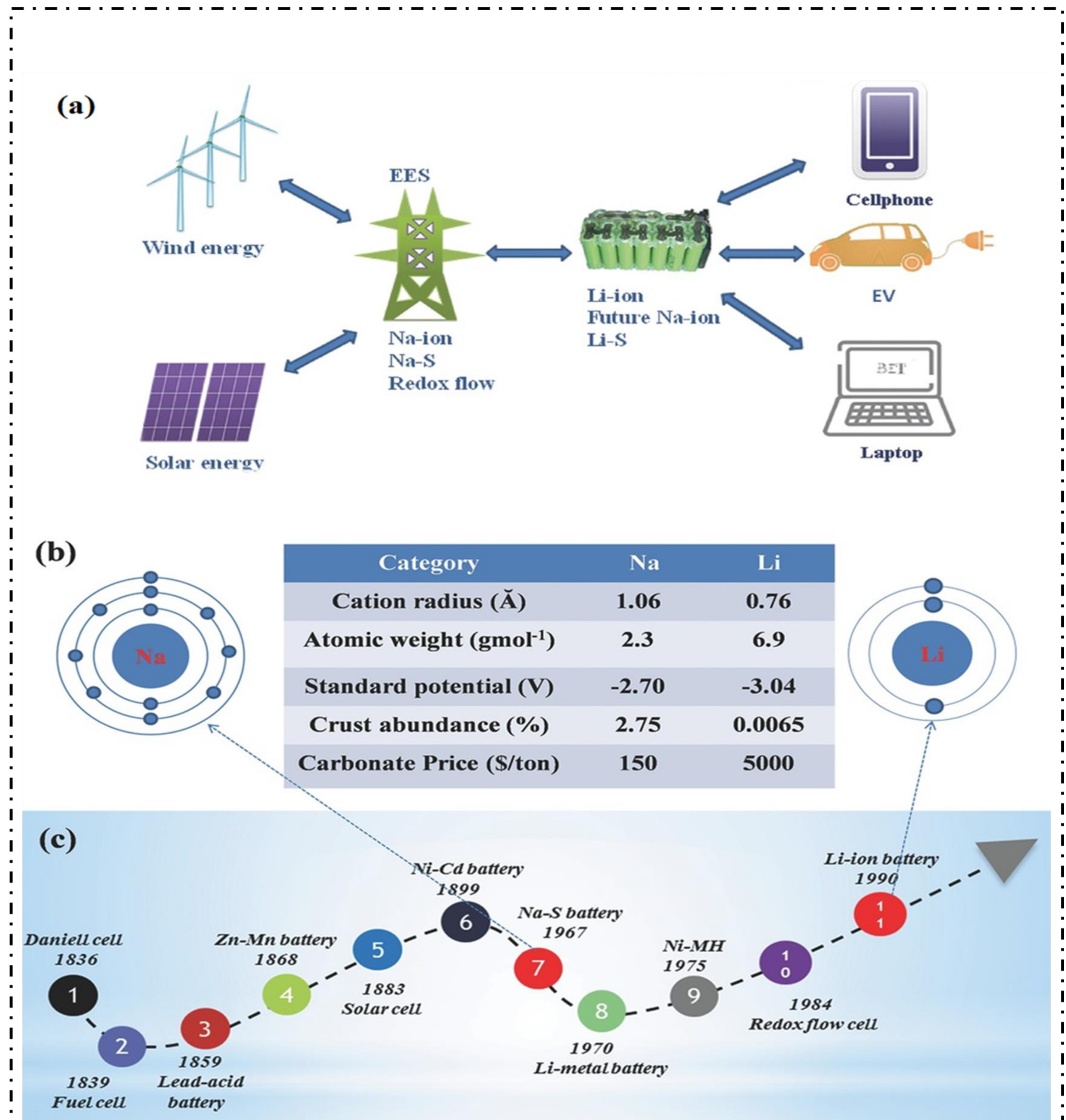

Fig.1.a) A schematic model showing interconnection of battery storage with grid and Utility b) Contrast between Na and Li c) Battery development history since past 200 years [1].

WORKING MECHANISM

- Na-ion battery employs the sodiation /de-sodiation process for charging /discharging.
- During charging, Na+ ion is extracted from cathode and inserted into anode with the electrons transport through outer circuit.
- The reverse process occurs for discharging.
- During this process under normal condition. The basic crystal structure should not be destroyed

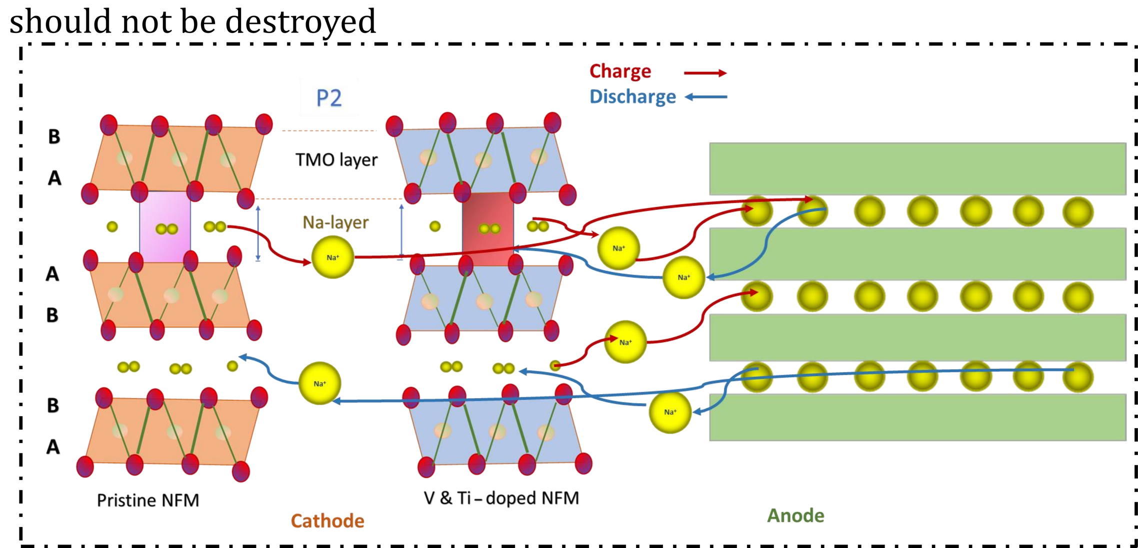

Fig.2 Working Principle of Sodium–ion Battery

METHODOLOGY FOR MATERIALS SYNTHESIS & BATTERY FABRICATION

DETAILED DESCRIPTION OF THE PROCESS

- An inexpensive and simple sol-gel process employed for preparing $Na_{0.6}Fe_{0.5-2x}Mn_{0.5}Ti_xV_xO_2$ (NFM-TV)with two step sintering process without pH control.
- Doping of Vanadium and Titanium substitute the Jahn-Teller prone Iron concentration to reduce multiple plateaus and capacity fading [2].

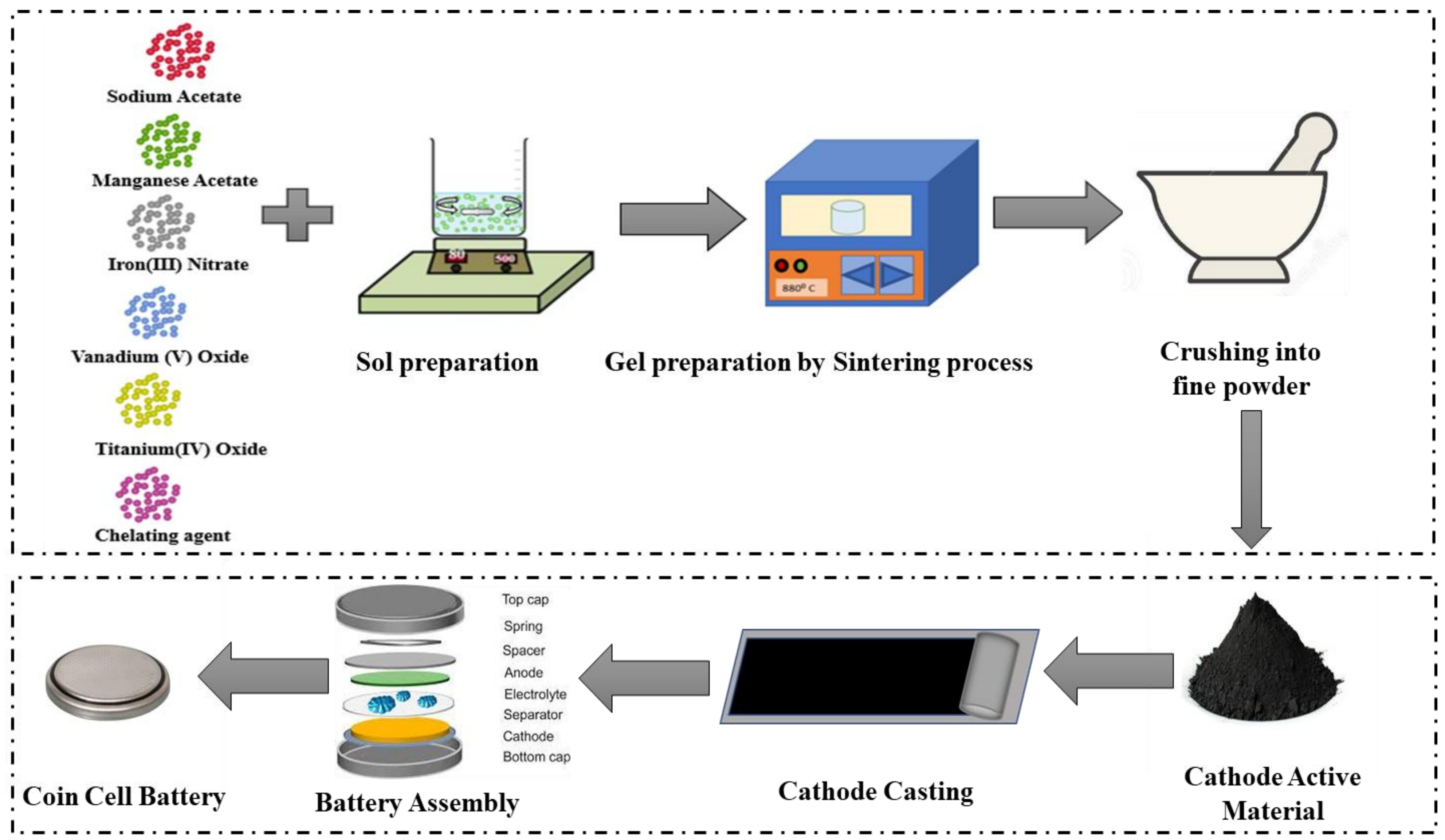

Fig.3 Battery Manufacturing Process by Sol-Gel Method

MORPHOLOGICAL ANALYSIS (FESEM & EDAX)

FESEM Analysis

- Primary particles are in nano-scaled pure hexagon structure (1 ~ 4 um).
- Self-assembled to form secondary particles, having granular shape with size of 40~50 um.
- Some needlelike nano-structures found to be formed with more Ti-V doping (NFM-TV 5%, NFM-TV 10%).
- Another significant finding is primary particles of NFM-TV materials gradually deviate from its pure hexagon shape (found in pristine NFM) when the doping is increased stepwise.

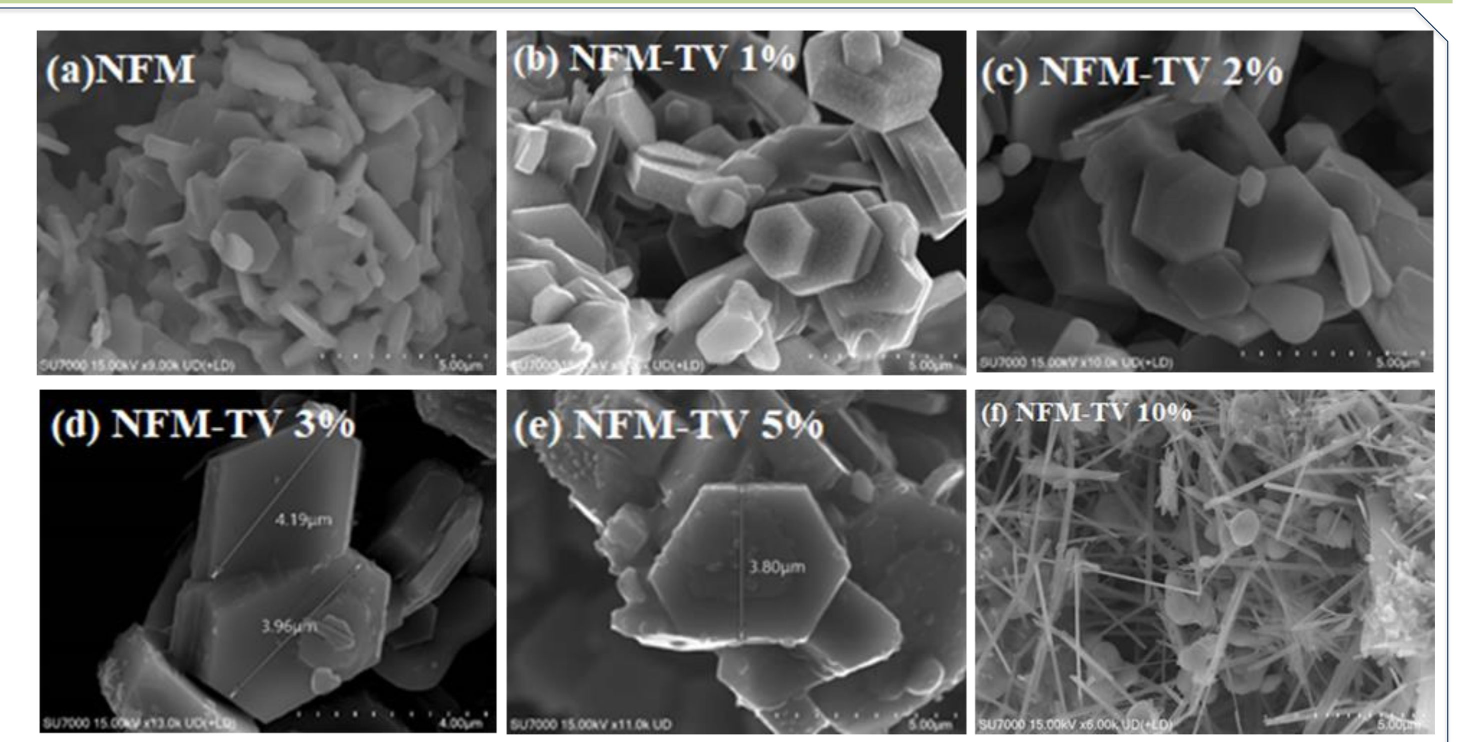

Fig.4 Scanning Electron Microscope Images of All Samples

EDAX Analysis

From the EDX elemental mapping figures, it is seen that all the elements – Mn, Fe, Ti, V and O are evenly distributed throughout the surface of the samples, validating Ti and V are doped well into the crystal structure

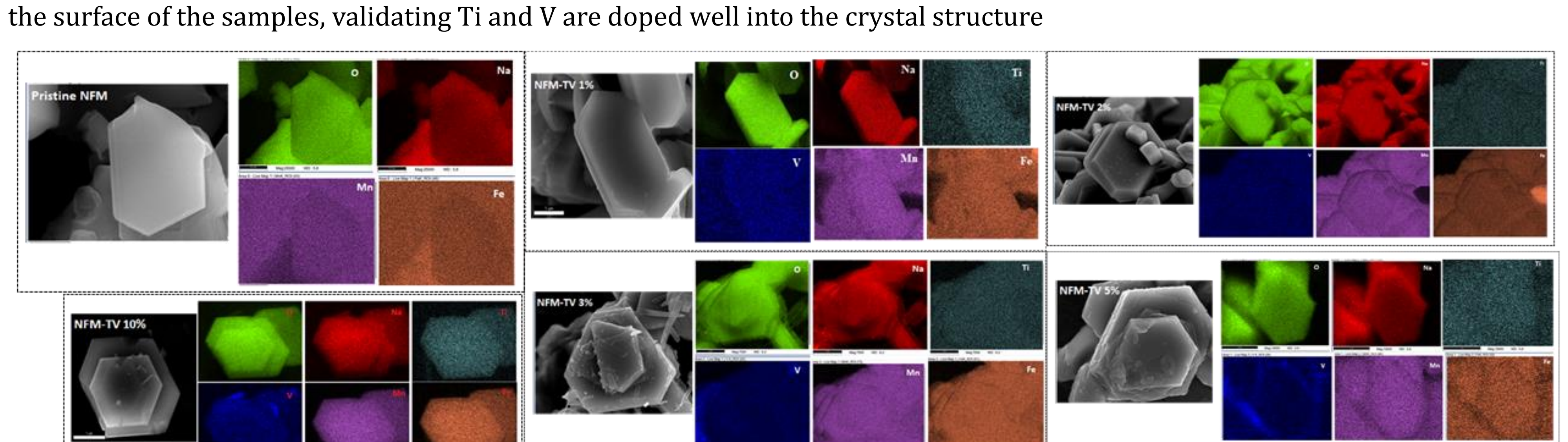

Fig.5 Elemental Mapping from EDAX Analysis of All Samples

MICROSTRUCTURAL ANALYSIS (XRD & RIETVELD ANALYSIS)

XRD Analysis

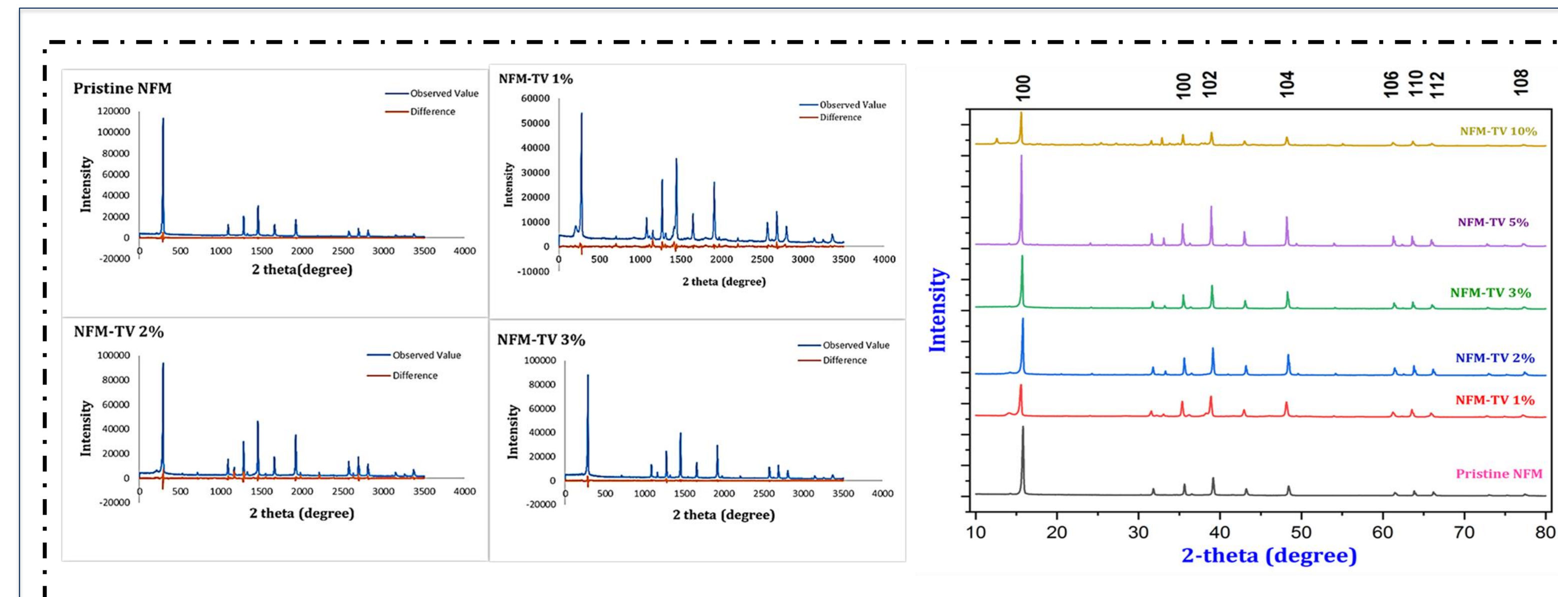

Fig.6 Comparative XRD Data Analysis of XRD Data of Samples $Na_{0.6}Fe_{0.5-2x}Mn_{0.5}Ti_xV_xO_2$ (x= 0.005-0.05)

- Diffraction peaks of all samples are well-indexed to the P63/mmc space group.
- No additional diffraction peaks in NFM-TV samples, even with increase of Ti & V doping to 5 %, indicating no extra phase generated with Ti-V doping.

Rietveld Refinement

- Rietveld Refinement is executed to obtain lattice parameters and d-spacing using PDXL software, as shown in Table 1.
- Both the lattice parameters a, c, and d-spacing increase with the doping of TV, except for NFM-TV 2%.
- The gradual decrease in TM-O bond length infers the structural stability with doping.
- The small values of reliability factors, R_{wp} and R_p (values <10) attest the reliability of the refinement calculation.

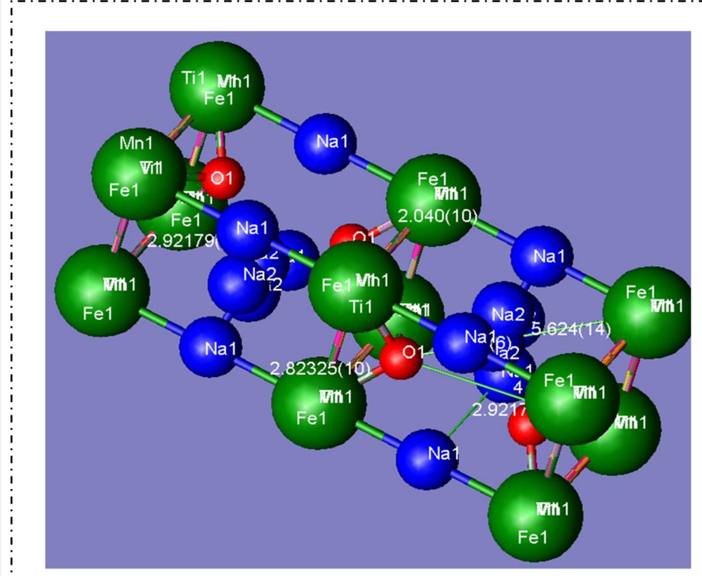

Fig.7 Refined Crystal Structure for NFM-TV 2%

Table 1. Refined Crystal Lattice Parameters of All Samples

Properties	NFM	NFM-TV 1%	NFM-TV 2%	NFM-TV 3%	NFM-TV 5%
a (Å)	2.92	2.92164	2.91819	2.92215	2.92103
c (Å)	11.29	11.2964	11.2975	11.2951	11.2909
Volume (Å^3)	83.3638	83.5048	83.3158	83.5243	83.4293
d (Å)	5.64	5.64896	5.64929	5.64756	5.64583
TM-O (Å)	1.93086	2.06948	1.993742	1.97514	1.93086
R_{wp}	7.8	7.28	8.59	6.29	5.46
R_p	5	4.89	5.71	4.12	3.96

DISCUSSION OF RESULTS

- From all the doped samples (NFM-TV's) while compared with the pristine NFM, it is found that NFM-TV 2% gives the desired structure as for this case, the lowest volume and the largest d-spacing. Therefore, Na+-ion conductivity and discharge current rate is higher for NFM-TV 2% than Pristine NFM and other doped NFM-TV samples.
- The lowest TM-O bond in NFM-TV 2% also validates the structural stability and FESEM figures justifies the surface morphology.

CONCLUSION AND FUTURE WORK

- In this research, a novel P2-type transition metal-oxide cathode $Na_{0.6}Fe_{0.5-2x}Mn_{0.5}Ti_xV_xO_2$ was synthesized by simple sol-gel method.
- A set of physicochemical analysis, including SEM and EDAX analysis, XRD and Rietveld analysis were performed to justify the morphological competence of the pristine NFM and doped NFM-TV.
- These exhaustive structural and morphological comparisons provided insights on the effects of V & Ti doping on stabilizing surface structures and promoting Na^+ carrier transport mechanism.
- The electrochemical analysis such as cyclic voltammetry and EIS analysis will be done in future for verifying the reversible capacity and rate capability.

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