UMSAEP (UM–UWC) ACADEMIC EXCHANGE PROGRAM PROJECT REPORT FOR 28 AUGUST – 28 OCTOBER 2022

Project Title: Understanding the relationship between Crystal Chemistry and Electrochemical Properties of Na_2MnSiO_4 and Li_2MnSiO_4 Nanomaterials in Secondary Na/Li-ion Batteries.

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UM Host: Dr. Amitava Choudhury
Associate Professor, Department of Chemistry, Missouri University of Science and Technology

Background

The exchange visit to the Missouri University of Science and Technology was originally planned for 2020. However, due to the COVID-19 pandemic and passport issues, the visit finally happened from the 28th of August – the 28th of October 2022, thanks to Prof Uphoff and Prof Iwuoha's great support. This represented the start of a productive research collaboration between SensorLab (University of the Western Cape Sensor Laboratories) with extensive expertise in nanomaterial synthesis and electrochemistry led by Prof Iwuoha and the Inorganic Solid-state and Materials Group at Missouri S&T, with wide experience in solid-state synthesis alongside single and powder X-ray crystallography, headed by Dr. Choudhury.

The main goal of the project was the fabrication and testing of cathode materials for lithium and sodium ion secondary batteries. The development and adoption of battery energy storage systems has become a global trend, due to the energy needs and climate commitments of many countries worldwide. Most especially, South Africa is currently facing massive loadshedding which is severely affecting its social and economic activities. Cost-effective and efficient batteries such as lithium and sodium ion batteries to store the energy produced by renewables and fed into the grid will play a huge role in reducing the huge shortfall in electricity supply and contribute towards enabling long-term energy security.

Project objectives

The original project objectives are listed below.

- Synthesis of pristine and doped nanomaterials of Na_2MnSiO_4, and Li_2MnSiO_4 and their coated composite with V_2O_5 as cathode materials
- Crystal structure refinement studies and electrochemical characterization of synthesized materials
- Fabrication of Na/Li-ion coin cells and galvanostatic charge/discharge studies of the pristine and nanocomposite cathode materials

The original project objectives were slightly altered by replacing the silicate nanomaterials (Na_2MnSiO_4 and Li_2MnSiO_4) with the highly sought-after superionic conducting solid state electrolyte materials for all solid-state batteries and transition metal phosphite cathode materials for lithium-ion batteries.

Amended objectives

- Superionic Li and Na argyrodite solid state electrolytes for all solid-state batteries.
- Transition metal phosphite cathode materials for lithium-ion batteries.

Research activities and outcomes

August 30, 2022 – September 9, 2022

- General introduction to Dr. Choudhury's lab, lab mates, Chemistry departmental staff and other staff members at Missouri S&T.
- Brief training on equipment in the lab and setting up reactions in the glove box.

September 12, 2022 – September 30, 2022

- Literature survey on Li and Na argyrodite solid-state electrolytes and possible aliovalent substitution on either the cationic or anionic sites.
- Online (Zoom) project meeting presentation with Dr. Choudhury and Prof Iwuoha.
- Attempted synthesis of Li_6PS_5Cl argyrodite based solid-state electrode.
- Synthesis of transition metal phosphite [$Li_2Mn(HPO_3)_2$] cathode material for lithium ion batteries.
- Single crystal X-ray and powder X-ray diffraction of the synthesized materials.
- Attending weekly Research Group meetings with Dr. Choudhury and other Group members.

October 03, 2022 – October 26,2022

The synthesized materials and attempted synthesis products were all identified using Dr. Ndipingwi's initials (MN).

- Various samples were prepared with the sample codes ranging from MN-1 to MN-18.
- MN-7 synthesis produced flat crystals with a major $Li_2Mn(HPO_3)_2$ phase and minor $MnHPO_3$ phase as confirmed by single crystal X-ray analyses.
- Li-ion coin cells were fabricated using the MN-7 material.
- Electrochemical experiments (cyclic voltammetry and galvanostatic charge-discharge) were performed with the Li-ion coin cells.
- Synthesis of MN-14 [$Li_2Fe(HPO_3)_2$] and MN-18 [$Li_2Mn_{1-x}Fe_x(HPO_3)_2$] materials.
- MN-14 and MN-18 were characterized by powder X-ray diffraction and Mössbauer spectroscopy.
- Li-ion coin cells were fabricated to investigate the charge storage performance of the materials.
- Figure 1 below shows the simulated pattern of MN-7 obtained from single crystal X-ray diffraction and powder X-ray diffraction patterns of MN-7, MN-14 and MN-18 materials obtained at a 2θ range of 5 to 90 degrees.
- Figure 2 shows the perspective view of the crystal structure of MN-7 [$Li_2Mn(HPO_3)_2$].

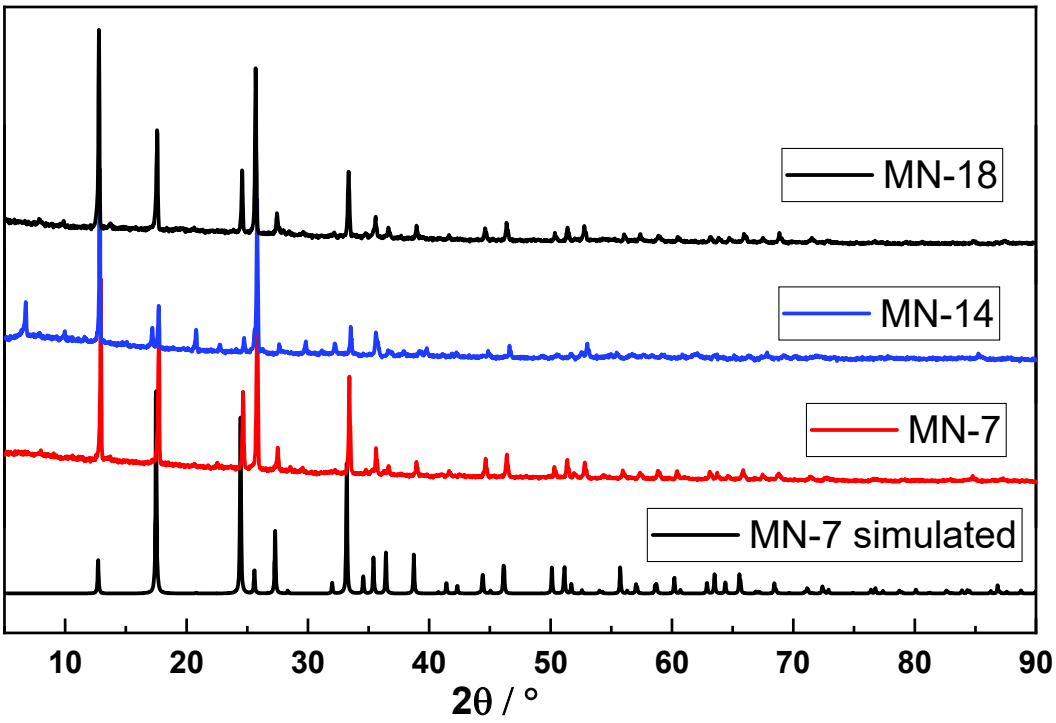

Figure 1: Simulated pattern of MN-7 and powder X-ray diffraction patterns of MN-7, MN-14 and MN-18.

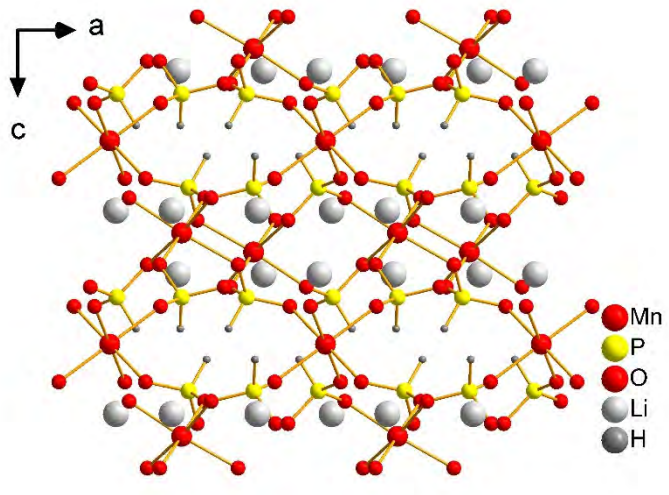

Figure 2: Figure shows the view of the crystal structure along *b*-axis.

Benefits of the exchange visit

- The exchange visit to Missouri S&T was my first visit to USA and I gained international exposure and experiences that will be very useful in enhancing my research skills and development as well as those of my colleagues at SensorLab, and building strong international collaborative networks.
- New friendships were made and I had a memorable experience taking part in the Celebration of Nations at Missouri S&T, that will last a lifetime.
- The project afforded me the opportunity to work with the world's largest database for identified inorganic crystal structures (ICSD) courtesy of Dr. Choudhury. This will be very beneficial in obtaining the crystallographic information files of different materials. I also gained experience in using crystal structure visualization softwares such as Vesta and Mercury.
- I was also exposed to Li-ion coin cell fabrication using organic electrolytes.

Impact of the visit and planned outputs

- This research collaboration has stimulated the advancement of scientific knowledge in the design and fabrication of Li and Na-ion battery technologies.
- Logical synergies from both teams will help in spreading the project results to a wider community.
- One of the highlights of the project is a manuscript that will be prepared from the work done on MN-7, MN-14 and MN-18 cathode materials for lithium-ion batteries.

Acknowledgement

I would like to express my sincere thanks to Prof Uphoff and the UWC leadership (Prof Bawa and Ms Wilson) and the entire UMSAEP committee for this opportunity and the support offered to me through my supervisor, Prof Iwuoha, to visit Dr. Choudhury's laboratory at Missouri S&T. Though it came with a lot of hurdles, I am so grateful to Prof Uphoff for his patience and most especially thankful to my supervisor for his support, kind consideration and guidance throughout the process. My profound appreciation goes to my host Dr. Choudhury for support and valuable discussions and to his wife (Dr Nath) for the excellent dinner. I would like to also extend my appreciation to his students (Sutapa and Santhoshkumar) for their support and assistance in the lab. I am also thankful to Ms Anklesaria at Residential Life at Missouri S&T for her kindness and assistance with accommodation.