A Project Report On

Ti_3C_2-Mxene/TiO_2 Anode For Sodium Ion Battery

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SARIFA REGINA FERNANDES

Roll No: 20P0490024

Under the guidance of

Dr. Anjani P. Nagvenkar

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CERTIFICATE

This is to certify that the dissertation entitled "synthesis of Ti_3C_2-Mxene/TiO_2 Anode for sodium ion Batteries" is a bonafide work carried out by Ms. Sarifa Regina Fernandes under the supervision in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry at the School of chemical sciences, Goa University, Taleigao-Plateau Goa.

Dr. Anjani. P. Nagvenkar
Guiding Teacher
Assistant Professor of School of Chemical sciences
Goa University

Prof. Vidyadatta Verenkar
Dean
School of Chemical sciences
Goa University

STATEMENT

I hereby declare that the matter presented in this dissertation entitled, 'synthesis of Ti_3C_2-Mxene/TiO_2 Anode for sodium ion Batteries' is based on a literature review held by me in the School of Chemical Sciences, Goa University, Goa under the supervision of Dr. Anjani. P. Nagvenkar and the same have not been submitted elsewhere for the award of a degree or diploma.

Ms. Sarifa Regina Fernandes
(M.Sc. Student)
20P0490024

Ti_3C_2-MXENE/TiO_2 ANODE FOR SODIUM ION BATTERY

INTRODUCTION

Electrochemical energy storage is considered to be an efficient energy storage technology because of its high energy alteration productivity, moderately compressed size and rapid response[1]. Amongst numerous electrochemical energy storage systems, the lithium-ion batteries have been widely used in life and production, from consumer electronics to mobile energy storage devices such as electric vehicles or energy storage power stations[2]. Due to the current dominance of lithium-ion in the battery markets are unsustainable, leading to research into use of alternative metal ions[2]. Sodium ion is well researched because of its similar chemistry to Li^+

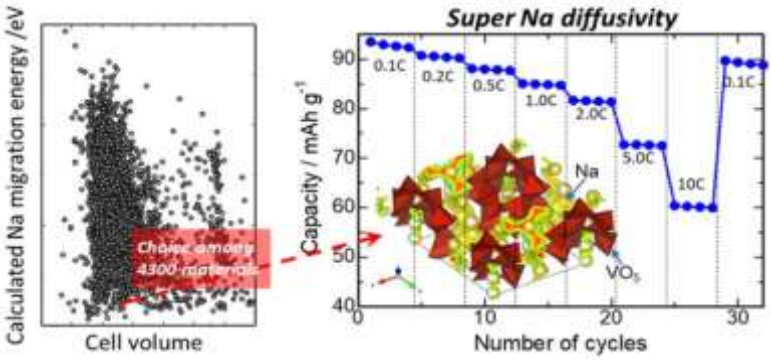

Fig.1: Schematic plot of life cycle of Na^+ and its cell

Due to their charge: mass ratio, the theoretical gravimetric capacities of sodium is low but its relative abundance in Earth's upper continental crust is greater than lithium and also its abundance in seawater making it cheap and apolitical resource[3]. Therefore, sodium ion battery can be used as an important complementary technology of lithium-ion battery in the field of large-scale energy storage, which has important economic value and strategic significance[2]. SIBs have suitable redox potential (E0 Na+/Na = 2.71 V vs SHE) and similar energy density to LIBs[4]. The solvation energy of sodium ion is lower than that of lithium ion, that is, it has better interfacial ion diffusion ability[5]. Fig.1 depicts the plot of the life cycle

provided by SIBs[6]. The internal resistance of sodium ion battery is slightly higher than that of lithium ion battery, which leads to less instantaneous heat and lower temperature rise in safety tests such as short circuit, which is one of the reasons for good safety performance[4]. SIBs become an ideal electrochemical energy storage device to replace LIBs.

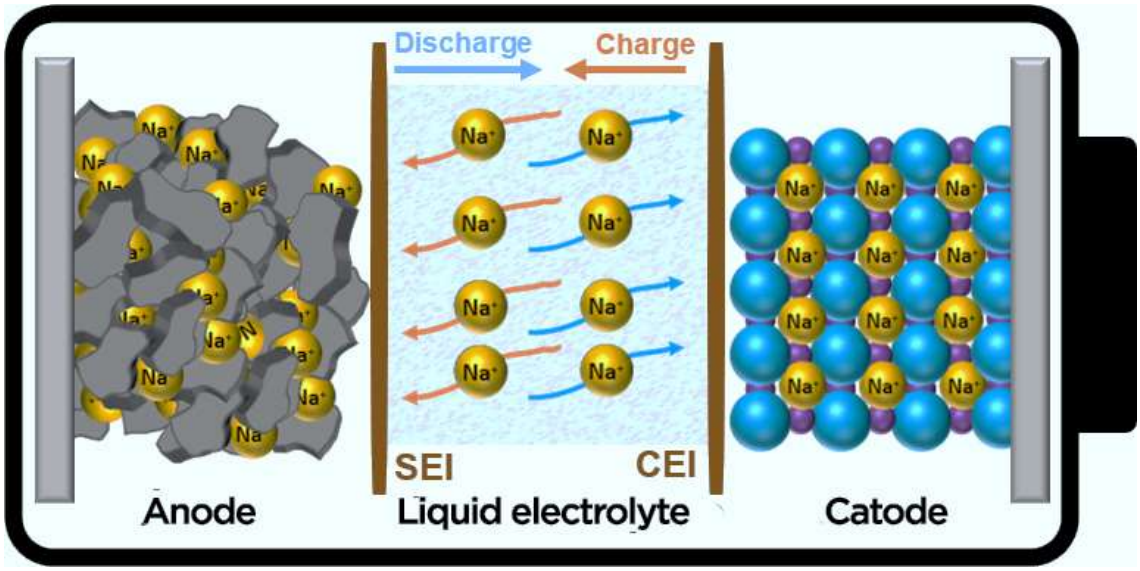

Fig.2: Schematic diagram of Sodium ion battery mechanism

Sodium-ion battery cells entail a cathode based on a sodium containing material, an anode (not certainly a sodium-based material) and a liquid electrolyte comprising of dissociated sodium salts in polar protic or aprotic solvents.[4] During charging, sodium ions are extracted from the cathode and introduced into the anode while the electrons travel through the external circuit; during discharging, the reverse process befalls where the sodium ions are extracted from the anode and re-inserted in the cathode with the electrons travelling through the external circuit doing useful work.[4] Fig.2 demonstrates schematic workup of sodium ion batteries.

Amongst all the aspects of a battery, the performance of EES (electrochemical energy storage) devices strongly depends upon the structure of electrode materials. In this project I propose to prepare an anode made of an inorganic material called as Mxene. Till date the research held up which is related to my project : 2D MXene/SnS_2 composites as high-

performance anodes for sodium ion batteries[7], Carbon-Reinforced Nb_2CT_x MXene/MoS_2 Nanosheets as a Superior Rate and High-Capacity Anode for Sodium-Ion Batteries[8], Hybrid Charge-Storage Route to Nb_2CT_x MXene as Anode for Sodium-Ion Batteries[9], MoS_2-Nanosheet-Decorated 2D Titanium Carbide (MXene) as High-Performance Anodes for Sodium-Ion Batteries[4], A chemically bonded $CoNiO_2$ nanoparticle/MXene composite as anode for sodium-ion batteries[10], MXene-derivative pompon-like $Na_2Ti_3O_7C$ anode material for advanced sodium ion batteries[11], $Ti_3C_2T_x$ MXene decorated with Sb nanoparticles as anode material for sodium-ion batteries[1], Alkali-induced 3D crinkled porous Ti_3C_2 MXene architectures coupled with NiCoP bimetallic phosphide nanoparticles as anode for high-performance sodium-ion batteries[12].

Here, the novelty is to prepare an anode made up of Ti_3C_2- Mxene/ TiO_2. Titanium Carbide (Ti_3C_2) is a novel type of 2D material known as a MXene, a compound composed of layered nitrides, carbides, or carbonitrides of transition metals[12].

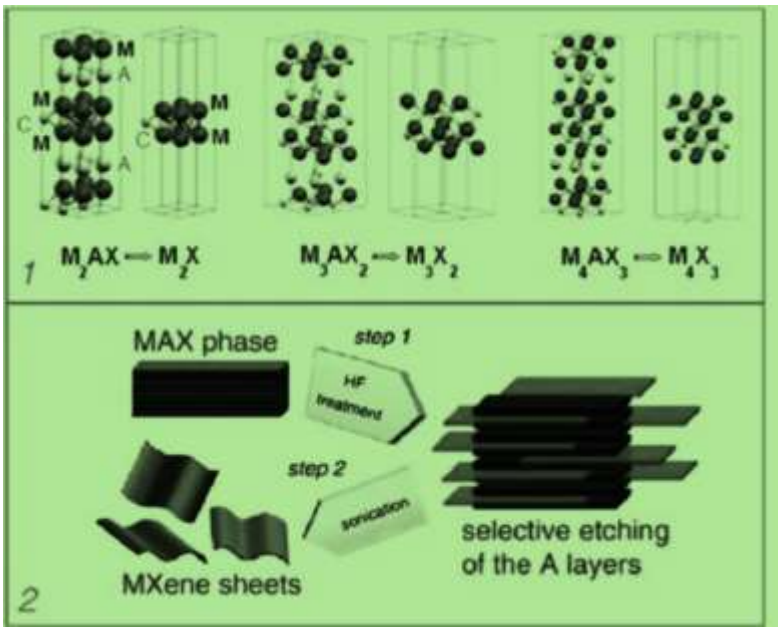

Fig.3: Schematic demonstration of Mxene synthesis

MXenes are synthesized via exfoliation or etching from a bulk three dimensional precursor MAX phase compound with the general formula $M_{n+1}AX_n$, where M is a transition metal, A is an element such as aluminium or silicon, and X is either carbon or nitrogen, with n=1, 2, or 3[13]. Selectively removing the A layer from the MAX phase material results in two dimensional layers of the MXene which can be separated by other ions (known as intercalation)[13].MXenes have excellent thermal and electrical conductivity, heat resistance and excellent volumetric capacitance[13]. In addition, owing to their large surface area, hydrophilicity, adsorption ability, and high surface reactivity, MXenes have attracted attention for many applications, e.g., catalysts, ion batteries, gas storage media, and sensors[13].

High rate capability is expected when Mxenes are used in preparation of the anode material. , as Na^+ ion is able to intercalate relatively quickly due to lower diffusion barriers, forming a mixture of mono and bilayers via redox chemistry with the surface[13]. TiO_2 itself is a very good photocatalytic material and having a bandgap of ~3.2ev it is a very good n-type semiconductor. As of now no such material for anode has been prepared and owning from their properties it might prove to be effective. The limitation of sodium ion battery is its low life cycle as compared to li^+ batteries, but using this synthesized material we can increase its efficiency. The limitations of the large size of Na^+ are totally eliminated here as Mxenes make its intercalation easier.

The motive of this novelty is to prepare a cheap and efficient anode used in sodium ion batteries so as to substitute the highly expensive and rare earth metals as Li+ and also increase its life cycle and decrease its discharging period.

IMPORTANCE OF THE PROJECT

Sodium-ion rechargeable batteries could soon be a cheaper and resource-saving alternative to current lithium-ion cells. Its relative abundance in Earth's upper continental crust is greater than lithium. Compared to lithium-ion batteries, current sodium-ion batteries have somewhat higher cost, slightly lower energy density and better safety characteristics. If in addition to cost improvements, the energy density is increased, then the batteries could be used for electric vehicles and power tools, and essentially any other application where lithium-ion batteries currently serves.

However, they are limited by a lack of anode materials with both an adequate lifespan and excellent rate capability. Sodium batteries are less powerful because they inevitably lose around 10% of their energy density due to a 0.3-volt lower cell voltage and hence they have low discharging cycles[2]. This is largely owing to the fact that the anodic material needed to be used in sodium-ion batteries should have the capacity to store the larger sodium ion in appreciable quantities. To address this issue, I plan to develop an anode made from an inorganic material of TiO_2 encrusted Mxene.

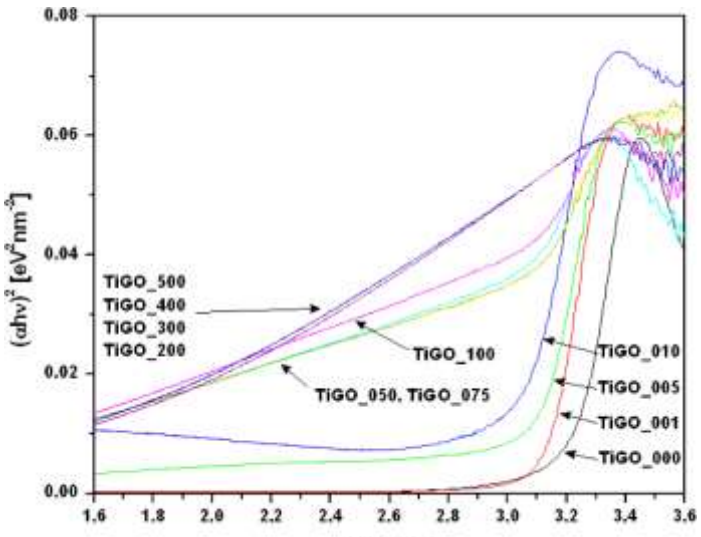

Fig. 4: Schematic plot of TiO_2 Band gap energy

MXenes are well known for their outstanding structural stability and superior electronic conductivities[12]. Thus, using MXenes as a host material for TiO_2 may improve its structural and electrical characteristics. Na^+ ion is able to intercalate relatively quickly in between the layers of Mxene due to its lower diffusion barriers, forming a mixture of mono and bilayers[12]. This will readily increase its life cycle. MXenes have excellent thermal and electrical conductivity, heat resistance and excellent volumetric capacitance[12]. In addition, owing to their large surface area, hydrophilicity, adsorption ability, and high surface reactivity it promises to produce high discharging cycle's [12].TiO_2 on the other hand is n-type semiconductor having a bandgap of ~3.2ev. Due to abundance, excellent safety, eco-friendliness, and low cost, titanium dioxide (TiO_2) has been considered a promising anode material for high power density[14]. Moreover, TiO_2 electrodes undergo small volume change (~5%) during the charge–discharge cycling[14]. The low electrical conductivity of TiO_2 is likely to be compensated by the exceptionally high electrical conductivity of MXene. MXene/TiO_2 electrochemical performance is enhanced in terms of higher initial discharge capacity, improved rate capability, and lower cell impedance[14]. The process employed here is quite simple, scalable without any complicated reaction steps compared to most of the published works. This project aims to derive high efficiency from the synthesized Mxene anode in order to shift to an environment friendly Sodium battery.

METHODOLOGY

The three-year work plan for the proposed research can be summarized in four major steps which includes synthesis of the Ti_3C_2 Mxene material and TiO_2 nanoparticles, Binding of the TiO_2 with Ti_3C_2 ,analyzing the properties of the prepared materials and testing its efficiency after having made an electrode. Synthesis is a very crucial step and hence will take atleast a year for it to be perfectly done.

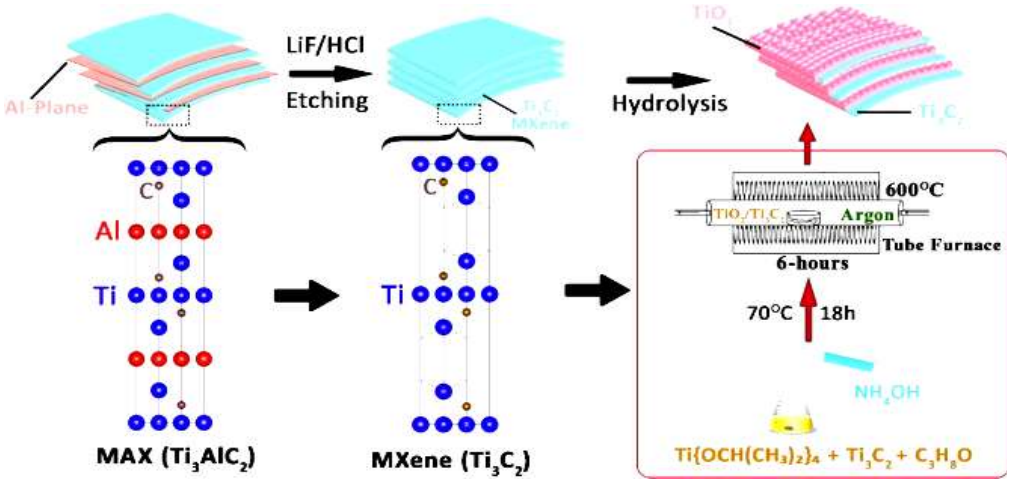

Fig. 5: Schematic illustration of binding of TiO_2 with Ti_3C_2

The methodology to be executed for the research that is put forward incorporates Synthesis of Ti_3C_2-MXene from MAX phase as a first step. Ti_3AlC_2 powder ought to be mixed slowly with an acidic mixture of LiF and HCL (pre-prepared) to result in simultaneous etching and delamination of Mxene[14]. Under these reaction conditions, the reaction must be allowed to continue for 24 h or even more until the desired product is obtained[14]. Nanoparticle-TiO_2 must be derived from a precursor of titanium isopropoxide[14]. The synthesized materials have to be investigated using an X-ray diffractometer, scanning electron microscope, Transmission electron microscopy, Energy-dispersive X-ray spectroscopy (EDX), TGA analyser and BET analysis methods[14].

TiO_2-Ti_3C_2 MXene nanocomposites will be synthesized by addingTi_3C_2-Mxene in solution of titanium isopropoxide (TTIP). The solution will be heated until a precipitate of the product is formed. This prepared material needs to be analysed for its properties by using various electron microscopy techniques like SEM, TEM, XRD, XRF, etc. This second step will be accomplished in the second year of our research.

The final step that shall be carried out during the third year basically comprises of developing an electrode from the prepared MXene nanocomposite and testing its efficiency. To start with the electrode preparation firstly, in n-methyl pyrrolidinone (NMP) solvent the active material (TiO_2 and MXene-TiO_2) needs to be mixed along with carbon black and polyvinylidene fluoride (PVDF) as a binder for about 6 hrs[14]. Next, the slurry will be later coated on copper foil (current collector) using a doctor blade and needs to be dried in a vacuum oven at 120 ◦C for 12 hrs to remove moisture traces. The dried electrode sheets shall be punched to get the electrodes[14].

To test its productivity, we will use a sodium metal as a counter electrode, while TiO_2 and MXene-TiO_2 electrodes ought to be used as an anode[14]. To investigate the electrochemical performance of the produced materials, it needs to be amplified with a tunable battery and the results will be obtained. This work plan requires shear dedication and relentless hard work to be executed and accomplished within these three years.

AFFIRMATIVE OUTCOME OF THIS WORK

As the demand for Li^+ commodity chemicals in enormous scale battery applications upsurges, primarily the geographically-constrained Li^+ mineral reserves will drive up the prices and this stresses to conduct a research into the use of an alternative metal ion in the batteries. Sodium ions on being one of the most copious elements on the earth and chipping in similar features with lithium ions certainly have to be the perfect alternative. The constructive upshot expected in this project is to achieve the maximum efficiency from the synthesized Ti_3C_2-Mxene/TiO_2 anode for the sodium ion batteries. With the purpose of increasing the batteries lifecycle, Mxene's which seem to possess outstanding properties as its large surface area, hydrophilicity, adsorption ability, and high surface reactivity makes the perfect candidate for the anode material. The ruination due to Na^+ ions large size is totally eliminated and the rate is expected to elevate as Na^+ ion is able to intercalate quite quickly owing to its lower diffusion barriers within the mono and bilayers of Mxene. To attain high stability and a good cell volume binding the synthesized Mxene with TiO_2 is necessary as it is a photocatalyst and will have high electron density. In addition to this, it undergoes small volume change (~5%) during the charge–discharge cycling which will produce affirmative results. Hence, TiO_2 has been considered a promising anode material for high power density. MXene/TiO_2 electrochemical performance will definitely be enhanced in terms of higher initial discharge capacity, improved rate capability, and lower cell impedance. The process employed here is quite trouble-free, scalable without any complex reaction steps compared to most of the published works.

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