

Preface

The present Thesis explores a few novel anode materials for both lithium-ion and sodium-ion rechargeable batteries. A series of layered metal titanium niobates have been synthesised and their electrochemical energy storage properties, ion transport, and reaction mechanisms are studied in detail. Alkali-titanium niobates such as Li-Ti-niobate (and its sodium counterpart) store lithium (sodium) via the conventional intercalation mechanism. Detailed experimental and theoretical investigations reveal interesting and non trivial ion transport, which are found to be strongly correlated to the electrochemical properties. Apart from intercalation, where amount of energy storage is limited by the crystal structure, energy storage via an alloying reaction is an important alternative strategy to boost specific capacities and energy densities of various battery systems. However, drastic volume changes during alloying/dealloying is detrimental for stable electrochemical function of the cell. The volume expansion problem associated with alloying anodes materials e.g. Sn for alkali-ion batteries have been tackled here via two different strategies. While one uses a flexible layered structure resulting in simultaneous intercalation and alloying process, the other approach uses a porous electrospun carbon fiber encapsulation for alloying compounds. The electrochemical properties as a function of Sn-content in a binary SnX (X: Sb) compound anode have been explicitly probed. This study provided invaluable information on alloying reaction mechanisms as well as identified the most optimum Sn-content for the long term stable battery operations. Usage of graphite as an anode in high energy density Li-ion cell has already been shown to be associated with severe safety issues. The thesis demonstrates a novel and very simple strategy to develop a stable non-carbonaceous anode for operation in the Li-ion (full) cell configuration. The thesis comprises of six chapters and a brief discussion of the content and highlights of the individual chapters are discussed below:

Chapter 1 briefly reviews the different materials (mainly anodes) and storage mechanisms in the context of lithium-ion and sodium-ion rechargeable batteries. Energy storage via different mechanisms in metal-ion batteries has its own advantages and disadvantages. Thus, design of alternative novel materials is absolutely essential to nullify the detrimental factors associated with various storage methods leading to highly efficient and safe alkali metal-ion rechargeable battery systems. Development of materials for efficient alkali metal-ion batteries are very pertinent even today as the next generation high energy density rechargeable batteries based on metal-S/metal-O₂ are still in the stages of infancy. They are far away from widespread

commercialization and thus, do not pose any threat to the rechargeable alkali metal-ion batteries. This chapter discusses the importance of diffusion of ions inside the electrode materials, which essentially determines the rate capability of half/full cells. Chapter ends with discussion on galvanostatic intermittent titration technique (GITT) which has been used extensively for calculating the diffusion coefficients of the electrodes.

Chapter 2 comprises of synthesis, characterization and investigation of electrochemical properties of novel Ti-based anode materials, namely Li-Ti-niobate and Na-Ti-niobate. These compounds are synthesized using a simple ion-exchange reaction from aqueous medium using KTiNbO_5 (potassium titanium niobate) as the parent compound. Li-Ti-niobate and Na-Ti-niobate are tested in Li and Na-battery respectively as an anode material. The effects of $\text{Ti}^{3+}/\text{Ti}^{2+}$ redox couple in the electrochemical performances are also investigated in the case of Li-Ti-niobate by altering the working potential window of the battery. The electrochemical performances of Li-Ti-niobate are further improved by downsizing the particle size followed by carbon coating through hydrothermal carbonization method.

Scheme 1: Layered structure of metal-titanium niobate. Electrochemical performance of Li-Ti-niobate in the voltage ranges (1-3) V and (0.2-2.75) V. The specific capacity of Li-Ti-niobate has been increased by downsizing the particles followed by carbon coating (cd-Li-Ti-niobate) in the voltage range (0.2-2.75) V.

In Chapter 2 we investigated the electrochemical properties of Li-Ti-niobate as an anode material for Li-ion battery. In Chapter 3 we probed the ion diffusion inside the material, an important physical property that determines the possibility of battery operation at higher current densities. Layered Li-Ti-niobate shows pseudo-1-D Li^+ ion diffusion, with ion transport taking place mainly along the crystallographic b-direction. Presence of line defects along crystallographic b-direction assists the diffusion to be pseudo-1-D in nature. Removal of line defects via sintering followed by studies on electrochemical properties suggests that presence of high density dislocation defects is crucial for superior rate performance of Li-Ti-niobate.

Scheme 2: Preferential direction of ion diffusion in Li-Ti-niobate

In the previous Chapters, the lithium ion intercalation behavior and its diffusion properties into titanium niobate layers have been investigated in detail. In Chapter 4, the same layered geometry has been explored to tackle the drastic volume expansion problem typically associated with anodes storing energy via the alloying method. Unique flexible non-

carbonaceous layered host viz. M-Ti-niobate (Ti: Titanium; M: Al³⁺, Pb²⁺, Sb³⁺, Ba²⁺, Mg²⁺) has been designed which can synergistically store both lithium-ions and sodium-ions via simultaneous intercalation and alloying mechanisms. M-Ti-niobate is formed by ion-exchange of the K-ions, which are specifically located in the galleries between the layers formed by edge and corner sharing TiO₆ and NbO₆ octahedral units in the sol-gel synthesized potassium titanium niobate (KTiNbO₅). The detrimental issues such as drastic volume changes (approximately 300-400%) typically associated with alloying mechanism of storage are completely tackled chemically viz. by the unique chemical composition and structure of the M-Ti-niobates. The free space between the adjustable Ti/Nb octahedral layers easily accommodates the drastic volume changes. Due to the presence of an optimum amount of multivalent alloying metal ions (50-75% of total K-ions) in the M-Ti-niobate, efficient alloying reaction takes place directly with the ions and completely eliminates any form of mechanical degradation of the electroactive particles. The M-Ti-niobate can be cycled over a wide voltage range (as low as 0.01 V) and displays remarkably stable Li⁺ and Na⁺ ion cyclability (> 2 Li⁺/Na⁺ per formula unit) for widely varying current densities over few hundreds to thousands of successive cycles. The simultaneous intercalation and alloying storage mechanisms demonstrated by the experiments is studied within the framework of density functional theory (DFT). DFT expectedly shows a very small variation in the volume of Al-titanium niobate following lithium alloying. Moreover, the theoretical investigations also conclusively endorse the occurrence of the alloying process of Li-ions with the Al-ions along with the intercalation process during discharge. The M-Ti-niobates studied here

demonstrates a paradigm shift in chemical design of electrodes and will pave the way for development of multitude of improved electrodes for different battery chemistries

Scheme 3: Scheme depicts the synergistic approach of charge storage in M-Ti-niobate anodes for alkali-ion rechargeable batteries. Colour changes in the layers indicate that the layers are electrochemically active.

Chapter 5 mainly focuses on a fully Li-alloy based anode such as SnSb for prospective application in rechargeable Li-ion batteries. The Sn-content variation in SnSb nanoparticles confined inside electrically conducting carbon nanofiber is observed to significantly influence the electrochemical performance. It is a major challenge to minimize the detrimental effects arising as a result of drastic volume changes (\approx few hundred times) occurring during repeated alloying-dealloying of lithium with Group IV elements e.g. tin (Sn). An important design

strategy is to have Sn as a component in a binary compound. SnSb, is an important example where the antimony (Sb) itself is redox active at a potential higher than that of Sn. The ability of Sb to alloy with Li reduces the Li uptake amount of Sn in SnSb compared to bare Sn. Thus, the volume changes of Sn in SnSb will expectedly be much lower compared to bare Sn leading to greater mechanical stability and cyclability. As revealed recently, complete reformation of SnSb (for molar ratio Sn:Sb= 1:1) during charging is not achieved due to loss of some fraction of Sn. Thus, molar concentration of Sn and Sb in SnSb is also absolutely

important for the optimization of battery performance. We discuss here SnSb with varying compositions of Sn encapsulated inside an electrospun carbon-nanofiber (abbreviated as CF). The carbon-nanofiber matrix not only provides electron transport pathways for the redox process but also provides ample space to accommodate the drastic volume changes occurring during successive charge and discharge cycles. The systematic changes in the chemical composition of SnSb minimize the instabilities in the SnSb structure as well as replenish any loss in Sn during repeated cycling. The composition plays a very crucial role as magnitude of specific capacities and cyclability of SnSb is observed to depend on the variable percentage of Sn. SnSb-75-25-CF, which contains excess Sn, exhibits the highest specific capacity of 550 mAh g⁻¹ after 100 cycles in a comparison with pure SnSb (1:1) anode material at current density (0.2 A/g) and shows excellent rate capability over widely varying current densities (0.2-5 A g⁻¹).

Scheme 4: Schematic depiction of lithiation and delithiation mechanism in SnSb. Bar diagram of specific capacity versus percentage of Sn present in SnSb-series of compounds. Percentage of Sn present is 0 %, 25%, 50%, 75% and 100% in Sb-CF, SnSb-25-75-CF, SnSb-50-50-CF, SnSb-75-25-CF and Sn-CF respectively.

In Chapter 6 we discuss a binary mixture of two non-carbon coated electroactive compounds viz. anatase-titanium dioxide (TiO₂) and vanadium pentoxide (V₂O₅) as a potential electrode for Li-based batteries. The binary mixture, whose components are synthesized using sol-gel methods and not carbon coated, can be reversibly cycled in the potential range (1.0-3.5) V against Li-metal. The physical mixture of the as-synthesized TiO₂ and V₂O₅ (w/w = 1:1) provides a high specific capacity (\approx 190 mAh g⁻¹ after 100 cycles at 100 mA g⁻¹) and higher compared to the bare anatase-TiO₂ and V₂O₅. Thus, this simple strategy enhances the operational potential of anatase-TiO₂ by 0.5 V to 3.5 V against lithium and also nullifies greatly the complexities of carbon electronic wiring of electroactive particles. A Li-ion cell,

comprising of the non-carbon coated binary mixture as anode and lithium manganese oxide (LiMn_2O_4) as the cathode, cycled in the potential range (0.2-3.5) V delivers a high specific capacity of nearly 80 mAh g⁻¹ at 100 mA g⁻¹ and is higher compared to the full cell capacities using the individual components as anodes. No signatures of SEI formation is observed from the cyclic voltammetry results. The presence of a second electroactive material may strongly suppress the SEI formation typically observed for Ti-oxide based materials when cycled to such a low potential (≈ 0.2 V). This may also account for the high percentage of reversibility and specific capacity of the full cell in this wide potential range. This simple approach enables the possibility of using Ti-oxide based anodes against the commercial intercalation cathodes without any compromise in the cell performance and also reduces the need for design of novel high voltage cathode materials.

Scheme 5: Scheme shows a design strategy for improvement in specific capacity as a result of presence of an additional redox active species in the Li-ion configuration.