

SYNTHESIS AND ELECTROCHEMICAL BEHAVIOUR OF TIN PHOSPHATE AS ANODE MATERIAL FOR LITHIUM ION CELLS

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ABSTRACT

This study aims to explore the possibility of tin phosphate application as anode material in lithium ion cells. Two batches of tin phosphates have been synthesized via a chemical route where one batch was synthesized with the sodium dodecyl sulfate surfactant to produce mesostructured tin phosphate and the other was synthesized without the surfactant. From X-ray diffraction (XRD) analysis, the synthesized tin phosphate which was calcined at 500°C showed crystalline characteristics whereas that of mesostructured tin phosphate maintained an amorphous nature. Electrochemical measurements showed reversible lithium ion reaction upon charging and discharging of the tin phosphate anodes within the potential range of 0 – 2V versus Li⁺/Li. Upon the first cycle, tin phosphate delivered a reversible capacity of 272 mAh/g whereas mesostructured tin phosphate delivered that of 590mAh/g. Substantial capacity losses and fading upon further cycling was experienced by both anodes due to the formation of irreversible phase and restriction in the reversible lithium-tin formation. It is believed that mesostructured tin phosphate anode exhibited better capacity retention because of its porous structure which minimized the effect of volume changes experienced by the anode during the charge-discharge cycling process.

INTRODUCTION

Graphite is commonly used as anode in commercial Lithium ion batteries but its capacity is only limited to 372 mAh/g. Alternative anode material with higher capacity are actively being pursued. One of such material is the tin oxide, which can deliver up to 991 mAh/g. However, this material showed poor capacity retention and cyclability. The cause of capacity fading of tin oxide anode was elaborated by Courtney and Dahn in a two-step reaction [1, 2]. In the first step, tin oxide reacts with lithium (Li) to form lithium oxide, Li₂O and metallic tin (Sn). Subsequently, further reaction of Sn with Li leads to the formation of Li-Sn alloy up to the composition of SnLi_{4.4}. The second step involves the reversible Li-Sn alloying and de-alloying process. Upon prolonged cycling tin atoms aggregate and form larger tin clusters which lead to large volume changes effects that eventually cause disintegration of the anode material [1, 2].

It has been suggested that a good anode material should be able to attain a structure and

composition that manage to prevent aggregation of tin while it still allows transport of lithium ions and electrons [3]. The presence of atoms such as phosphorus which are indirectly involved in the electrochemical reaction, create a matrix where tin atoms are embedded, may have beneficial effect on the electrochemical performance of these materials [3-5]. Mesoporous materials have attracted considerable attention due to its potential application in catalysts, molecular sieves and electrodes in ionic devices. Recently Kim *et al* reported mesoporous/crystalline tin phosphate composite exhibited reversible pore changes during reaction with lithium [6]. The group incorporated mesoporous structure as a buffer layer in which the mesopores could alleviate volume changes effects during the lithium alloying/de-alloying.

In this study, tin phosphate and mesostructured tin phosphate were synthesized via a chemical route and their performances as anode material for lithium ion cells were investigated.

EXPERIMENTAL METHOD

Two batches of tin phosphate were prepared for this study. The mesostructured tin phosphate was prepared by mixing tin (IV) chloride (SnCl_4 , 99%, Aldrich) with 1M sodium dodecyl sulphate ($\text{NaCl}_2\text{H}_{25}\text{SO}_4$, Fluka) aqueous solution. 1M of phosphoric acid (H_3PO_4 , 86%, J.T Baker) was then added into this mixture. The mixed solution gradually turned into a block of whitish and very viscous gel. The gel was then loaded into a Teflon lined stainless steel vial which was then placed into a vacuum oven and aged at 100°C for 5 days. The resulting product was filtered, washed with purified water and dried at ambient temperature. For comparison purpose, tin phosphate without the mesostructure was synthesized by mixing 1M aqueous SnCl_4 solution with 1M phosphoric acid at room temperature. A whitish, viscous gel was then formed. The gel was then aged, recovered, washed and dried in an identical manner. All precursors were preheated at 200°C for 2 h in air and then calcined at 300, 400 and 500°C for 4 h. The resultant powders were then ground in an agate mortar.

Thermogravimetric analysis (TGA) was conducted with a Netzsch Simultaneous Thermal Analyser (STA409C) in Argon atmosphere. Powder X-Ray Diffraction (XRD, BRUKER Advance D-8 X-Ray Diffractometer) measurements using Cu K_α radiation were used to characterise the structures of the synthesised powders. Nitrogen adsorption-desorption isotherms were recorded with an adsorption apparatus from Quantachrome (Autosorb 1-C). The sample was degassed overnight at 100°C .

For electrochemical study, the electrode was prepared by mixing the tin phosphate (70% in weight) with a blend of acetylene black and polyvinylidene fluoride (30% in weight) in an agate mortar. The mixture was spread and pressed on a stainless steel mesh. The electrode was then dried around 120°C in the oven. All electrochemical test cells were assembled in Argon filled glove box. Cyclic voltammetry was carried out on an EG&G model 273 potentiostat/galvanostat with the synthesized tin phosphate as the working electrode and lithium foil as the reference and counter electrodes. A 1M LiPF_6

in a 1:2 mixture of EC:DMC (ethylene carbonate: dimethyl carbonate) was used as the electrolyte. The potential was scanned between 0 and 2 V versus Li^+/Li at a rate of 0.167mV/s. Charge and discharge performance tests were carried out at a constant current of 0.5mA between the within the potential range of 0–2V versus Li^+/Li with WonATech Battery Cycler System (WBCS3000).

RESULTS AND DISCUSSION

Thermal Analysis

TGA curve for the tin phosphate synthesized with the surfactant, sodium dodecyl sulphate is shown in Figure 1. This analysis has been conducted to investigate the decomposition of the surfactant using a heating rate of 10°C/min. There are two significant weight losses observed at ~100-220°C and ~300-400°C. The first weight loss is assigned to the evaporation of moisture and initial decomposition of organic matter. Subsequent weight loss is attributed to the combustion of sodium dodecyl sulphate indicating that complete removal of surfactant and formation of mesoporous tin phosphate occur at 400°C.

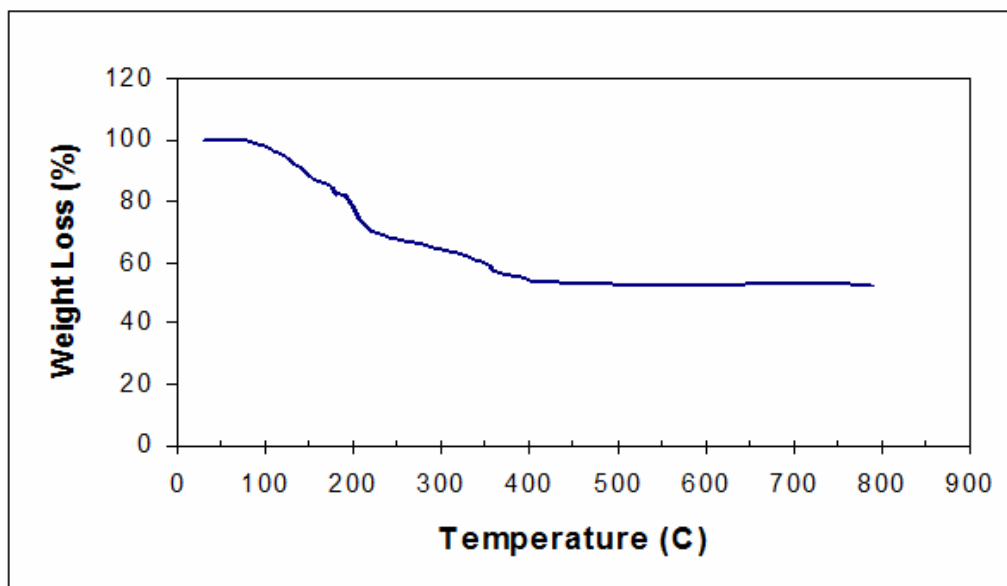


Figure 1: TGA analysis of tin phosphate synthesized with surfactant

Structural Characterization

The X-Ray diffraction patterns of as-synthesized and calcined tin phosphate which was produced without sodium dodecyl sulfate are shown in Figure 2. No diffraction peaks are observed in the pre-calcined tin phosphate indicating an amorphous state. Peaks begin to form at 300°C which marks the evolution of a crystalline phase. Clear diffraction peaks observed for tin phosphate calcined at 400 and 500°C are attributed to $\text{Sn}_3(\text{PO}_4)_4$.

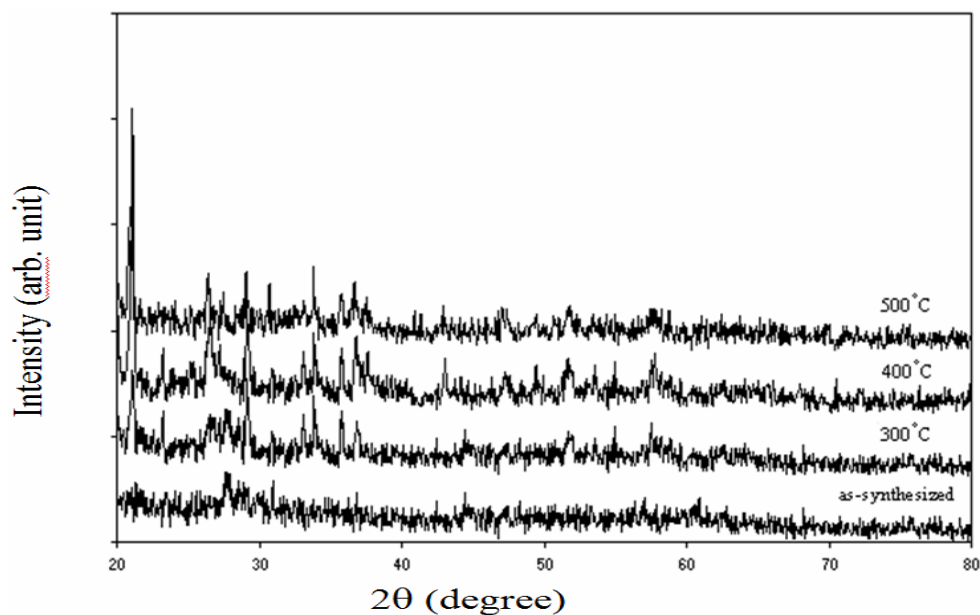


Figure 2: XRD pattern of tin phosphate.

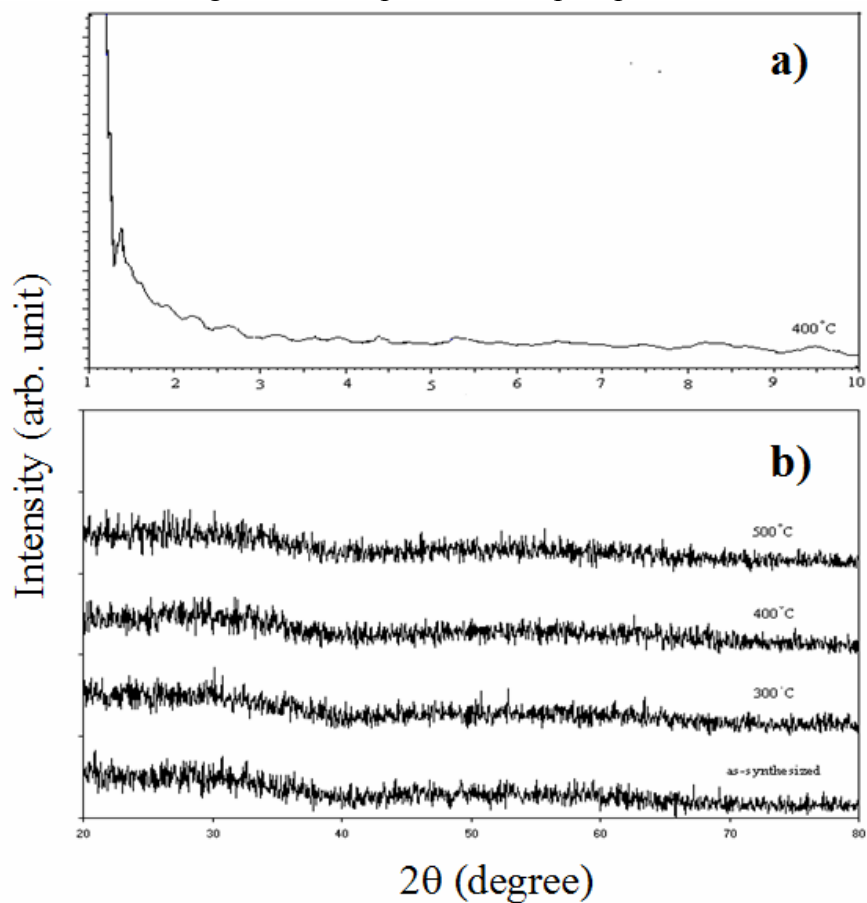


Figure 3: XRD pattern of mesostructured tin phosphate at; a) $2\theta = 1-10^\circ$ and b) $2\theta = 20-80^\circ$

Figure 3 shows the X-Ray diffraction pattern of tin phosphate synthesized with sodium dodecyl sulphate. Figure 3a showed the XRD pattern for mesostructured tin phosphate calcined at 400°C at $2\theta = 1-10^\circ$ which exhibited a single low angle reflection that is characteristic of a mesostructured material. No obvious peaks were identified in the $2\theta = 20-80^\circ$ region for as-synthesized and calcined samples. The intensities observed are generally weak which indicates that the mesostructured tin phosphate is largely amorphous even when calcined up to 500°C.

Nitrogen adsorption-desorption isotherm recorded for mesostructured tin phosphate calcined at 400°C is shown in Figure 4. The shape of this hysteresis is indicative of mesoporous material with open slit-shaped pores. The mesostructured tin phosphate produced at 400°C has a Brunauer-Emmett-Teller (BET) surface area of 110.13 m²/g. Inset in Figure 4 showed the pore size distribution for the mesostructured tin phosphate. The average pore size is 18nm as determined using the Barrett-Joyner-Halenda (BJH) model and the desorption branch isotherm.

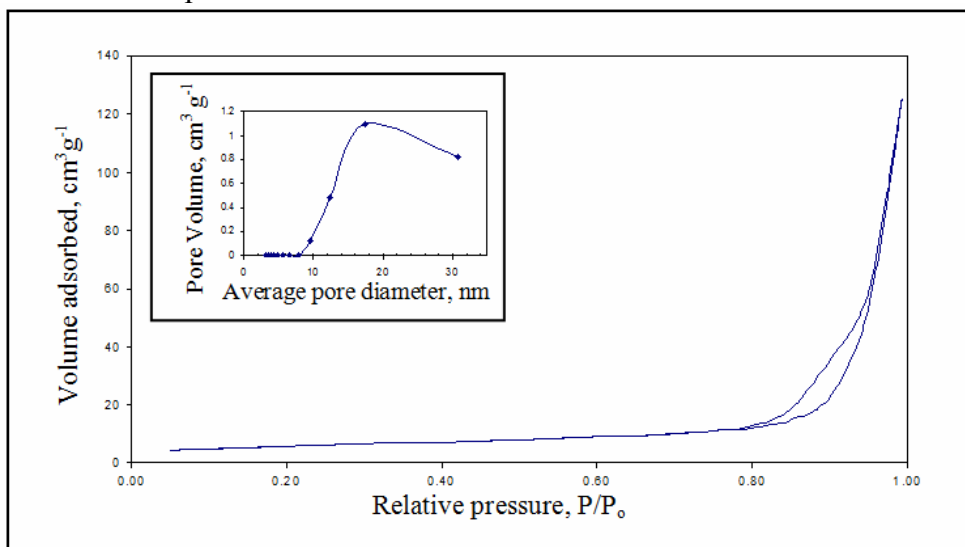


Figure 4: N₂ sorption isotherm of mesostructured tin phosphate calcined at 400°C. Inset shows pore size distribution determined using BJH model and the desorption branch isotherm

Electrochemical Characterization

Cyclic Voltammetry

Cyclic voltammograms of tin phosphate and mesostructured tin phosphate calcined at 400°C are shown in Figure 5 and Figure 6, respectively. In both voltammograms, the first cycle voltammetric response is noticeably different compared to the subsequent second and third cycle. In Figure 5, the initial cathodic scan showed a large peak occurring at 1.23V but this peak is no longer visible in the second and third scan. This

indicates the electrochemical reaction that gives rise to this peak is irreversible. The next cathodic peak was found around 0.18V followed by an oxidation peak at 0.52V on the reverse anodic scan. According to Courtney and Dahn [4], the large first cycle irreversible cathodic peak could be due to the reduction of tin phosphate to tin and formation of irreversible lithium phosphate phases. This is then followed by reversible lithium-tin insertion and extraction reaction.

The voltammogram for mesostructured tin phosphate as shown in Figure 6 does not have a similar curve when compared to that of the tin phosphate in Figure 3. There are three visible irreversible cathodic peaks at 1.65, 1.12 and 0.68V. Reaction occurring at 1.65V may be due to electrolyte decomposition on the active anode surface [7-8]. A pair of reversible redox peak is observed at 0.16V and 0.56V for all three cycles which may probably be associated with the reversible Li-Sn insertion and extraction reaction. The different voltammetric response exhibited by the mesostructured and non-mesostructured tin phosphate is believed to be strongly influenced by their structural state. The two extra cathodic peaks at 0.68V and 1.12V observed during the initial scan of mesostructured tin phosphate indicate two different energetic sites that lithium ion (Li^+) may reside during the initial decomposition of the tin phosphate which could be due to the complex nature of mesostructured configuration. A pair of reversible redox peaks at 0.16V and 0.56V for all three cycles is attributed to the reversible lithium-tin reaction.

Electrochemical reaction which have been reported [7-8] attributed decomposition of tin phosphate and the formation of metallic tin with the following stoichiometry;

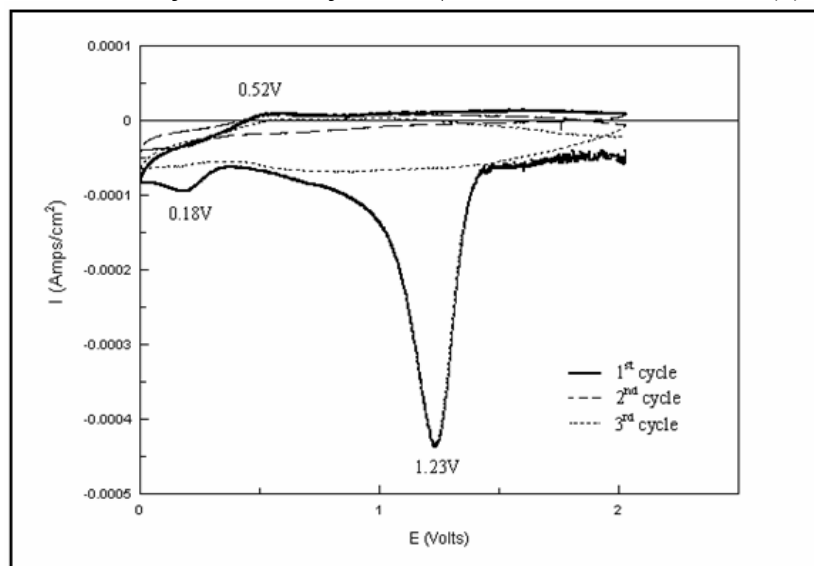
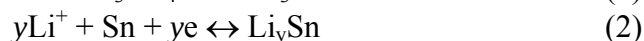
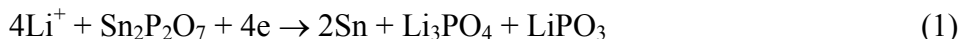


Figure 5: Cyclic voltammogram of tin phosphate

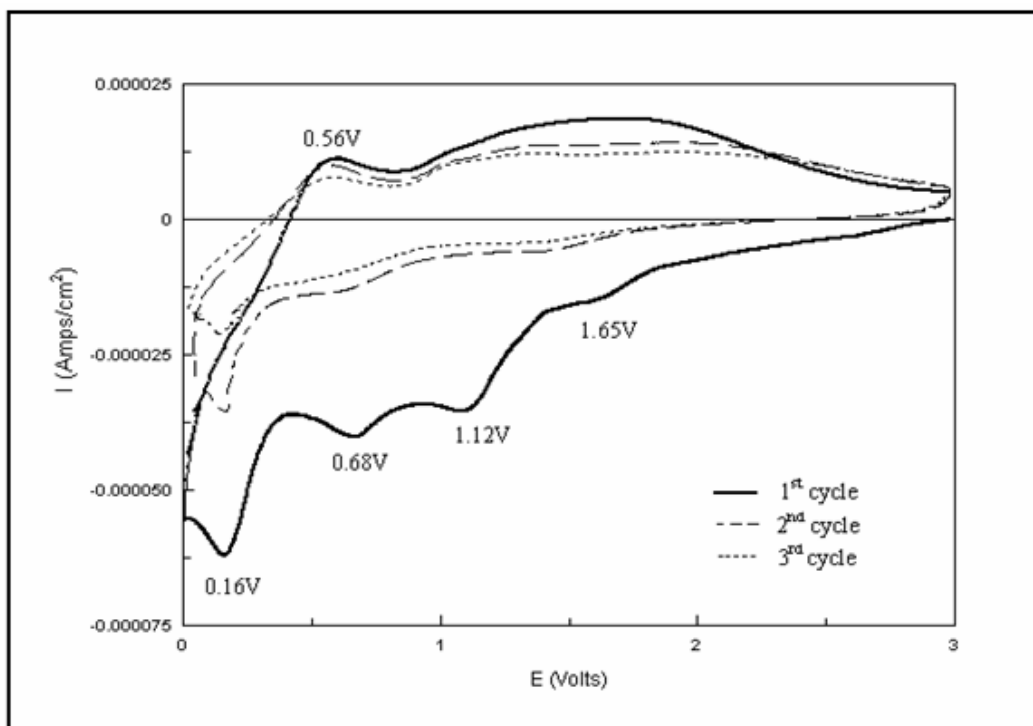


Figure 6: Cyclic voltammogram of mesostructured tin phosphate

Charge-Discharge Performance

Charge (Li^+ insertion) and discharge (Li^+ extraction) capacity profile for tin phosphate and mesostructured tin phosphate are shown in Figure 7 and Figure 8, respectively. Referring from Figure 7, the initial Li -ion storage capacity for tin phosphate is 821 mAh/g which is quite close to the theoretical capacity of tin oxide (991 mAh/g). However, upon the subsequent discharging in the first cycle, tin phosphate experience a 67% loss in capacity, retaining only about 273 mAh/g in reversible capacity. This capacity gradually fades and upon reaching the 10th cycle, only about 69 mAh/g of reversible capacity was retained.

As for mesostructured tin phosphate, initial Li -ion storage capacity achieved was 2872 mAh/g as shown in Figure 8. This value is very much higher than that of tin phosphate and tin oxide anode materials. The higher Li -ion storage capacity is an indication of additional loss of irreversible capacity. The subsequent Li -ion discharging in the first cycle up to 2.0V returned a capacity of 590 mAh/g, suffering a 79% of losses. Capacity fading was also evident for this anode, where upon reaching the 10th cycle, a reversible capacity of only 235 mAh/g was retained. This value is still very much higher than that retained for tin phosphate anode.

The large losses capacity in the first cycle are caused by reaction between lithium and tin phosphate to form irreversible lithium phosphate phases (Li_3PO_4 and LiPO_3) and metallic tin which could then be used to store and release Li ion reversibly [7]. This finding is in agreement with results obtained from cyclic voltammograms from Figure 5

and Figure 6. Gradual capacity losses with further cycling observed for both anodes may be due to aggregation of tin into clusters when subjected to repeated reversible reaction with lithium which increases mechanical stresses in the material leading to electrical connectivity losses and subsequent capacity fading.

The ability of mesostructured tin phosphate anode to store high amount of Li^+ and retain higher reversible capacity may be due to its complex mesostructure, amorphous network which is believed to play an important role in buffering against large volume changes during the Li insertion and extraction process. It is believed that the lithium-tin phosphate form a flexible, mesostructured framework that could minimized the consequence of tin aggregation upon further charge-discharge cycling [6]. The mesostructured tin phosphate is more effective in confining the tin particles in its framework thus retarding the aggregation of tin atoms into large clusters that could lead to the disintegration of the anode material compared to that of non-mesostructured tin phosphate. Capacity fading is also evident in mesostructured tin phosphate as in tin phosphate and this may be due to the deterioration of mesostructured characteristics upon further cycling.

Although both anode materials exhibited low Coulombic efficiency of less than 35% in the first cycle, the efficiency improved more than 90% upon further cycling (Figure 7 and Figure 8). Both anodes showed good charge-discharge efficiencies upon further cycling.

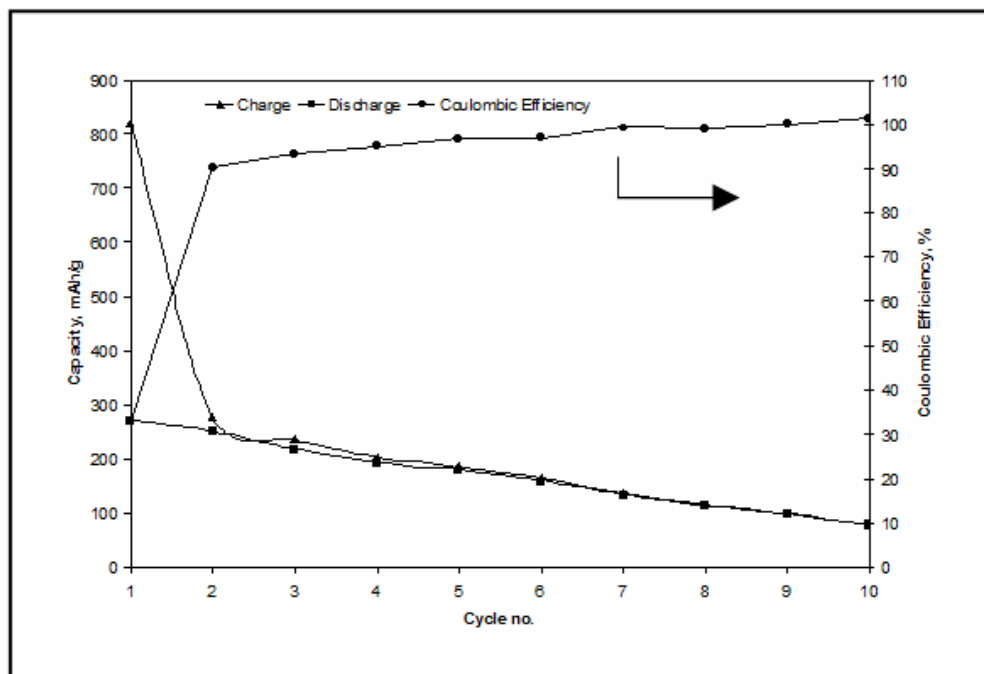


Figure 7: Charge-Discharge capacity profile for tin phosphate

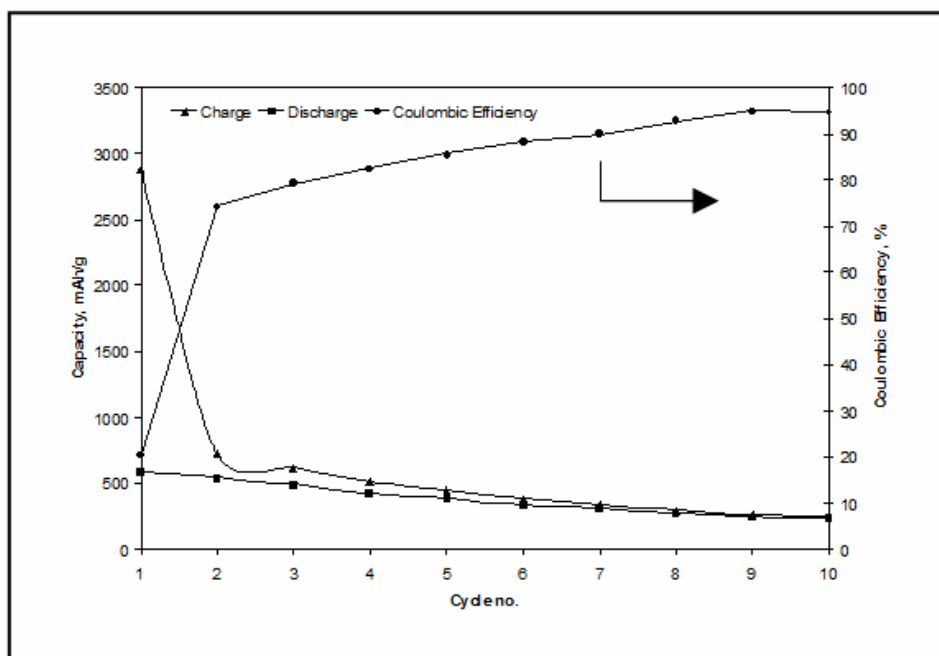


Figure 8: Charge-Discharge capacity profile for mesostructured tin phosphate

CONCLUSION

Tin phosphate exhibited a lithium-ion storage capacity of 821 mAh/g whereas mesostructured tin phosphate exhibited much higher lithium-ion storage capacity of 2872 mAh/g. However both anodes suffered large losses in irreversible capacity of more than 60%. The irreversible losses are due to the reduction of tin phosphate to lithium phosphate phases and formation of metallic tin. Capacity fading observed for both anode materials may be due to aggregation of tin into clusters. A reversible capacity of 69 mAh/g and 235 mAh/g upon reaching the 10th cycle was achieved for tin phosphate and mesostructured tin phosphate, respectively. Extensive work is currently in progress to investigate the mesostructure and amorphous state in tin phosphate and its influence on the electrochemical reaction with lithium.

ACKNOWLEDGEMENT

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