CHAPTER 6

Discussions on lithium tin oxide and vanadium tin oxide

6.1 Discussions on lithium tin oxide obtained from tin dioxide and lithium hydroxide

The XRD pattern of a sample obtained by heating "home-made" tin dioxide with lithium hydroxide monohydrate agrees well with the JCPDS: 31-0761 of dilithium stannate, Li_2SnO_3.

Hence a possible reaction for the formation of this mixed oxide is:

$$SnO_2.H_2O + 2LiOH.H_2O \xrightarrow[10\ hr]{650^oC} Li_2SnO_3 + 4H_2O$$

It is to be noted that we have written the formula of tin dioxide as $SnO_2.H_2O$. This is in line with FTIR spectrum of the final product heated 800°C which still shows trace amount of water and therefor rendering initial water of crystallization to be less than 1.6. To the nearest whole number the amount of water of crystallization is one.

Complete Li_2SnO_3, formation is obtained after heating the reacting materials at 650°C for 10 hr this shows that Li_2SnO_3 can be

produced at relatively low temperature compared to that obtained by Courtney and Dahn, (1997).

In their method, Li_2SnO_3 was prepared by blending equemole amount of Li_2CO_3 and SnO_2 this blend was heated in an alumna heating boat at 10°C/min to 1000°C in air in Lindbrg tube furnace. The heated blend was soaked for 7 hr and cooled slowly to room temperature. The resultant product is a white powder, which is the same as that obtained in the present work.

Li_2SnO_3 has been used as a cathode material in rechargeable lithium ion coin cells. It demonstrates discharge capacities on the other of 1000 mAh/(g Sn). Which is consistent with the alloying capacity limit of 4.44 Li atoms per Sn atom or 991mAh/(g Sn).

When using Li_2SnO_3 as a cathode material, the observed, first discharge capacity is 1200 mA hr/g. This is about the same as the calculated first discharge capacity based on the formation of Li_2O and subsequent alloying which is 1244 mA hr/g. The observed second discharge capacity less than 1.0 V is 550 mA hr/g and the calculated second disharge capacity based on alloying is 652 mA hr/g.

SEM micrograph of lithium tin oxide shows the sample constitute of small spherical agglomerates of diameter small as 1μm. Thus the total surface area to volume ratio will be larger. The radius of the spherical agglomerates this could be the explanation as to why there is a spontaneous reaction between tin dioxide and lithium

hydroxide even by soft mixing as indicated by XRD pattern Fig. (5.1). Once again FTIR shows spontaneous reaction upon mixing tin dioxide with lithium hydroxide as shown in Fig. (5.8) upon heating water is removed this supports our formation mechanism of Li_2SnO_3, the FTIR peaks after 650°C is more distinct than that before heating, this shows that the materials is well formed after heating at 650°C.

6.2 Discussion on lithium tin oxide obtained from tin monoxide and lithium hydroxide

The formation of lithium tin oxide is same as that of SnO_2 $1.6H_2O$ and $LiOH.H_2O$ using the $SnO.9H_2O$ as starting material. However the mixture must be heated to 650°C for 10hr.

In this process SnO was converted to SnO_2 this is also proven by X-Ray diffraction Fig. (3.15). Lithium tin oxide obtained is more crystalline using SnO as the starting materials than the one using SnO_2 as a starting materials.

Several differences are observed when mixing tin monoxide and lithium hydroxide at room temperature when compared to the mixing of tin dioxide and lithium hydroxide at room temperature. Firstly, the XRD shows an intense peak at $2\theta = 43°$ when tin monoxide was softly mixed with lithium hydroxide. Whereas, in the case of mixing tin dioxide with lithium hydroxide, the XRD pattern obtained upon

grinding the mixture containing tin monoxide exhibits an amorphous hump in the XRD pattern.

FTIR spectrum of tin dioxide mixed with lithium hydroxide before heating Table (6.1) and after heating Table (6.2).

Table (6.1): FTIR peaks of the mixture of tin monoxide and tin dioxide with lithium hydroxide at room temperature.

SnO_2+LiOH Peaks at r.t [cm^{-1}]	1627.8	1504.3	1437.0	993.7	864.7	823.4	500
SnO+LiOH Peaks at r.t [cm^{-1}]	1628.7	1532.6	1448.7	966.4	906.4	754	504.2
Difference [cm^{-1}]	0.9	28.3	11.7	-27.3	41.7	-69.4	-4.2

Table (6.2): FTIR peaks of the mixture of tin monoxide and tin dioxide with lithium hydroxide after heating to 650°C

SnO_2+LiOH Peaks at 650°C [cm^{-1}]	1508.1	1438.0	867.6
SnO+LiOH Peaks at 650°C [cm^{-1}]	1516.8	1441.2	864.3
Difference [cm^{-1}]	8.1	3.2	-3.3

Table (6.2) shows that there is a similarity between the peaks that exist after heating at 650 °C. For both starting materials mono and dioxide tin, the Li_2SnO_3 shows same vibration frequencies. At room temperature, two peaks are existed in the mixture of tin monoxide and lithium hydroxide (1107.3 cm^{-1}, 661.9 cm^{-1}) but are not existed in the mixture tin dioxide and lithium hydroxide. This is related to the

different formation mechanism of lithium tin oxide as confirmed by XRD pattern Fig. (5.3).

6.3 Discussion on vanadium tin oxide

In the present work vanadium tin oxide has been prepared by heating the mixture of vanadium oxide dihydrate (brown) (which was prepared by the sol-gel process following the method of Znaidi et al, (1989). This compound exists as a yellow powder.

The preparation method is summarised by:

$$x/2\ V_2O_5.\ 2H_2O\ +\ SnO_2.H_2O \xrightarrow{500^{\circ}C} V_xSn_{1-x}O_{2+y}\ (5\ \text{mol}\ \%V)$$

The chemical formula for the solid solution could probably be $V_{0.05}Sn_{0.95}O_{2.025}$. According to a recent study (Melghit et al, 1999), the maximum percentage of vanadium that can be incorporated into tin dioxide is 5 mol %V.

Table (6.3) shows the preparation of the phase AB using A and B as starting materials.

Table (6.3): The preparation of the phase AB

Materials oxide (A)	Materials oxide (B)	The minimum temperature reached for the synthesis of (AB)
V_2O_5 Commercial	SnO_2 commercial	1200°C
V_2O_5 oxalate	SnO_2 commercial	600°C
V_2O_5 Soft chemistry	SnO_2 Soft chemistry	500°C
SnO_2 Commercial	Li_2CO_3 Commercial	1000°C
SnO_2 Soft chemistry	$LiOH.2H_2O$ Commercial	650°C
SnO_2 Soft chemistry	$LiNO_3$ Commercial	650°C
SnO Commercial	$LiOH.2H_2O$ Commercial	1000°C
SnO Soft chemistry	$LiOH.2H_2O$ Commercial	650°C

The results in Table (6.3) are summarised in three cases:

First case: A and B are commercial materials with well-defined phases (A and B are oxide, nitrate or carbonate)

$$A\ (commercial) + B\ (commercial) \xrightarrow{T_1} AB$$

T_1: Reaction temperature

Second Case: In this case, (A) is prepared by a soft chemistry technique. Materials prepared by this way exist in amorphous or semi-amorphous phases (semi-amorphous phase means that XRD

pattern are characteristic of crystalline materials but with broad and weak diffraction peaks)

$$\text{A (soft chemistry)} + \text{B (commercial)} \xrightarrow{T_2} \text{AB}$$

T_2: Reaction temperature

Third case: Both of A and B are prepared by soft chemistry techniques, A and B are amorphous or semi-amorphous phases:

$$\text{A (soft chemistry)} + \text{B (soft chemistry)} \xrightarrow{T_3} \text{AB}$$

T_3 : Reaction temperature

We can easily see that the last reaction will have the lowest temperature, i.e. T1 > T2 > T3.

According to the literature (Volkov and Buldakova, 1994), vanadium tin oxide when prepared using commercially available vanadium oxide and tin dioxide heated to 1200°C exists as a yellow solid-solution. This material is used as pigments for tiles and pottery.

$$\underset{\text{(crystalline)}}{NH_4VO_3/V_2O_5} + \underset{\text{(crystalline)}}{SnO_2} \xrightarrow{\textbf{1200°C}} \underset{\text{(crystalline)}}{\text{Solid solution of vanadium tin oxide}}$$

In order to enhance the vanadium tin oxide reaction, oxalic acid can be added to convert vanadium oxide to vanadium oxalate (*in-situ*)

(Volkov and Buldakova, 1994). The addition of oxalic acid dramatically decreases the reaction temperature to 600°C.

$$x/2V_2O_5 + SnO_2 \xrightarrow{600°C} V_xSn_1\text{-}xO_{2+y}\ (18\ \text{mole}\ \%V)$$

with oxalic acid (crystalline) (crystalline)

In the present study, the physical nature of the starting materials affects the reaction conditions. Both the reactants are amorphous materials and the product, which can be obtained only at 500°C, exists as a crystalline solid. This result suggests that amorphous materials would be more suitable reactants in soft chemistry reaction.

For most synthesis, commercial oxides, nitrates or carbonates are the starting materials. These have well-defined phases and large crystallite sizes. If the observation on non-crystallinity is correct, then these properties can adversely affect their reactivity in solid state reaction

6.4 Summary

The formation of lithium tin oxide begins with the disruption of the lithium hydroxide structure, which is followed by a re-arrangement of the tin, lithium, oxygen atoms within the structure. The re-arrangement of atoms is accelerated by heating and is

facilitated by the evaporation of water that is bonded in both materials.

The study also shows that when lithium hydroxide is mixed with tin monoxide, the structure of lithium hydroxide collapses, and the collapse is followed by the formation of a new structure that has been characterised by new peaks in both the X-ray diffractograms and infrared spectra. Upon heating this phase, lithium tin oxide is obtained (Wen and Huggins, 1980; Brousse et al, 1998).

The XRD used for identification of impurities in materials and the nature of the phases, the investigation of vanadium tin oxide and lithium tin oxide showed a high purties and an overlap of the peaks recorded with JCPDS cards.

For the syntheses of lithium and vanadium tin oxide, poor crystallinity and small particle sizes favour high reactivity. Semi amorphous tin dioxide ($SnO_2.1.6H_2O$) has been used to prepare vanadium tin oxide and lithium tin oxide at relatively low temperatures. Tin monoxide in place of tin dioxide as reagent shows a higher reactivity in the preparation of lithium tin oxide. Lithium hydroxide reacts spontaneously with both tin dioxide and tin monoxide at room temperature to give new phases, as shown by thermal analysis, X-ray diffraction and infrared spectroscopy.