CHAPTER 3

METHODOLOGY

3.1 Introduction

$LiNiVO_4$ was synthesised by solution evaporation method and polymer modified solution evaporation method. Chitosan was used as polymer host in this work. $LiNiVO_4$ obtained by chitosan modified solution evaporation method was coated with ZnO. Different concentration (in wt %) of ZnO was coated on $LiNiVO_4$. The structural properties and morphological studies of the cathode materials were evaluated using x-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). Electrochemical performance was tested with cyclic voltammetry (CV) and charge-discharge performance of batteries using the prepared cathode materials.

3.2 Solution evaporation method and chitosan modified solution evaporation method

Before going further, we would like to clarify that the solution evaporation method mentioned here follows the same procedure as the sol-gel method. In the sol-gel method, carboxylic acid chelating agent is usually used. At the appropriate concentration of chelating agent, a gel can be finally formed. In this work, we do not use such chelating agents. Instead we used nitric acid to make the solution acidic. In the solution precipitation method by Fey et al (1999) a pH of 3 will produce a complete material that will exhibit good cycling performance when the material is used in the cathode of the cell. In this work, we used a pH of 2. The method adopted by Fey et al (1999) is the solution precipitation method where the product was evaporated at room temperature. The method used in this

work is simpler and the starting materials are commonly available. Solution evaporation and chitosan modified solution evaporation method were used to prepare $LiNiVO_4$. Stoichimetric amounts of lithium acetate (Fluka), nickel acetate (Fluka) and ammonium metavanadate (Ajax chemicals) were used as starting materials. Ammonium metavanadate was dissolved in hot distilled water until the solution become clear yellow solution. Then ethanol was added to the solution to ensure complete dissolution before lithium acetate was added to the solution. After the lithium acetate salt has dissolved completely, nickel acetate was added to the mixture. Nickel acetate turns the solution to green upon the dissolution. At this point, nitric acid was added dropwise until pH=2 and a clear green solution obtained. The mixture was continuosly stirred and heated on the magnetic stirrer. The temperature was controlled until the solution was just boiling. The temperature was reduced accordingly as the solid precursor starts to form. The precursor was sintered at different sintering temperatures of 500 °C, 600 °C, 700 °C and 800 °C for 3 hours separately.

Similar steps were followed for chitosan modified sol gel method. Polymer solution which was prepared separately using 1 g chitosan in 100 ml 1 % acetic acid was added to the mixture after the nitric acid. This additional step gives chitosan modified sol gel method. The method is summarized as shown in Fig.3.1.

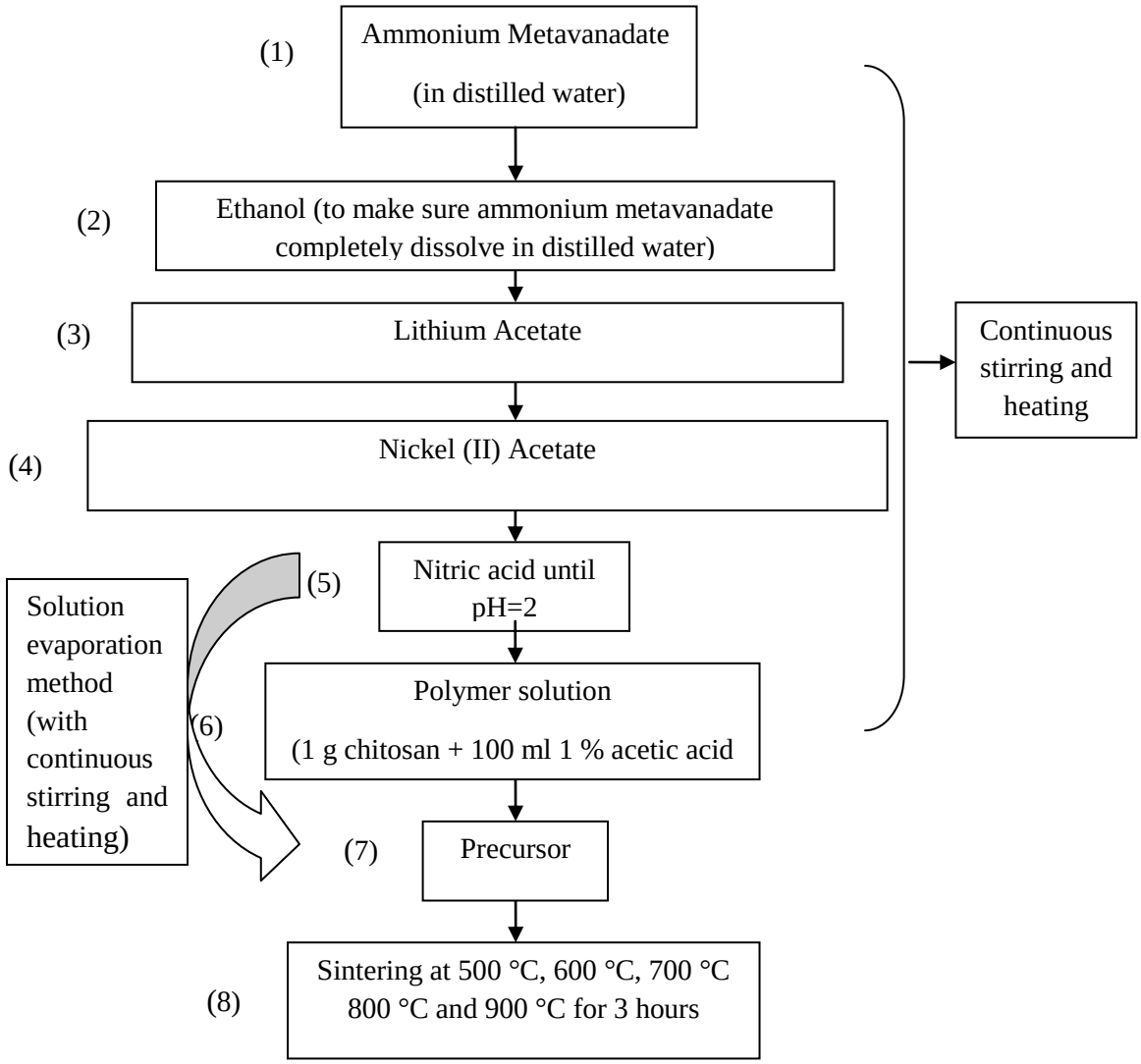


Fig.3.1: Chitosan modified solution evaporation method. By passing step 6 gives the solution evaporation method.

3.3 ZnO coated $LiNiVO_4$

Zinc acetate (Fluka) was dissolved in distilled water and heated until clear. $LiNiVO_4$ was added into the clear solution and continuosly heated until a solid precursor was formed. The solid precursor was sintered at 500 °C, 600 °C, 700 °C and 800 °C. In this work, $LiNiVO_4$ by with

smallest crystallite size and prepared by chitosan modified sol gel method was chosen as candidate that will be coated with ZnO. Fig.3.2 summarizes the coating process on $LiNiVO_4$.

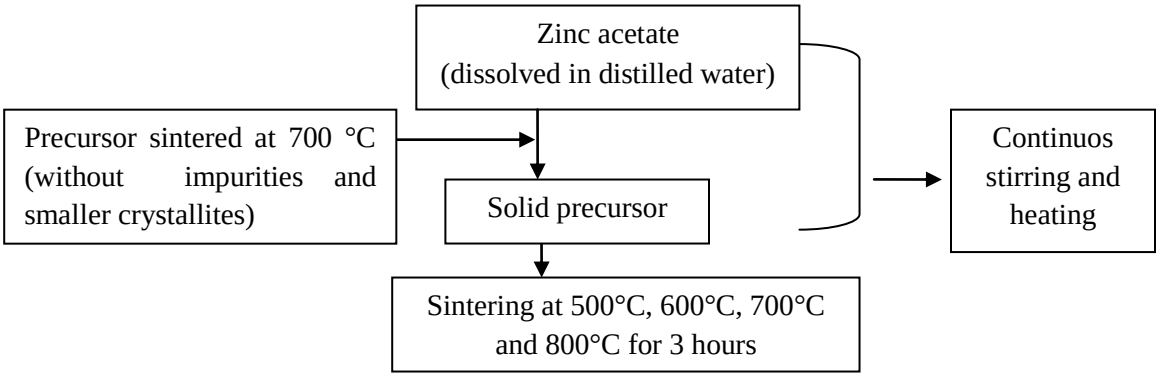


Fig.3.2: Preparation of ZnO coated $LiNiVO_4$

3.4 CHARACTERIZATION

3.4.1 X-ray diffraction (XRD)

X-ray diffraction is an important method in research because it can provide useful information about the crystalline structure. Diffraction occurs based on Bragg's Law (Fig 3.3):

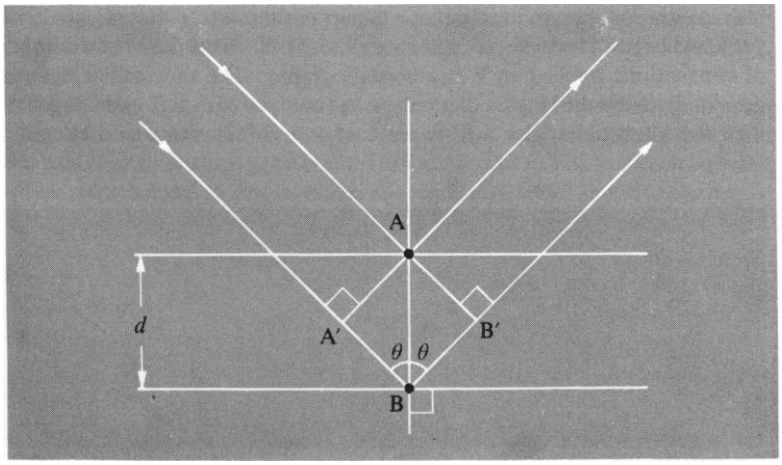


Fig 3.3 Reflection of Bragg's law

From the diagram,

$$\lambda = 2d \sin\theta$$

Cubic structure takes the equation relating lattice constant, a with interplanar spacing, d_{hkl} and plane indices (*hkl*) as follows:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

X-ray diffraction (XRD) was carried out on (Siemens D5000) with Cu Kα (40 kV, 40 mA) to identify crystalline phase of the product. XRD data in the range of 2θ = 0° to 80° were collected with a step size of 0.05°. Crystallite size (*d*) of the samples was calculated using Scherrer's equation (Yi et al., 2006; Molenda et al., 2007)

$$d = \frac{0.9\lambda}{\beta \cos\theta}$$

β is the Full width half maximum (FWHM) of the most intense diffraction peak (311) plane in radians, θ = Bragg angle of the diffraction peak and λ = the wavelength of CuKα X-radiation.

3.4.2 Transmission electron microscopy (TEM)

Properties of materials depend mainly on structure. Composition, heat treatment, processing methods, etc affect the structure. Transmission electron microscope (TEM) is an instrument which can provide chemical and physical information. It enables better understanding of materials. The operation of an electron microscope is based on scattering

processes when the electron beam passes through the sample. There are two types of scattering which can be classified as elastic and inelastic. Elastic scattering occurs between the electrons and potential field of the nuclei. No energy loss occurs in elastic scattering. Inelastic scattering occurs between electrons in the sample. There is energy loss in inelastic scattering. Both scatterings produce information about the samples (Thomas and Goringe., 1979).

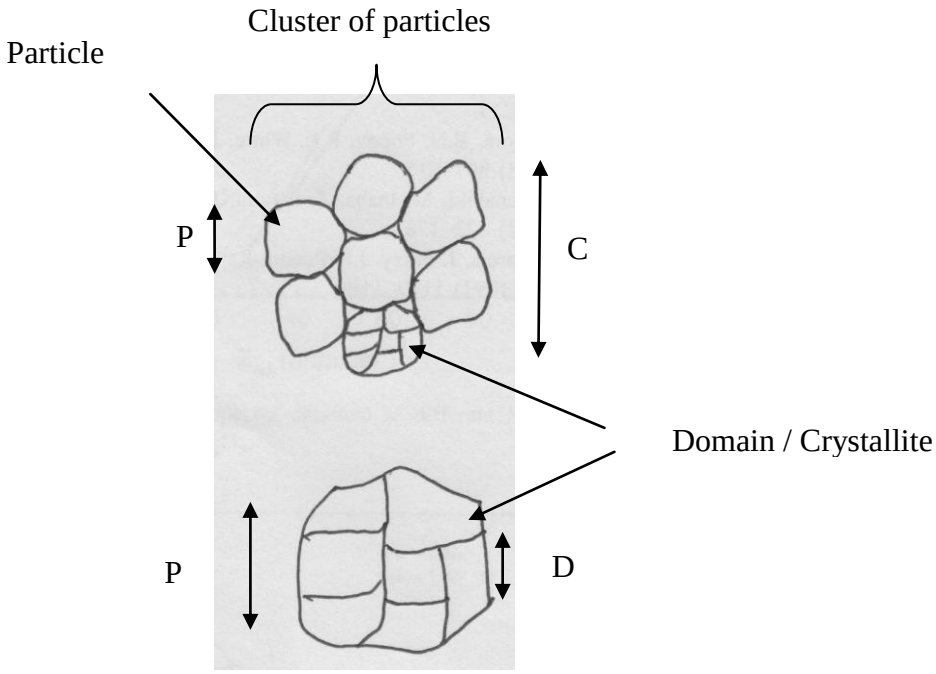
TEM samples were prepared by sonicating the cathode material with ethanol. The solution was dropped onto a carbon coated copper grid and left to drying. TEM was performed using Leo Libra 120 electron microscope with a LaB_6 filament as electron source at 12.5 kV.

3.4.3 Scanning electron microscopy (SEM)

Scanning electron microscope is a tool to observe surface morphology. When the electron beam strikes the surface of the samples, signals from secondary electrons, backscattered electrons, Auger electrons, characteristic x-rays and photons of various energies are produced. However, secondary and backscattered electrons are the main signals of attention because of its use in surface morphology (Joseph et al., 1981).

Crystallites and particles

Crystallite sizes obtained from X - ray diffraction are domains which reside in particles. The domains are not detected by TEM and SEM. Particle size can be observed by TEM. SEM can provide morphology of the sample which consists of cluster of particles.



$D \leq P \leq C$

Size of particle clusters is bigger compared to particles. The particles contain the smaller crystallites/domains.

3.4.4 Fabrication of batteries

20 mg of the active material was ground with 8 mg teflonized acetylene black (TAB) into thin film with few drops of ethanol. The thin film was pressed on stainless steel mesh. The film was then heated in a furnace at 200°C for 3 hours to eliminate moisture from the samples. Electrochemical cells were assembled in a glove box filled with argon. Lithium metal was used as counter and reference electrodes. The electrodes were separated from the working electrode by a 1 mm thick fiberglass soaked in an electrolyte, which consists of 1 M $LiPF_6$

dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) in the volume ratio of 1:2. Electrochemical tests were performed at room temperature using an Autolab PG12 potentiostat-galvanostat equipment. The cut off voltages were fixed at 4.8 V for charging and 3.0 V for discharging respectively.

3.4.5 Cyclic voltammetry

Cyclic voltammetry can be used as a tool to determine the redox potentials, chemical reactions and the kinetics of the electron transfer. The ratio of peak currents (i_{pa}/i_{pc}) and the separation of peak potentials (E_{pa} - E_{pc}) are the interested parameters in the cyclic voltammetry.

Summary

Results and discussion from these techniques on the materials prepared will be displayed in the following chapters.