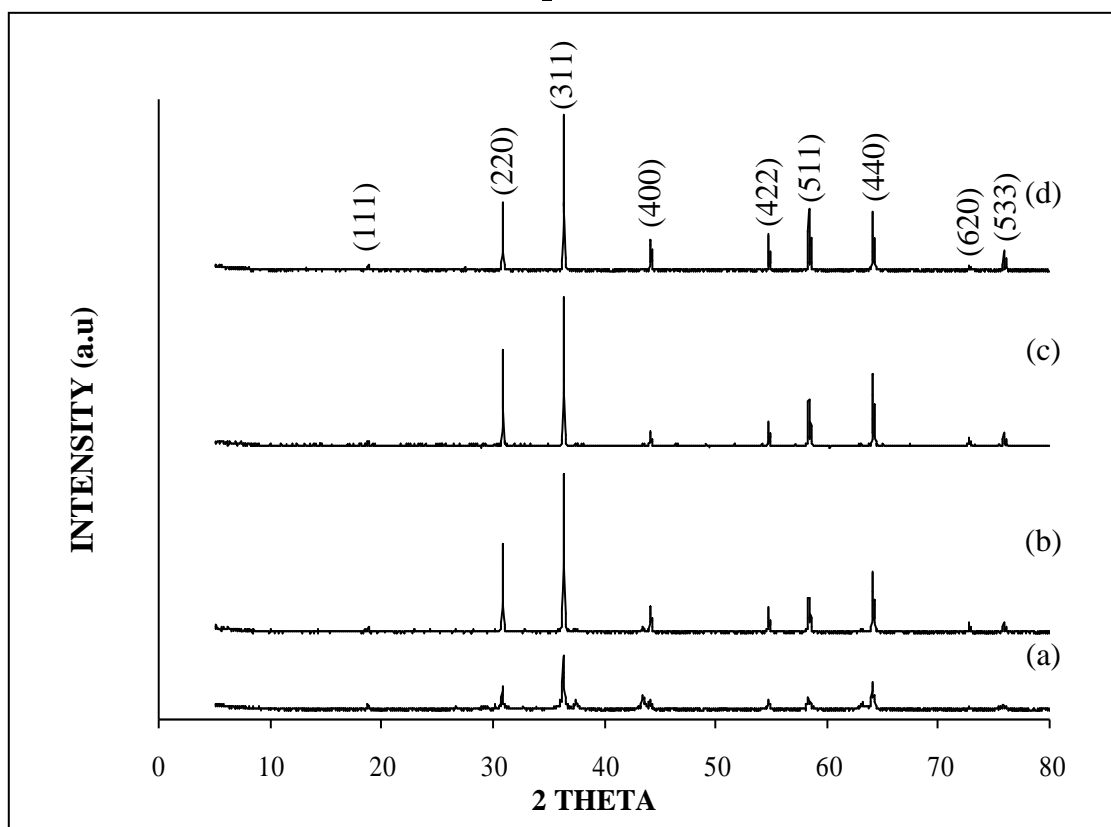


**CHAPTER 5****LiNiVO<sub>4</sub> BY CHITOSAN MODIFIED SOLUTION EVAPORATION METHOD****5.1 Introduction**

In this chapter, characterization results from LiNiVO<sub>4</sub> synthesized by the polymer modified solution evaporation method are presented. Chitosan was used as the polymer. Precursors sintered at different temperatures were characterized by XRD, SEM, TEM, CV and charge-discharge cycling performance.

**5.2 X-ray diffraction (XRD)**

XRD analysis was performed on the samples for the purpose of identification. Fig. 5.1 depicts X-ray diffractograms of LiNiVO<sub>4</sub> synthesized by chitosan modified solution evaporation method. Acetates of lithium and nickel and ammonium metavanadate were used as starting materials in this method. All the diffractograms show patterns corresponding to the face centered cubic spinel structure in  $Fd\bar{3}m$  space group as compared to JCPDS data 73-1636. XRD exhibit weak (111) Bragg line and strong (220) line confirming the structure of LiNiVO<sub>4</sub> has vanadium on the tetrahedral  $8a$  site (Kalyani et al., 2002, Bhuvaneshwari et al., 2005). Extra peaks at  $2\theta = 37.3^\circ$  and  $43.5^\circ$  at the sintering temperatures of 500 °C and 600 °C are evidence of the presence of NiO as impurity. The NiO impurity can be eliminated by sintering at temperatures above 600 °C. This clearly shows that LiNiVO<sub>4</sub> can be successfully obtained by the polymer modified sol gel method. Diffractograms for precursors sintered above 600 °C also did not show presence of Li<sub>3</sub>VO<sub>4</sub> as have been reported in previous literature (Fey *et al.*, 1997; Reddy *et al.*, 2007).



**Fig. 5.1: XRD of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method Sintering temperatures of (a) 500 °C (b) 600 °C (c) 700 °C (d) 800 °C**

Table 5.1 gives lattice parameters for LiNiVO<sub>4</sub> prepared by chitosan modified sol gel method at different sintering temperatures. Lattice parameters show the values of 8.205 and 8.212 at sintering temperatures of 500°C and 600°C. It is to be remembered that these samples contain impurities. The lattice parameter of the sample sintered at 700°C is also 8.212 and is maintained at this value to four significant figures even at 800°C.

Table 5.1: Lattice parameter of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at different sintering temperatures

500°C

hkl	2θ	d	$h^2 + k^2 + l^2$	$(h^2+k^2+l^2)^{1/2}$	a
220	30.834	2.89758	8	2.8284	8.1956
311	36.307	2.47236	11	3.3166	8.1999
400	44.116	2.05114	16	4.0000	8.2046
422	54.745	1.67538	24	4.8990	8.2077
333	58.353	1.5801	27	5.1962	8.2104
440	64.101	1.45158	32	5.6569	8.2114

Calculated average lattice parameter is 8.205

600°C

hkl	2θ	d	$h^2 + k^2 + l^2$	$(h^2+k^2+l^2)^{1/2}$	a
220	30.799	2.90081	8	2.8284	8.2047
311	36.254	2.47586	11	3.3166	8.2115
400	44.085	2.05254	16	4.0000	8.2102
422	54.703	1.67657	24	4.8990	8.2135
333	58.328	1.58073	27	5.1962	8.2137
440	64.065	1.45229	32	5.6569	8.2154

Calculated average lattice parameter is 8.212

700°C

hkl	2θ	d	$h^2 + k^2 + l^2$	$(h^2 + k^2 + l^2)^{1/2}$	a
220	30.801	2.90062	8	2.8284	8.2042
311	36.256	2.47574	11	3.3166	8.2111
400	44.08	2.05275	16	4.0000	8.2110
422	54.693	1.67685	24	4.8990	8.2149
333	58.304	1.5813	27	5.1962	8.2167
440	64.054	1.45251	32	5.6569	8.2166

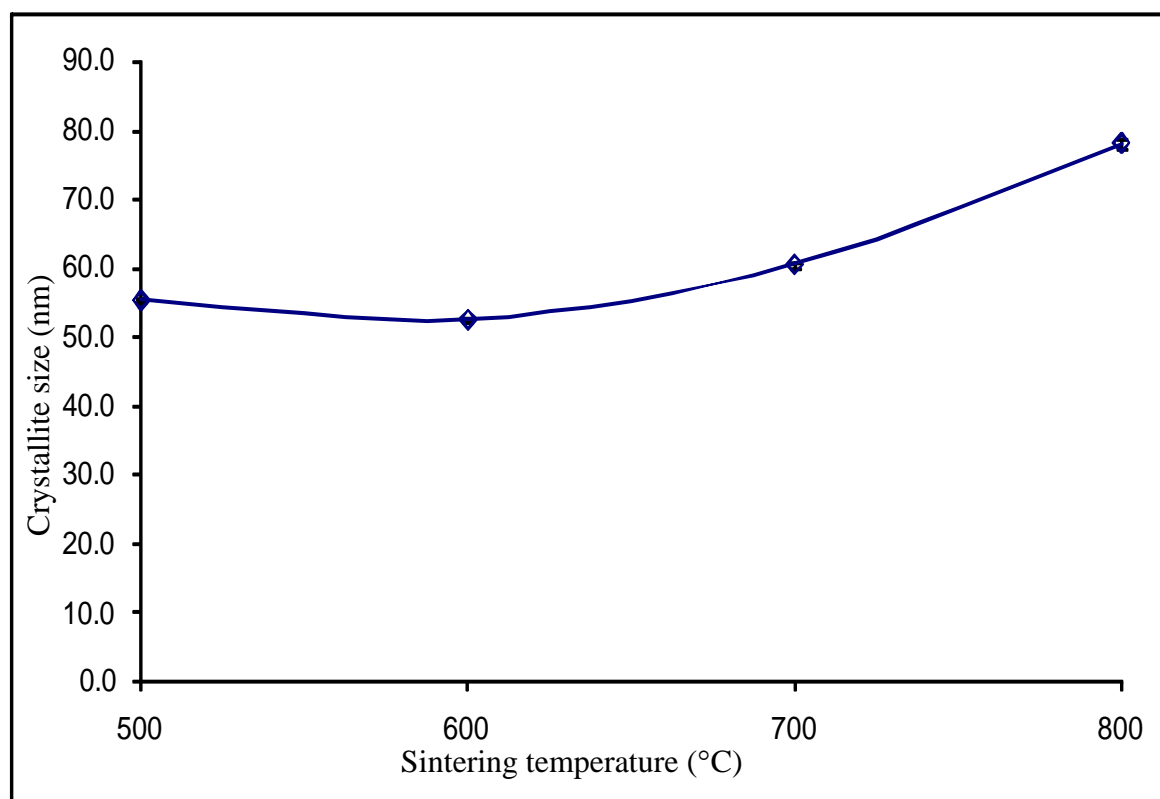
Calculated average lattice parameter is 8.212

800°C

hkl	2θ	d	$h^2 + k^2 + l^2$	$(h^2 + k^2 + l^2)^{1/2}$	a
220	30.802	2.9005	8	2.8284	8.2039
311	36.254	2.47585	11	3.3166	8.2115
400	44.085	2.05254	16	4.0000	8.2102
422	54.7	1.67666	24	4.8990	8.2139
333	58.324	1.58081	27	5.1962	8.2141
440	64.058	1.45243	32	5.6569	8.2162

Calculated average lattice parameter is 8.212

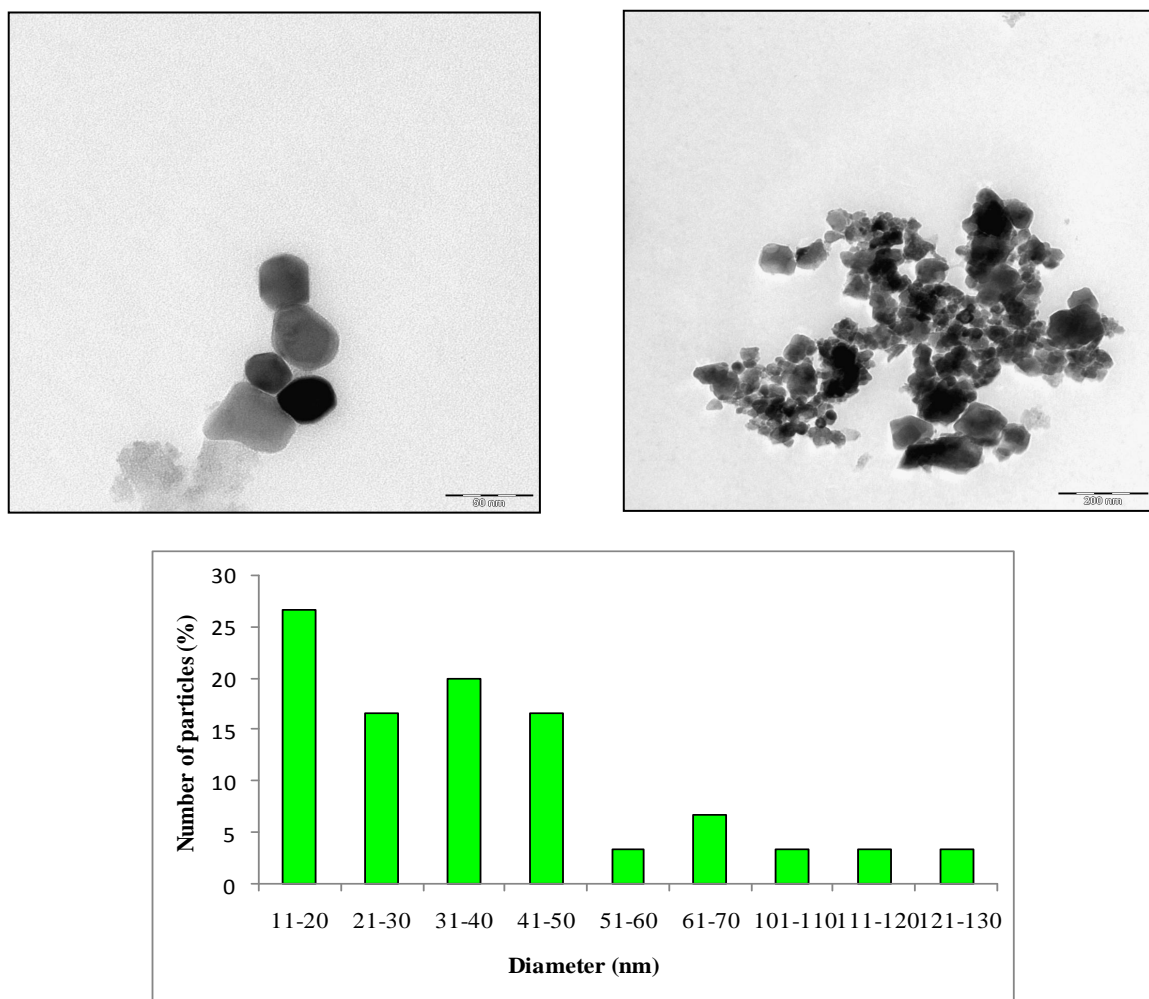
Fig. 5.2 presents crystallite size of LiNiVO<sub>4</sub> prepared by chitosan modified solution evaporation method at sintering temperatures of 500 °C to 800 °C. The samples by chitosan modified sol gel method gives more smaller crystallites of 55.3 nm, 52.5 nm, 60.5 nm and 78.1 nm for sintering temperatures of 500 °C, 600 °C, 700 °C and 800 °C respectively. This shows that the chitosan modified solution evaporation method can produce crystallite of nanosize.



**Fig. 5.2: Crystallite size of LiNiVO<sub>4</sub> chitosan modified by solution evaporation method at different sintering temperatures**

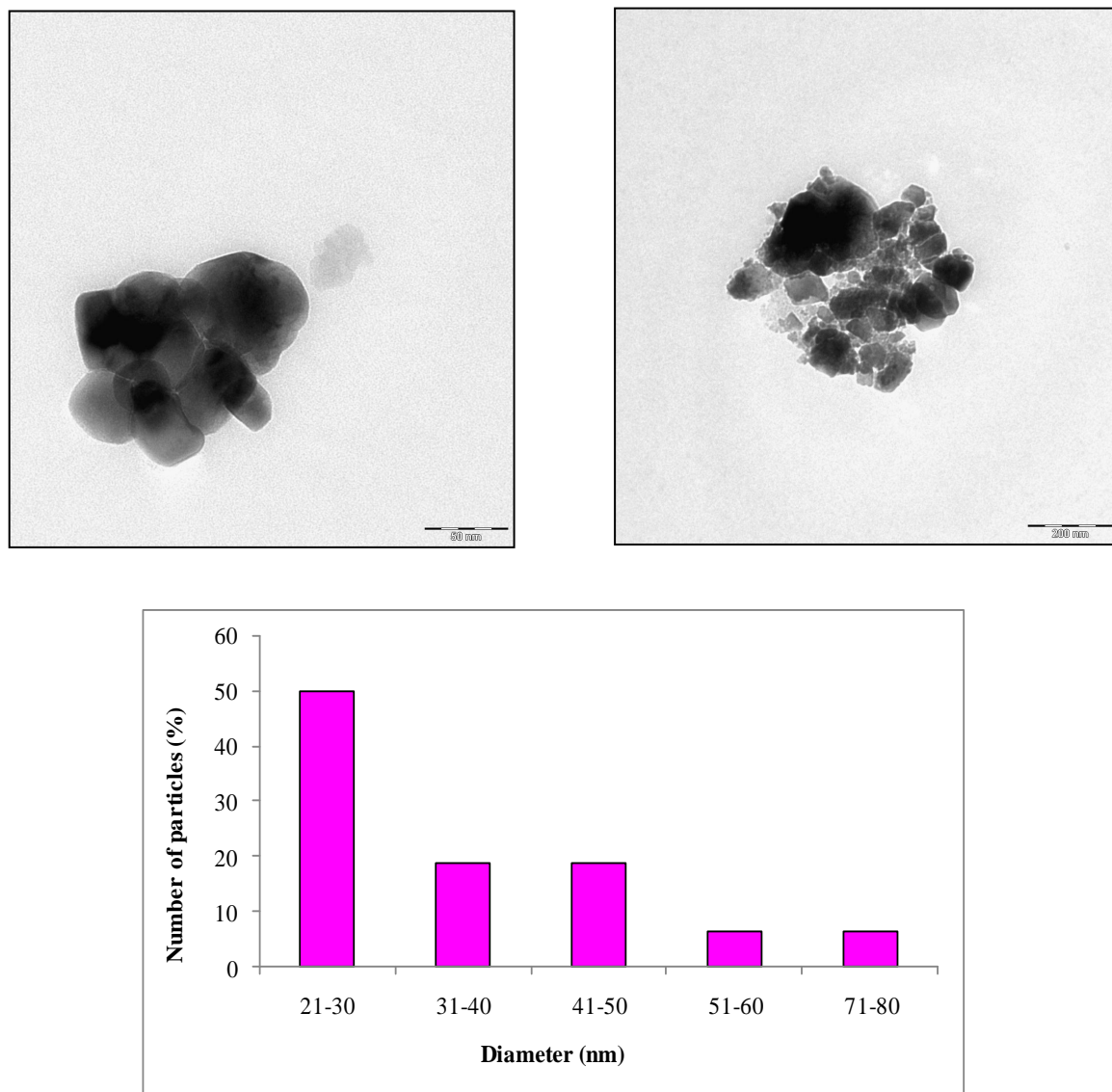
### 5.3 Transmission electron microscopy (TEM)

TEM images for samples by chitosan modified solution evaporation method at different sintering temperatures are shown in Fig. 5.3 to Fig 5.7. Diameter of the particles ranges between 11 nm to 130 nm when sintered at 500 °C. 26.7 % of the particles have diameter within 11 nm to 20 nm followed by 20 % of particles with diameter 31 nm to 40 nm. The diameter ranging between 21 nm to 30 nm and 41 nm to 50 nm represents 16.7 % of particles are respectively. Only 3.3 % of particles with diameter in the range of 51 nm to 60 nm, 101 nm to 110 nm, 111 nm to 120 nm and 121 nm to 130 nm respectively.



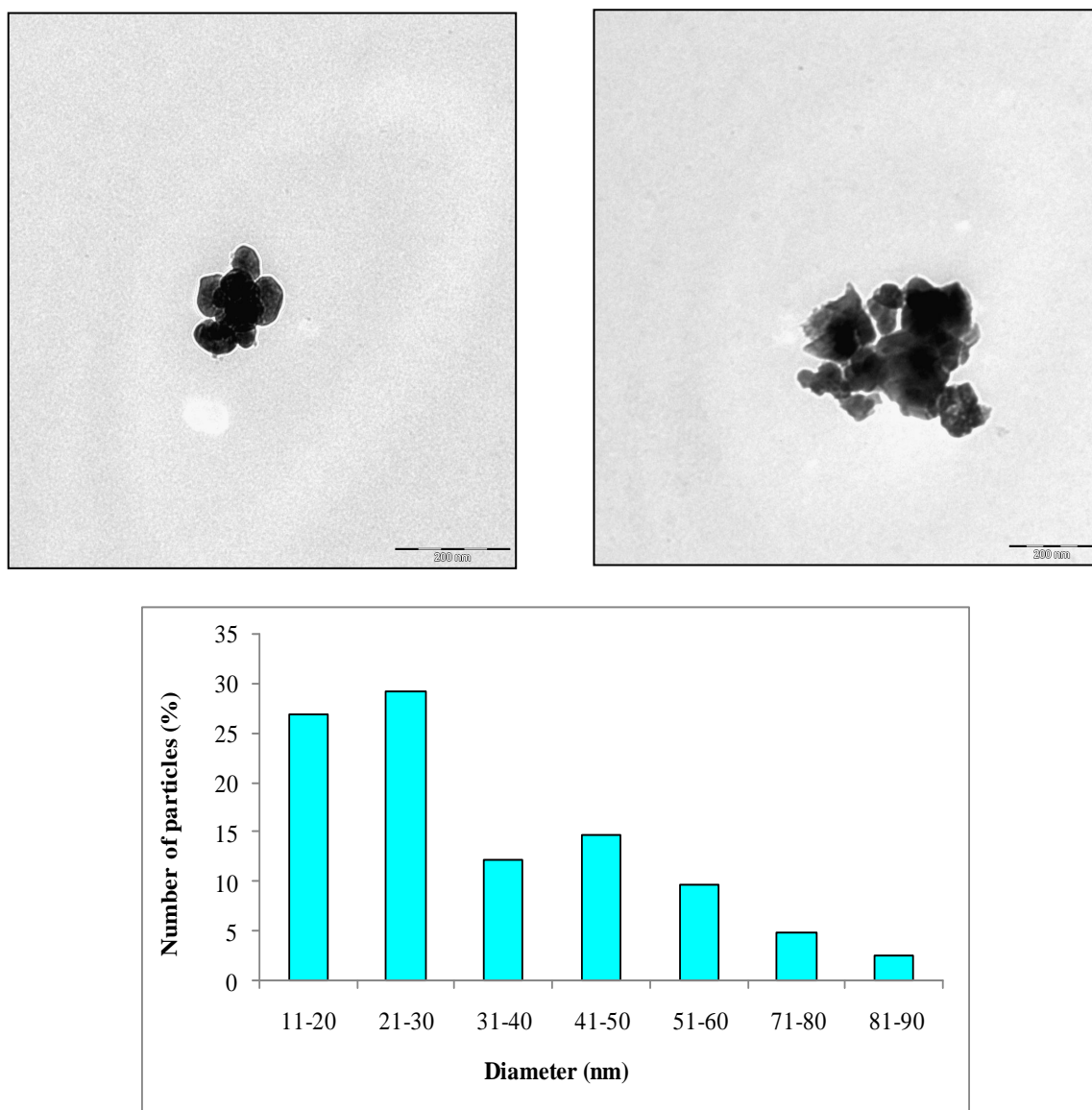
**Fig. 5.3:** TEM images of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 500 °C

The diameter of the particles for the samples sintered at 600 °C ranges between 21 nm to 80 nm as shown by Fig. 5.4. The highest numbers of particles have diameter ranging between 21 nm to 30 nm. There are also particles of diameters within the range between 31 nm to 40 nm and 41 nm to 50 nm which covers 37.6 % of the distribution. 6.3 % of the particles are with diameter range 51 nm to 60 nm and 71 nm to 80 nm. The distribution indicates non-uniformity of particle size.



**Fig. 5.4:** TEM images of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 600 °C

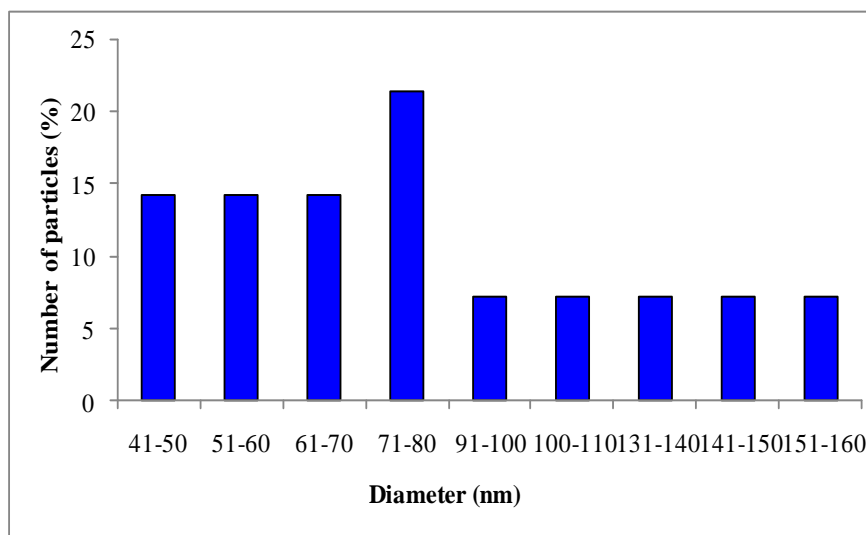
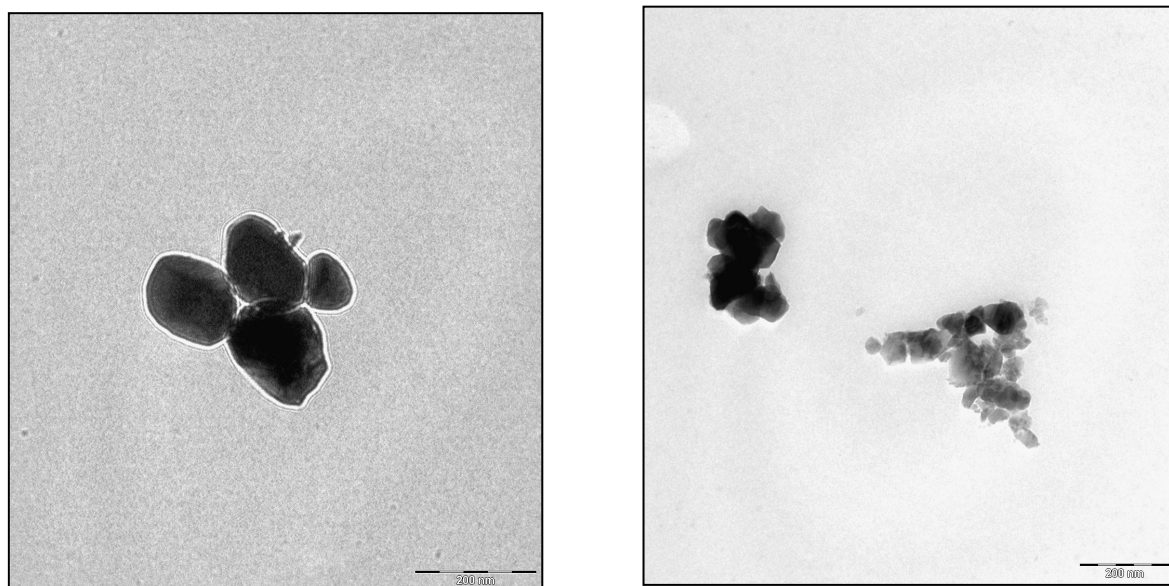
Fig. 5.5 states that the precursor sintered at 700 °C produced particles of size in the range of 11 nm to 90 nm. 29.3 % of the particles are with diameter in the range of 21 nm to 30 nm and 26.8 % of the particles in the range of 11 nm to 20 nm. The diameter ranging from 31 nm to 40 nm, 41 to 50 nm and 51 to 60 nm represents 12.2 %, 14.6 % and 9.8 % of the distribution respectively. 4.9 % of the particles have distribution is in the diameter range of 71 nm to 80 nm. About 2.4 % of the particles have diameter ranging from 81 nm to 90 nm.



**Fig. 5.5: TEM images of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 700 °C**

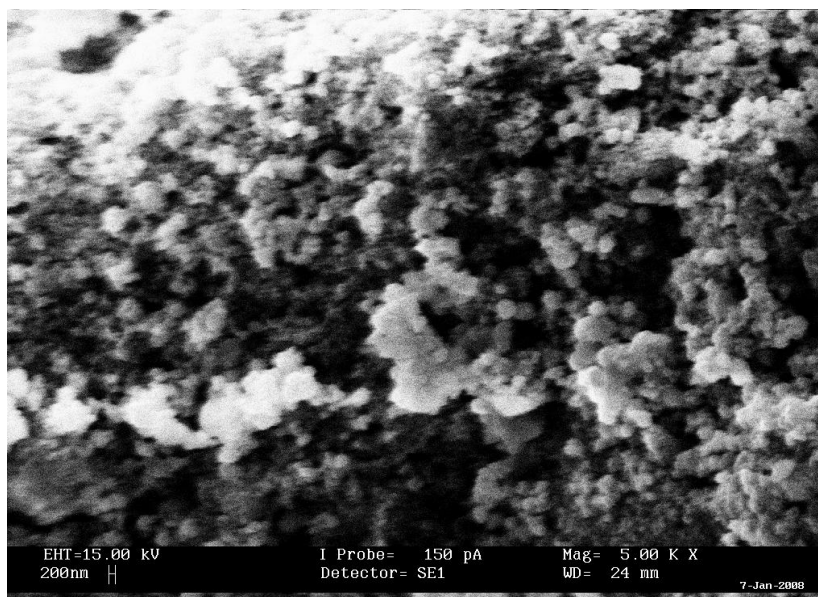


Sintering the precursor for 3 hours at 800 °C produced particles of size in the range of 41 nm to 160 nm as displayed in Fig. 5.6. It can be deduced that the particles have agglomerated giving rise to larger particles. However the particles are most likely to have sizes in the range between 71 nm and 80 nm which covers 21.4 % of the distribution. 14.3 % of the particles are with diameter ranging from 41 nm to 50 nm, 51 nm to 60 nm and 61 nm to 70 nm. 35.5 % of the particles are with diameters between 91 nm and 160 nm.



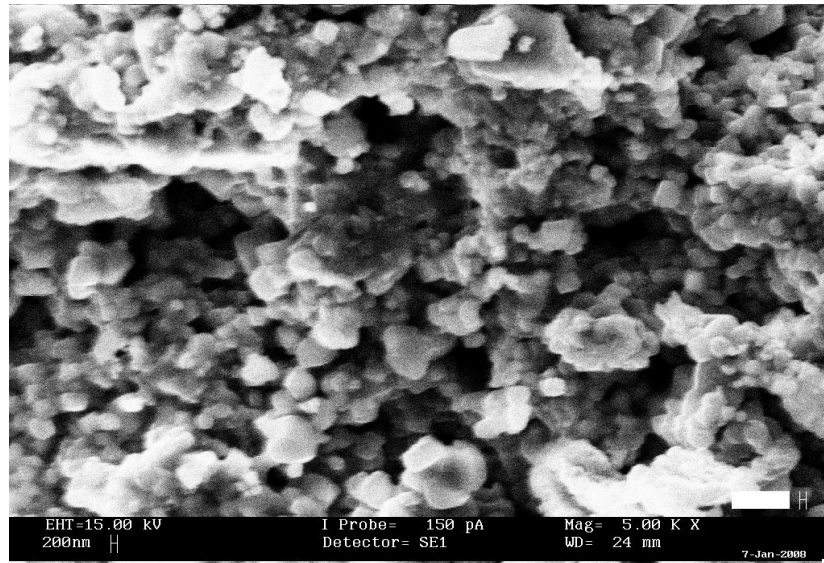
**5.4 Scanning electron microscopy (SEM)**  
Fig. 5.6 TEM images of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 800 °C

The morphologies of LiNiVO<sub>4</sub> prepared by chitosan modified solution evaporation method at sintering temperatures of 500 °C and 600 °C are depicted in Fig. 5.7 and Fig. 5.8. The formation of the samples can be observed at different sintering temperatures. At sintering temperatures of 500 °C and 600 °C which lasted for 3 hour, small grains of impure LiNiVO<sub>4</sub> are obtained.

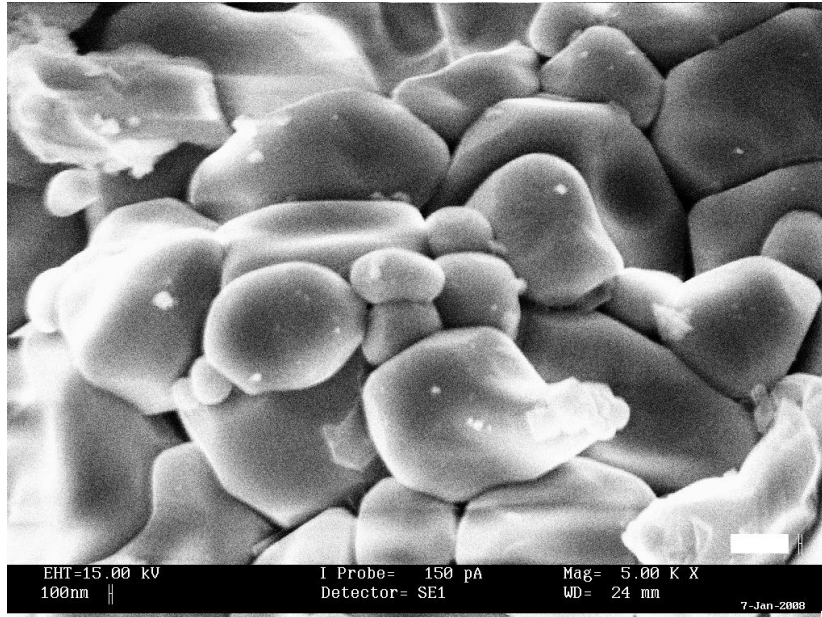


**Fig. 5.7: SEM images of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 500 °C**

Pure LiNiVO<sub>4</sub> are formed and the grains agglomerate to form larger particles of different sizes at temperature greater than 600 °C. The sizes of the particles are as shown in the histogram. The smooth surfaces of grains with clear edges formed at sintering temperature of 700 °C is presented in Fig 5.9.

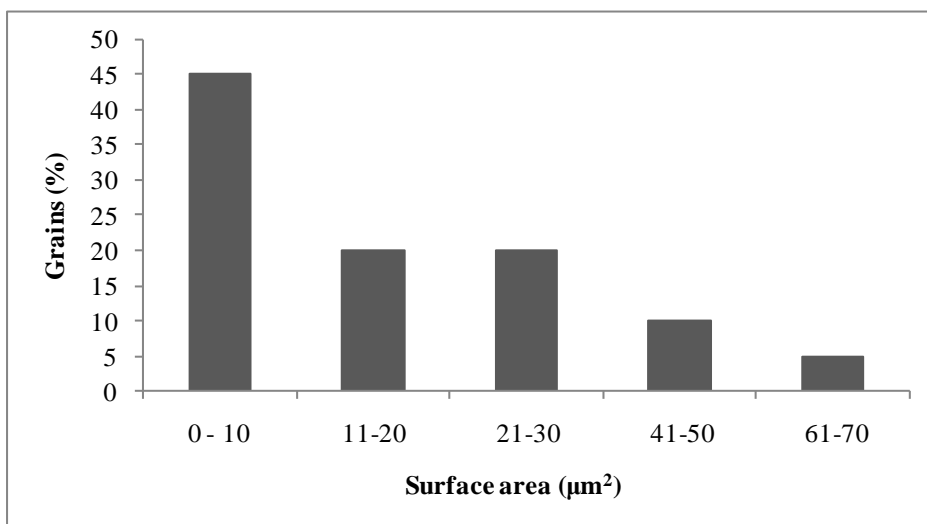


**Fig. 5.8:** SEM images of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 600 °C



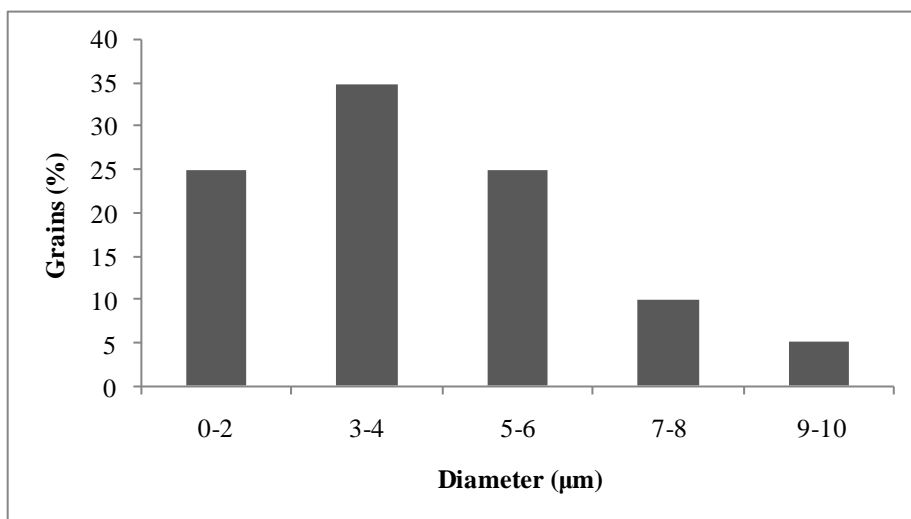
**Fig. 5.9:** SEM images of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 700 °C

Fig. 5.10 shows the distribution of surface area of LiNiVO<sub>4</sub> by chitosan modified sol gel method at sintering temperature of 700 °C. Surface area of 45 % of the grains is within 10 μm<sup>2</sup>. 20 % of the grains have surface area in the range 11 μm<sup>2</sup> to 20 μm<sup>2</sup> and 21 μm<sup>2</sup> to 30 μm<sup>2</sup> respectively. 10 % of grains cover the surface area in the range of 41 μm<sup>2</sup> to 50 μm<sup>2</sup> and 5 % of grains with surface area of 61 μm<sup>2</sup> to 70 μm<sup>2</sup>.



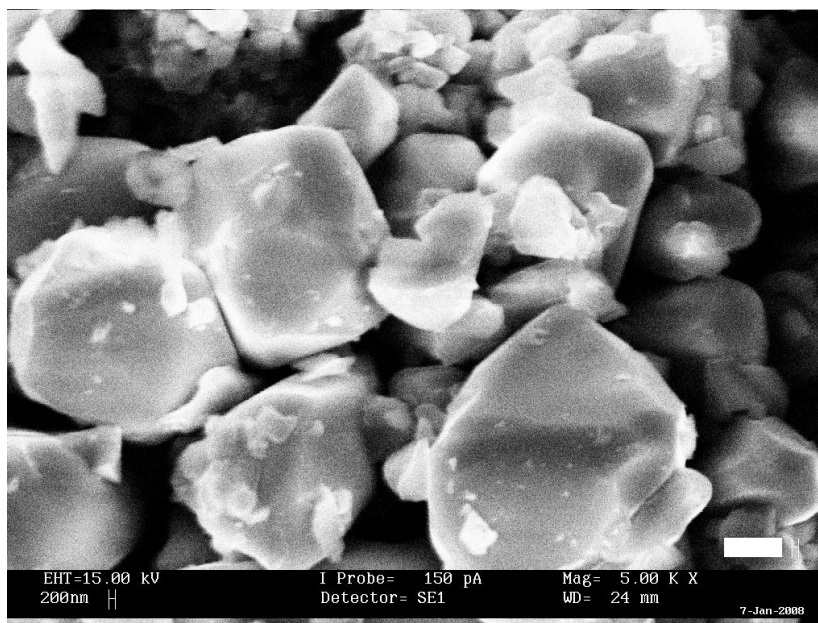
**Fig. 5.10: Distribution of surface area of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 700 °C**

Diameter distribution of the sample is depicted in Fig 5.11. About 35 % of the grains with diameter in the range of 3 μm to 4 μm. 25 % of the grains are within diameter 2 μm. 25 % of the grains have diameter in the range of 5 μm to 6 μm. 10 % of the grains have diameter ranging from 7 μm to 8 μm and 5 % with diameter from 9 μm to 10 μm.



**Fig. 5.11** Distribution of diameter of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 700 °C

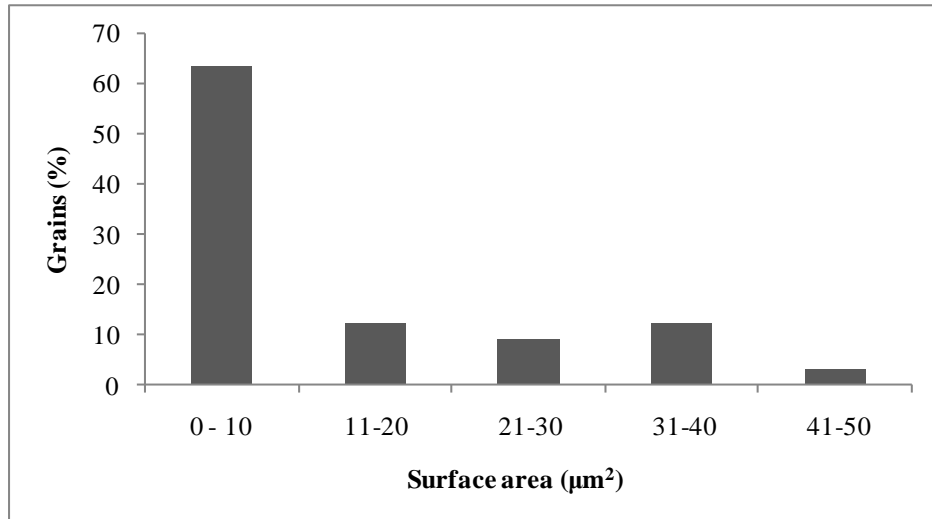
The SEM micrograph of the LiNiVO<sub>4</sub> product at 800 °C is shown in Fig 5.12.



**Fig. 5.12:** SEM images of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 800 °C

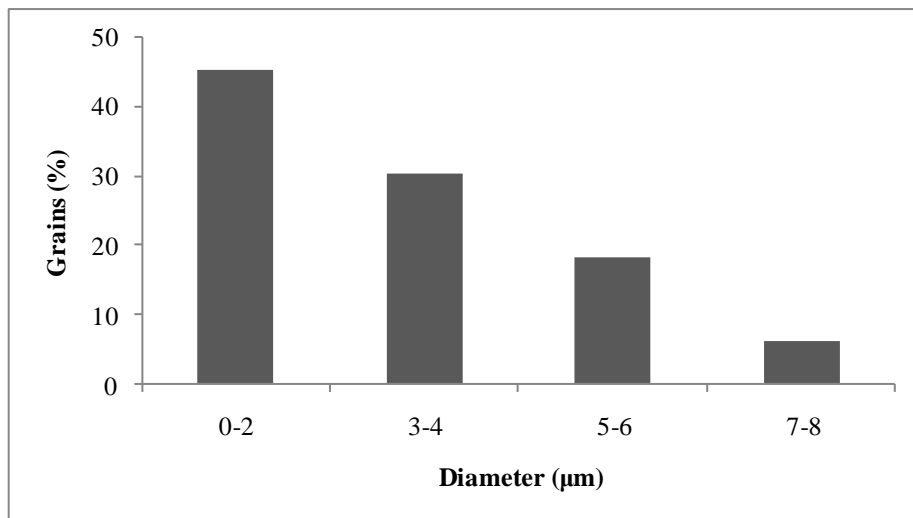
Fig. 5.13 states the distribution of surface area of LiNiVO<sub>4</sub> by chitosan modified sol gel method at sintering temperature of 800 °C. More grains are with surface area within 10 μm<sup>2</sup>. 12.1 % of the grains are grouped into the surface area ranging from 11 μm<sup>2</sup> to 20 μm<sup>2</sup>

and  $31 \mu\text{m}^2$  to  $40 \mu\text{m}^2$ . The surface area range of  $21 \mu\text{m}^2$  to  $30 \mu\text{m}^2$  contains 9.1 % of grains. Only 3.0 % of the grains have surface area in the range of  $41 \mu\text{m}^2$  to  $50 \mu\text{m}^2$ .



**Fig. 5.13: Distribution of surface area of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 800 °C**

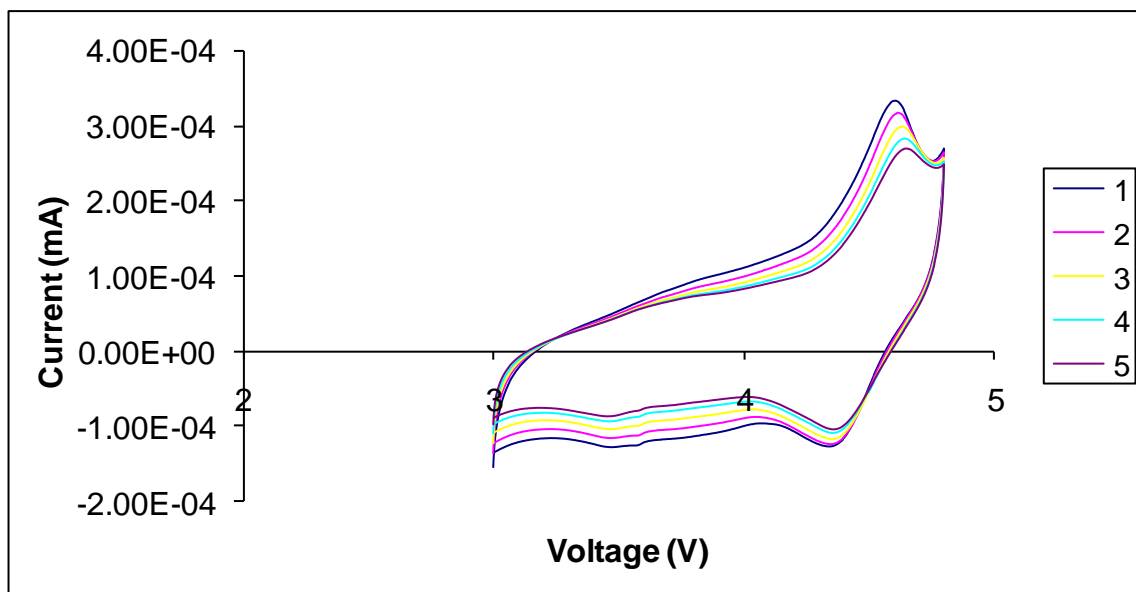
Fig. 5.14 clearly displays the distribution of diameter of the grains formed at sintering temperature of 800 °C. 45.4 % of the grains have diameter size within 2  $\mu\text{m}$ . The diameter between 3  $\mu\text{m}$  and 4  $\mu\text{m}$  is covered by 30.3 % of the grains. The diameter range of 5  $\mu\text{m}$  to 6  $\mu\text{m}$  consists of 18.2 % of grains. 6.1 % of grains are with diameter 7  $\mu\text{m}$  to 8  $\mu\text{m}$ .



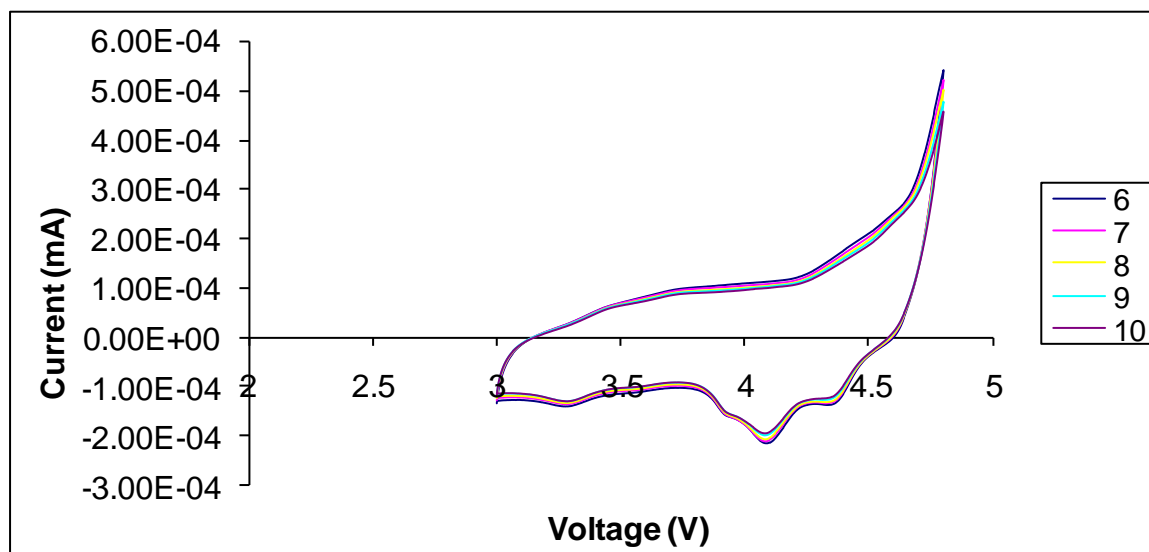
**Fig. 5.14: Distribution of diameter of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 800 °C**

### 5.5 Cyclic voltammetry

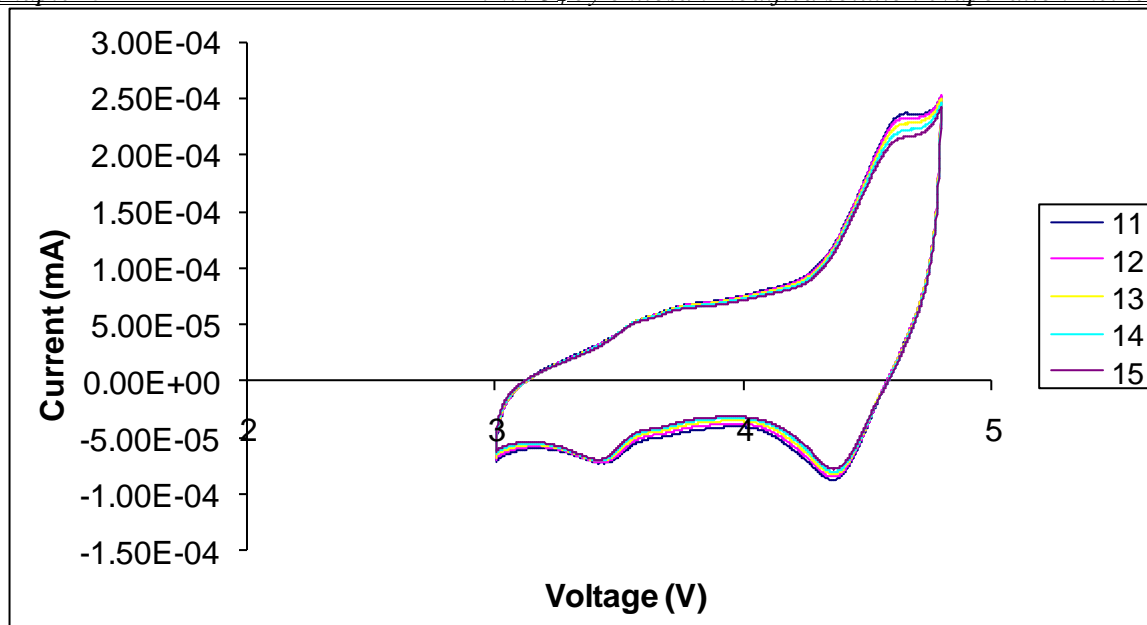
Cyclic voltammetry of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 700 °C is shown in Fig. 5.15. The voltammogram depicts stabilization of the material performance with increased cycling.



Cyclic voltammetric of LiNiVO<sub>4</sub> (1st-5th cycles)



Cyclic voltammetric of LiNiVO<sub>4</sub> (6th-10th cycles)



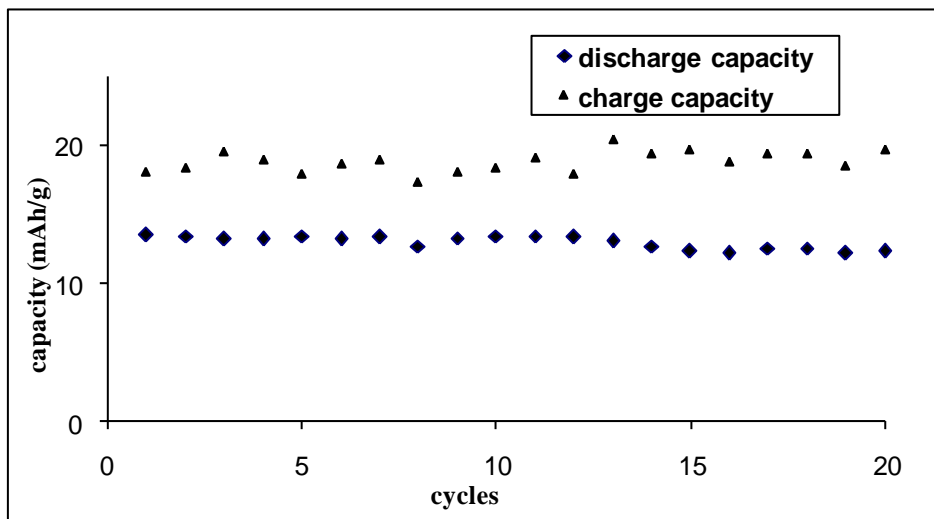
Cyclic voltammetric of LiNiVO<sub>4</sub> (11th-15th cycles)

Fig. 5.15: Cyclic voltammetry of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method at sintering temperature of 700 °C

## 5.6 Charge discharge characteristics

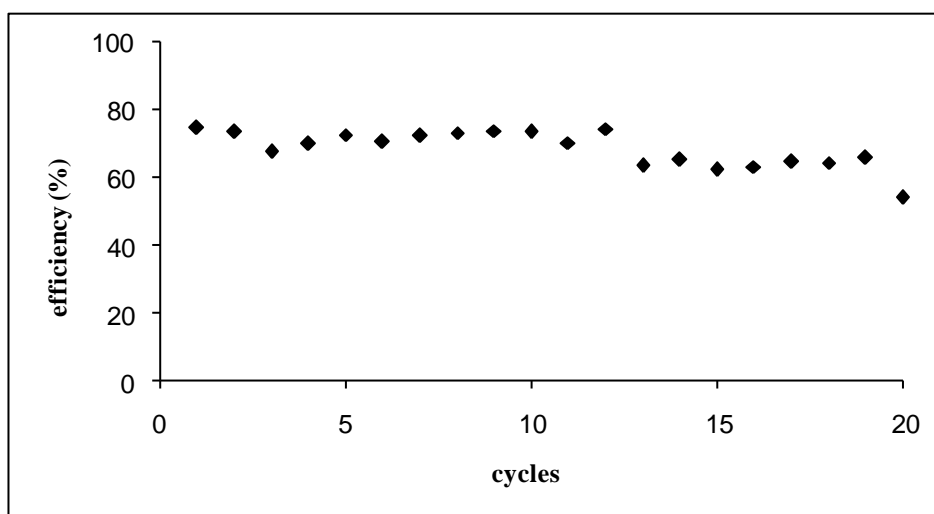
Charge-discharge performance of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method is presented in Fig. 5.16. First discharge capacity of the cell was recorded as 13.5 mAhg<sup>-1</sup> and it reached 12.3 mAhg<sup>-1</sup> at the end of 20<sup>th</sup> cycle. First charge capacity is about 17.9 mAhg<sup>-1</sup> which is lower compared to 19.5 mAhg<sup>-1</sup> at third cycle. However the charge capacity rises to 19.6 mAhg<sup>-1</sup> at 20<sup>th</sup> cycle.





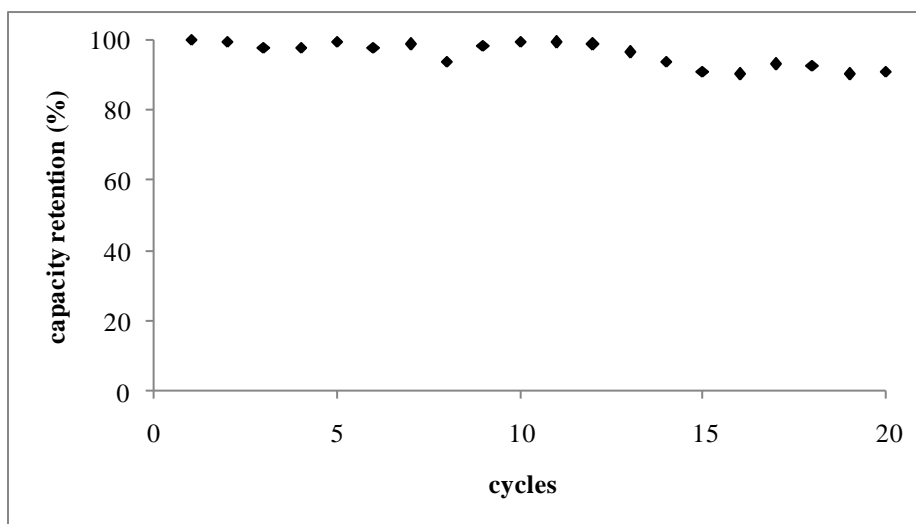
**Fig. 5.16: Charge-discharge studies of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method**

The efficiency of the cell is displayed by Fig. 5.17. 74.8 % efficiency was achieved during the first cycle. The efficiency is about 65.6 % until the 19<sup>th</sup> cycle. Only 62.4 % of efficiency remained at the 20<sup>th</sup> cycle. The efficiency is quite stable during continuous cycling performance.



**Fig. 5.17: Cycling efficiency of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method**

Fig. 5.18 explains the capacity retention of the cell with LiNiVO<sub>4</sub> by chitosan modified solution evaporation method as cathode. The capacity retains about ~ 90 % until 20<sup>th</sup> cycle which credits only 91.1 %. The loss of capacity compared with initial discharge capacity is ~ 8.9 %. This clearly explained that LiNiVO<sub>4</sub> by chitosan modified solution evaporation method improved the capacity retention compared to sol gel method as stated in previous chapter.



**Fig. 5.18: Capacity retention of LiNiVO<sub>4</sub> by chitosan modified solution evaporation method**

### Summary

LiNiVO<sub>4</sub> was successfully obtained by chitosan modified solution evaporation method. XRD results coincide well with JCPDS data 73-1636. LiNiVO<sub>4</sub> is completely formed at sintering temperature of 700 °C. Calculated crystallite size using Scherrer equation is in the range of 52.5 nm - 78.1 nm. LiNiVO<sub>4</sub> obtained by chitosan modified solution evaporation method improved the capacity retention.