CHAPTER 4

$LiNiVO_4$ BY SOLUTION EVAPORATION METHOD

4.1 Introduction

In this chapter, $LiNiVO_4$ is prepared by the solution evaporation method. The precursor for $LiNiVO_4$ was sintered at different temperatures and were followed by characterization with XRD, SEM, TEM, CV and charge-discharge cycling performance.

4.2 X-ray diffraction (XRD)

JCPDS data 73-1636 was referred to determine the XRD results. Fig. 4.1 shows X-ray diffraction patterns of $LiNiVO_4$ from acetates of lithium and nickel and ammonium metavanadate as starting materials. The product obtained was identified as face centered cubic $LiNiVO_4$ by JCPDS data 73-1636. NiO impurity was present after sintering 500 ºC and 600 ºC for 3 hours at $2\theta = 37.3°$ and 43.5° in the diffractogram. Impurities due to Li_3VO_4 which should exhibit peaks at $2\theta = 16.2°$, 21.5°, 22.8° and 24.3° which were found to be observed by Fey *et al*., (1999) and Reddy *et al*., (2007) were not observed in this work. The presence of (111) Bragg line which should be weaker than (220) line confirm that the product has an inverse spinel structure (Chitra *et al*., 2000).

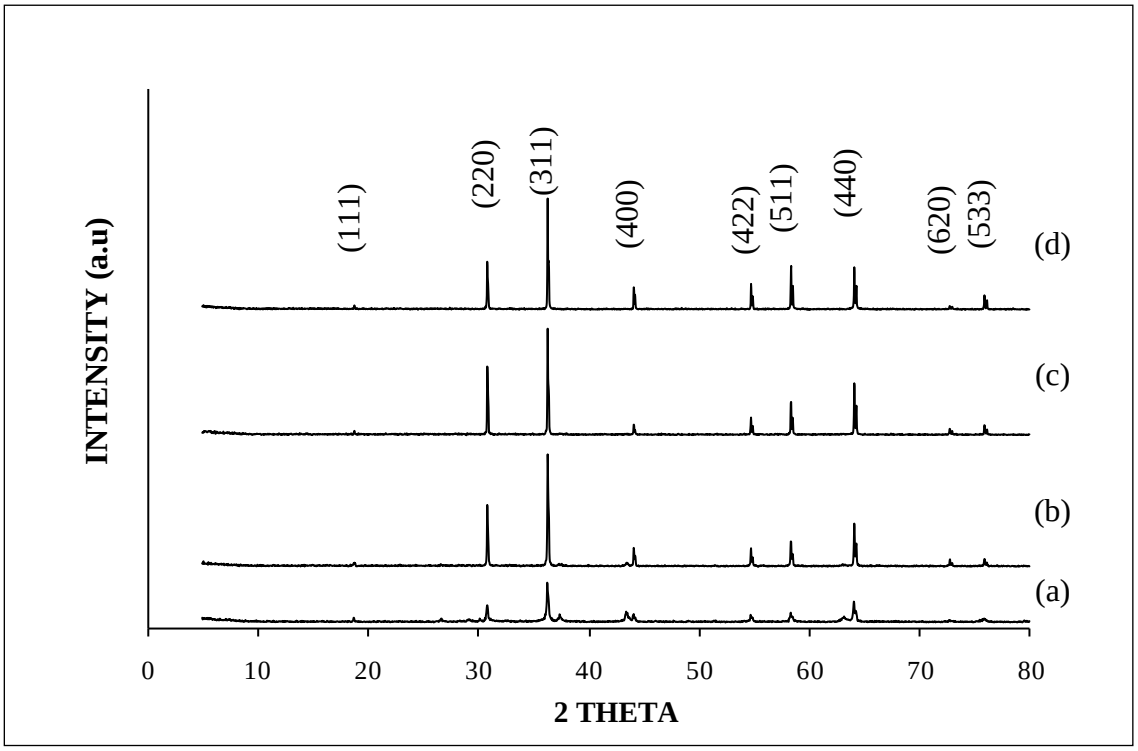


Fig. 4.1: XRD of $LiNiVO_4$ by sol gel method at sintering temperatures of (a) 500 °C (b) 600 °C (c) 700 °C (d) 800 °C

The lattice parameters of the samples synthesized by solution evaporation method are tabulated in Table 4.1 above. The average values at sintering temperatures of 500°C and 600°C are 8.205 and 8.209 respectively. These contain impurities as recorced by XRD. Average lattice parameter increases from 8.208 to 8.209 when the sintering temperature is increased from 700°C to 800°C.

Table 4.1: Lattice parameter of $LiNiVO_4$ by sol gel 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	30.842	2.89684	8	2.8284	8.1935
311	36.304	2.47255	11	3.3166	8.2005
400	44.113	2.05128	16	4.0000	8.2051
422	54.738	1.67560	24	4.8990	8.2087
333	58.357	1.58000	27	5.1962	8.2099
440	64.090	1.45179	32	5.6569	8.2126

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	30.864	2.89486	8	2.8284	8.1879
311	36.326	2.47109	11	3.3166	8.1957
400	44.129	2.05059	16	4.0000	8.2024
422	54.756	1.67507	24	4.8990	8.2061
333	58.378	1.57948	27	5.1962	8.2072
440	64.123	1.45112	32	5.6569	8.2088

Calculated average lattice parameter is 8.209

700°C

hkl	2θ	d	$h^2 + k^2 + l^2$	$(h^2+k^2+l^2)^{1/2}$	a
220	30.867	2.89453	8	2.8284	8.1870
311	36.323	2.47132	11	3.3166	8.1964
400	44.117	2.05042	16	4.0000	8.2017
422	54.757	1.67505	24	4.8990	8.2060
333	58.380	1.57943	27	5.1962	8.2070
440	64.127	1.45104	32	5.6569	8.2083

Calculated average lattice parameter is 8.208

800°C

hkl	2θ	d	$h^2 + k^2 + l^2$	$(h^2+k^2+l^2)^{1/2}$	a
220	30.848	2.89632	8	2.8284	8.1920
311	36.322	2.4714	11	3.3166	8.1967
400	44.133	2.05041	16	4.0000	8.2016
422	54.765	1.67483	24	4.8990	8.2050
333	58.393	1.57912	27	5.1962	8.2053
440	64.124	1.4511	32	5.6569	8.2087

Calculated average lattice parameter is 8.209

Crystallite size of the sample at different sintering temperatures was calculated using Scherrer equation. Fig. 4.2 shows crystallite size of $LiNiVO_4$ synthesized by sol gel method at sintering temperatures of 500 °C to 800 °C. The crystallite size of $LiNiVO_4$ at sintering

temperature at 500 °C is 48.6 nm and become 68.5 nm, 97.2 nm and 132.6 nm at sintering temperatures of 600 °C to 800 °C. Eventhough the crystallites are smaller at sintering temperatures of 500 °C and 600 °C, they contain NiO impurity.

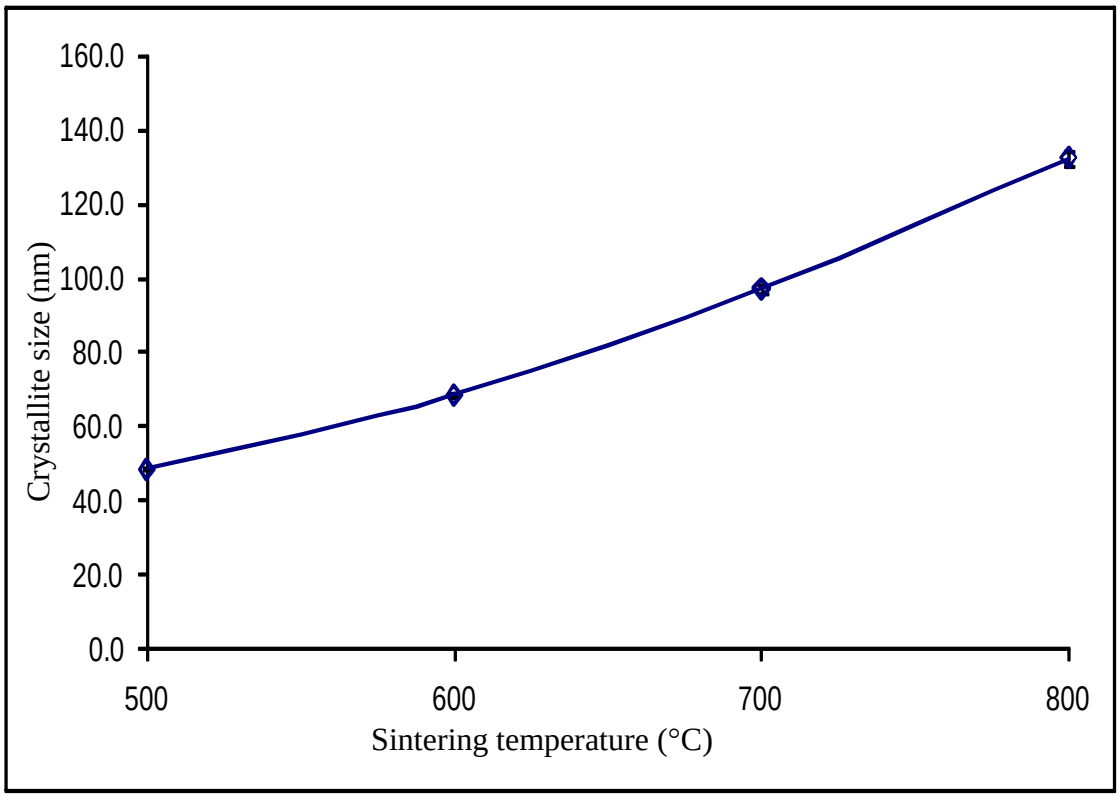


Fig. 4.2: Crystallite size of $LiNiVO_4$ by sol gel method different sintering temperatures

4.3 Transmission Electron Microscopy (TEM)

TEM results in Fig. 4.3 shows the diameter of the particles for the samples sintered at 500 °C. The diameter of product obtained at sintering temperature of 500 °C is in the range of 11 nm to 80 nm. A large number of particles are in the range from 21 nm to 30 nm. This is

folowed by particles with size between 31 to 40 nm. These results are in agreement with results from XRD.

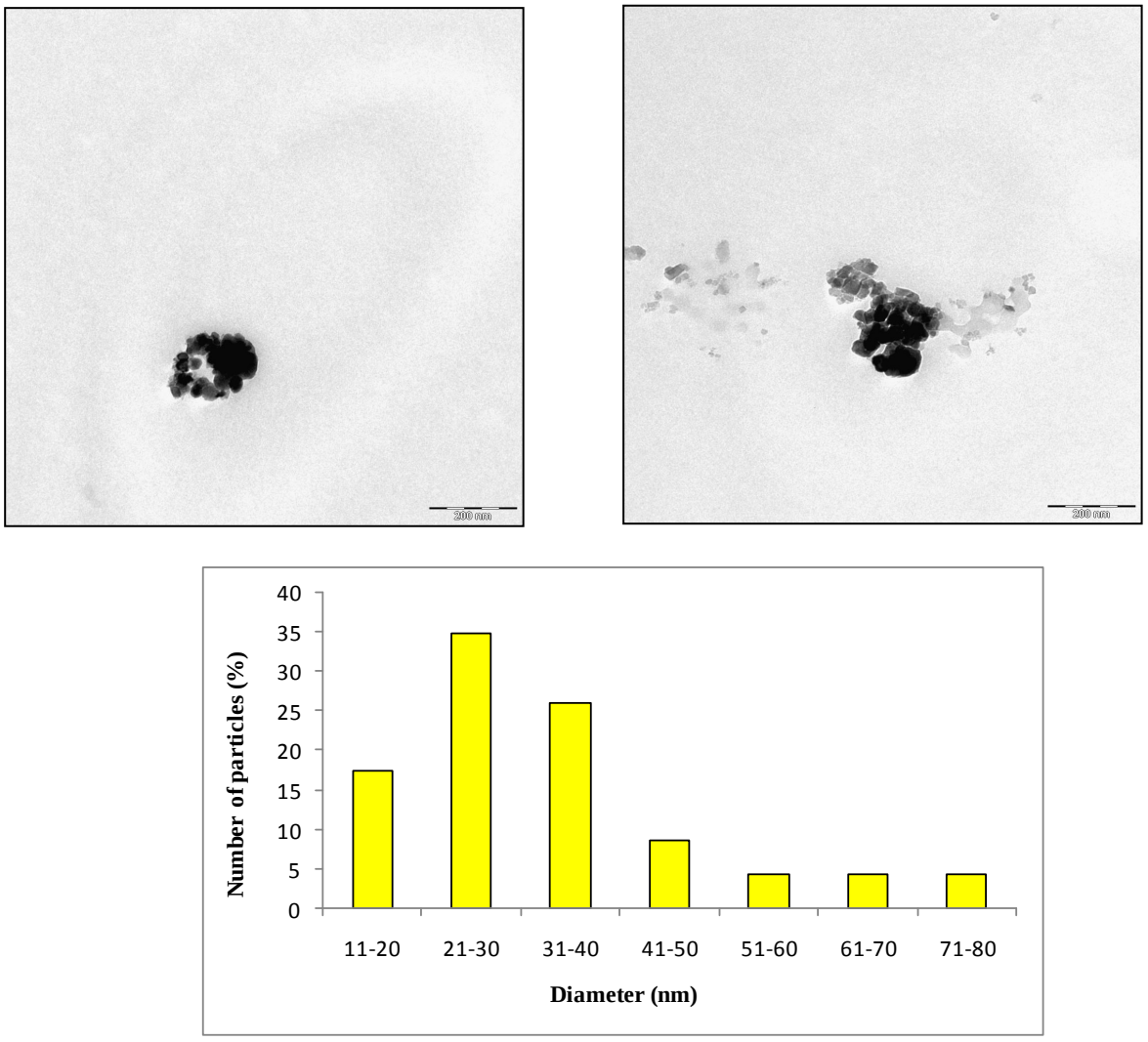


Fig. 4.3: TEM images of $LiNiVO_4$ by solution evaporation method at sintering temperature of 500 °C

The range is almost similar for particles obtained when the precursor was sintered 600 °C which is 21 nm to 80 nm. Fig 4.4 depicts that the diameter of particles are mostly in the range from 31 nm to 40 nm and 51 nm to 60 nm. Less than 10% of particles have diameter between 61 nm and 80 nm.

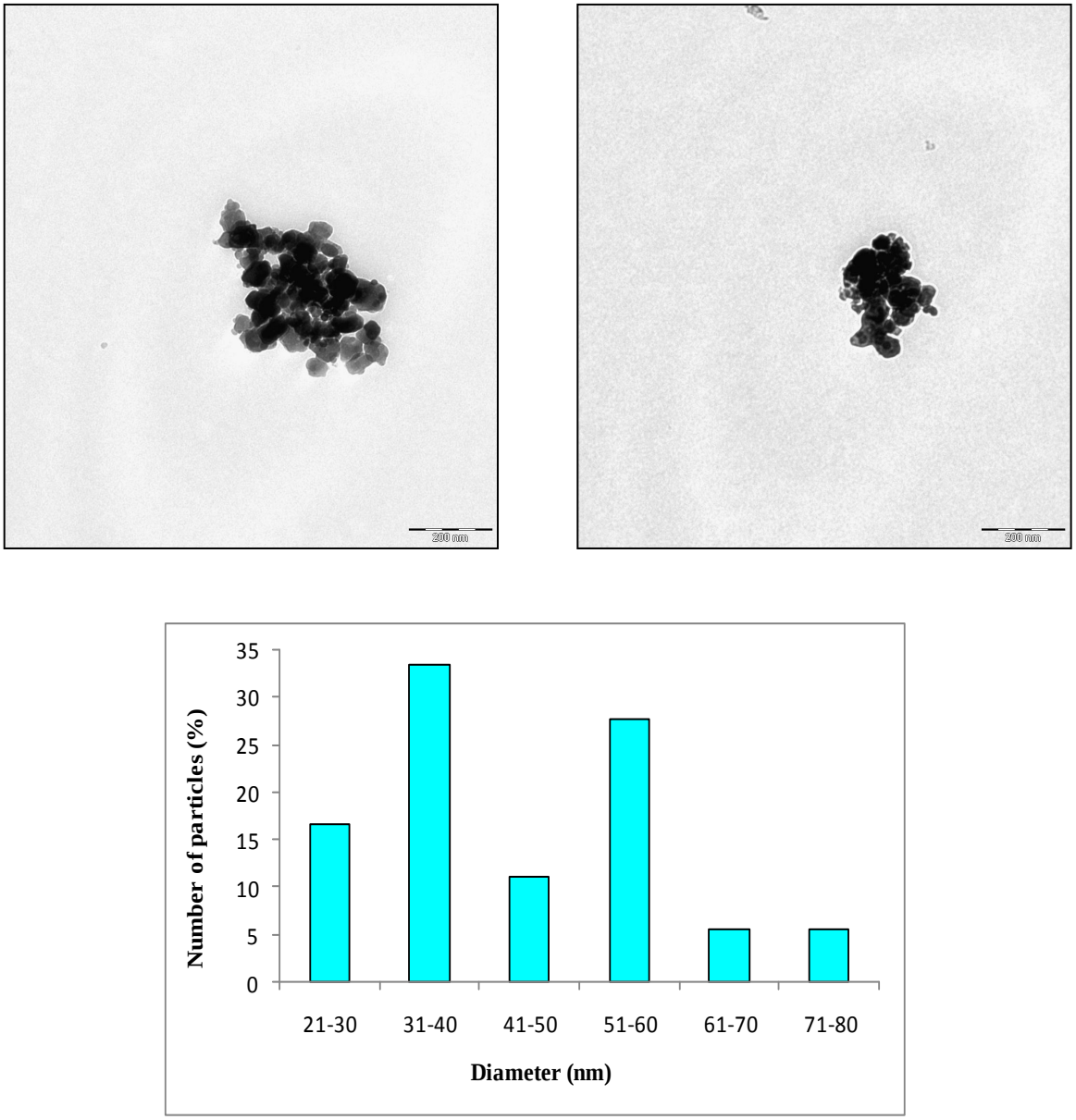


Fig. 4.4: TEM images of $LiNiVO_4$ by solution evaporation method at sintering temperature of 600 °C

Particles of sample sintered at 700 °C show sizes in the range from 21 nm to 90 nm as shown in Fig 4.5. Fewer particles have sizes between 61 nm and 90 nm. The distribution clearly exhibits that more particles are in the range between 31 nm and 60 nm.

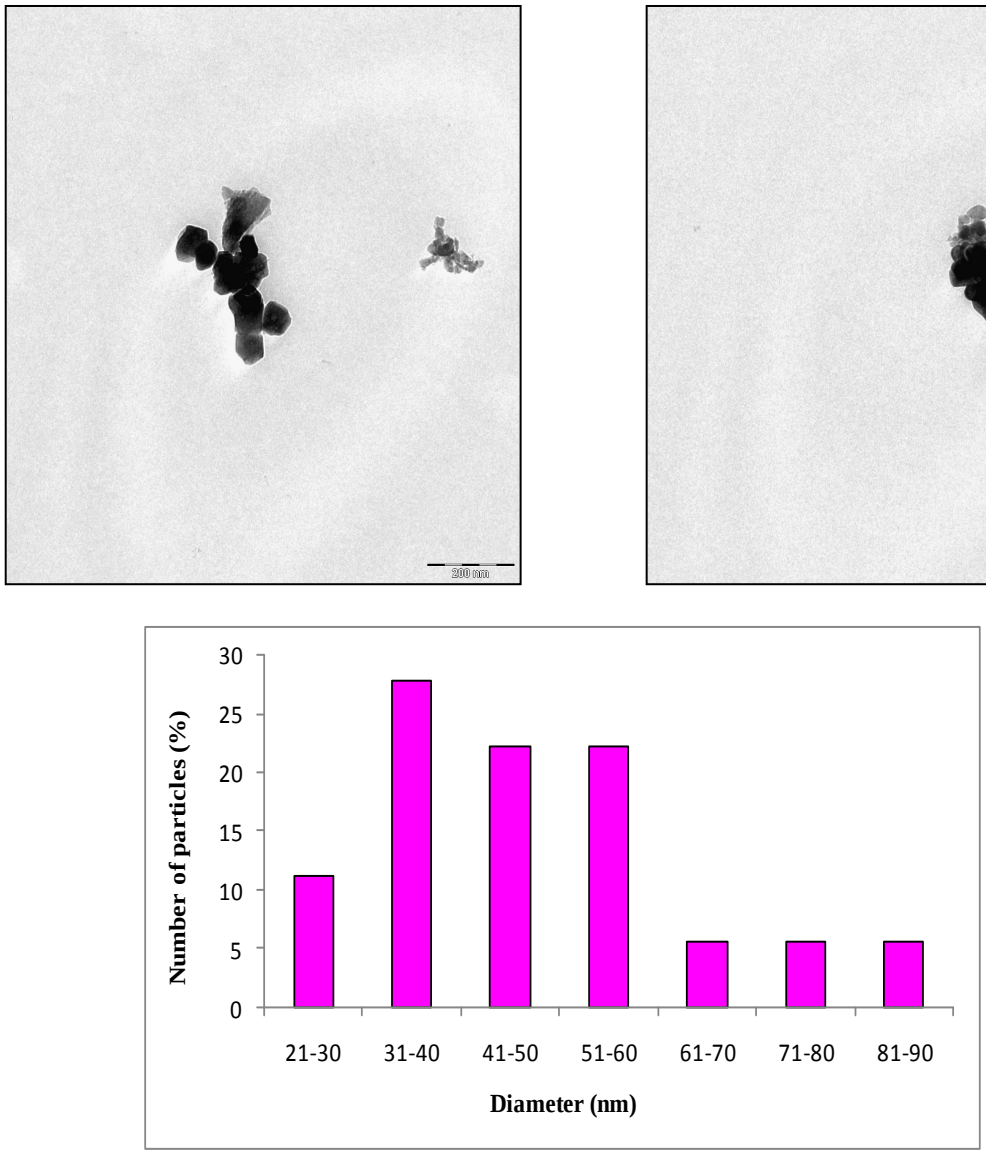


Fig. 4.5: TEM images of $LiNiVO_4$ by solution evaporation method at sintering temperature of 700 °C

Fig 4.6 shows that the particle sizes increase at sintering temperature of 800 °C. More amples are in the range from 51 nm to 60 nm and 81 nm to 90 nm. 33.3% of the particles with diameter 51 nm to 60 nm and 22.2 % in the diameter of 81 nm to 90 nm. There are some particles with size of greater than 100 nm.

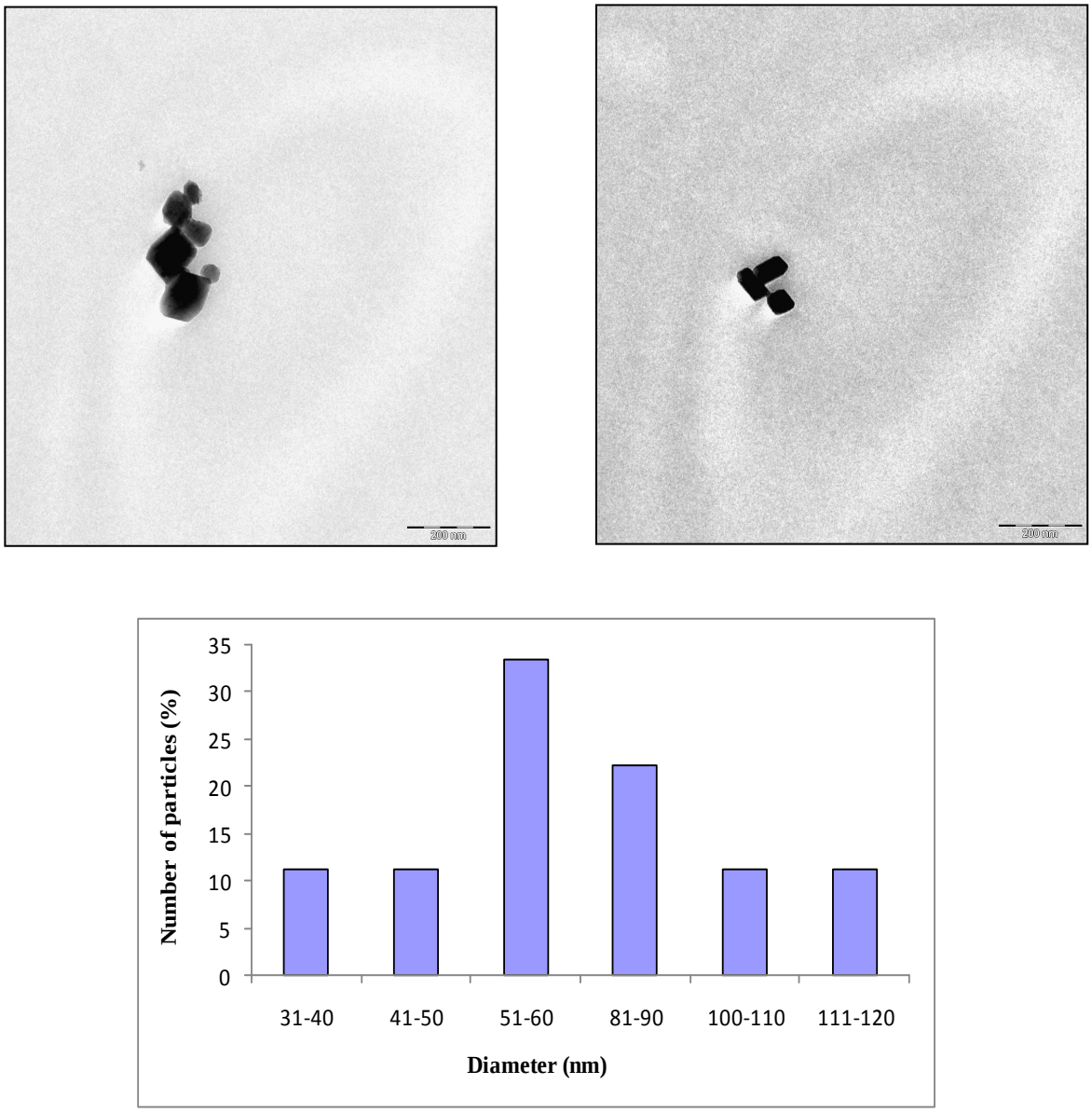


Fig. 4.6: TEM images of $LiNiVO_4$ by solution evaporation method at sintering temperature of 800 °C

4.4 Scanning Electron Microscopy (SEM)

SEM micrographs of $LiNiVO_4$ by sol gel method at sintering temperatures from 500 °C to 800 °C can be observed in Fig 4.7. The particles are not completely formed at sintering temperatures of 500 °C and 600 °C as shown in Fig 4.7 and 4.8.

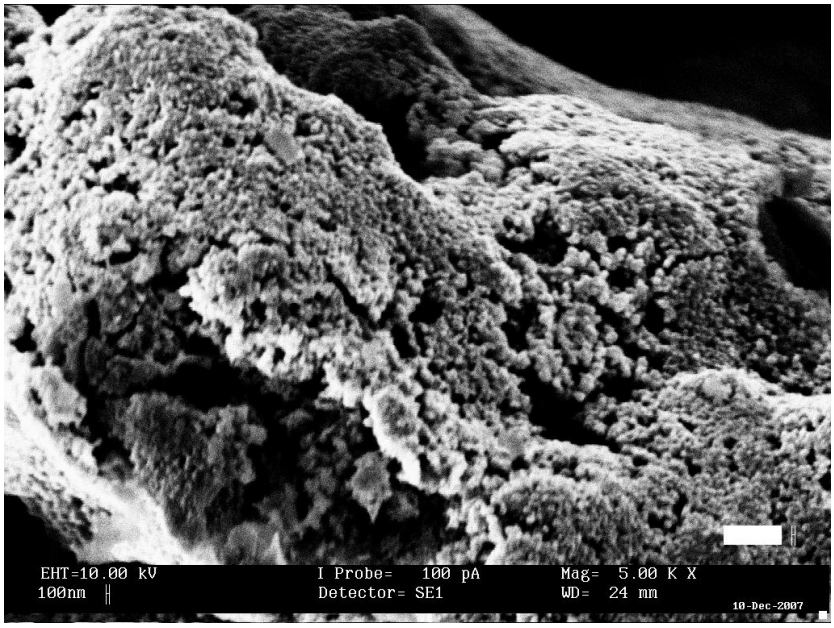


Fig. 4.7: SEM image of $LiNiVO_4$ by solution evaporation method at sintering temperature of 500 °C

The particles are completely formed with clear edges at sintering temperature of 700 °C. The grains are however not uniform in size as depicted in Fig 4.9.

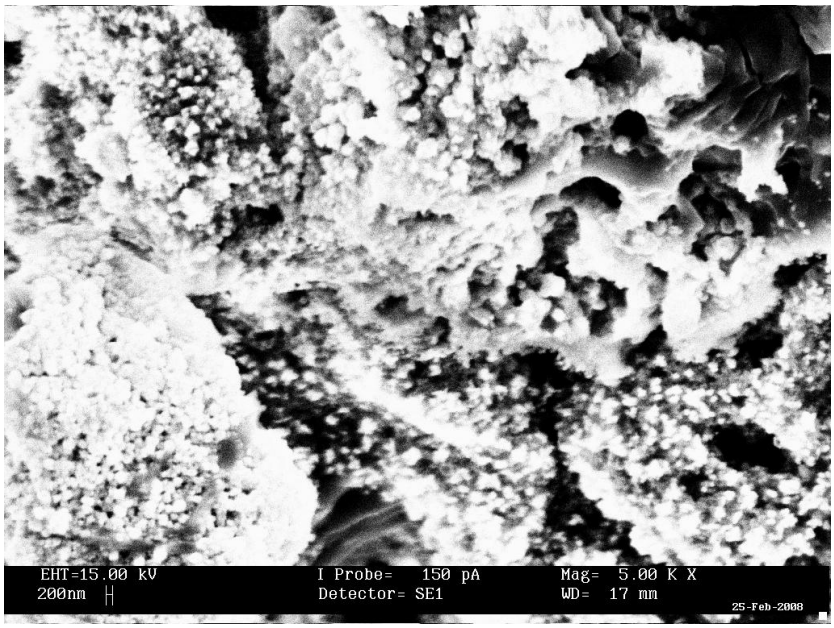


Fig. 4.8: SEM image of $LiNiVO_4$ by solution evaporation method at sintering temperature of 600 °C

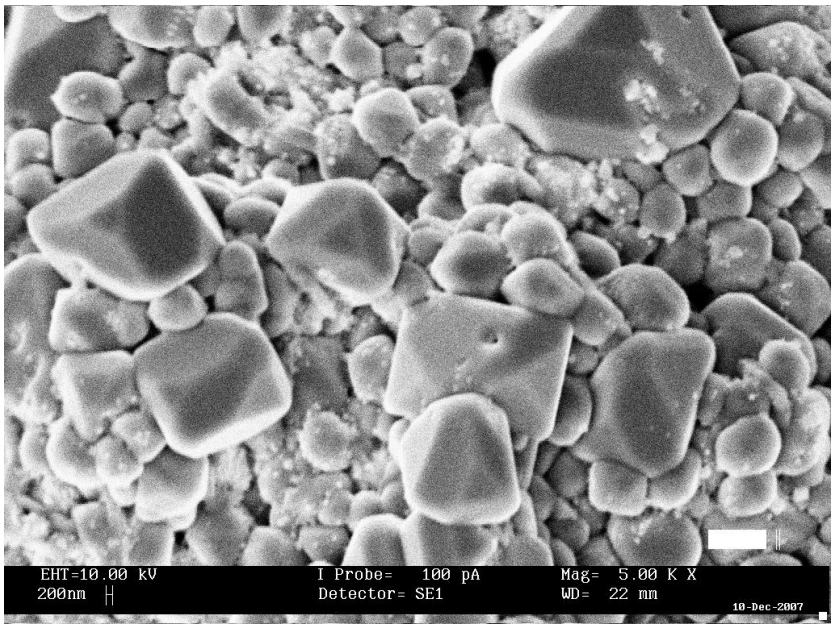


Fig. 4.9: SEM image of $LiNiVO_4$ by solution evaporation method at sintering temperature of 700 °C

Surface areas of the grains are most likely in the range of 0 μm – 10 μm^2. About 90 % of the particles are within the stated range. Only ~10 % of particles with surface area 11μm^2 – 20 μm^2 as shown in Fig 4.10.

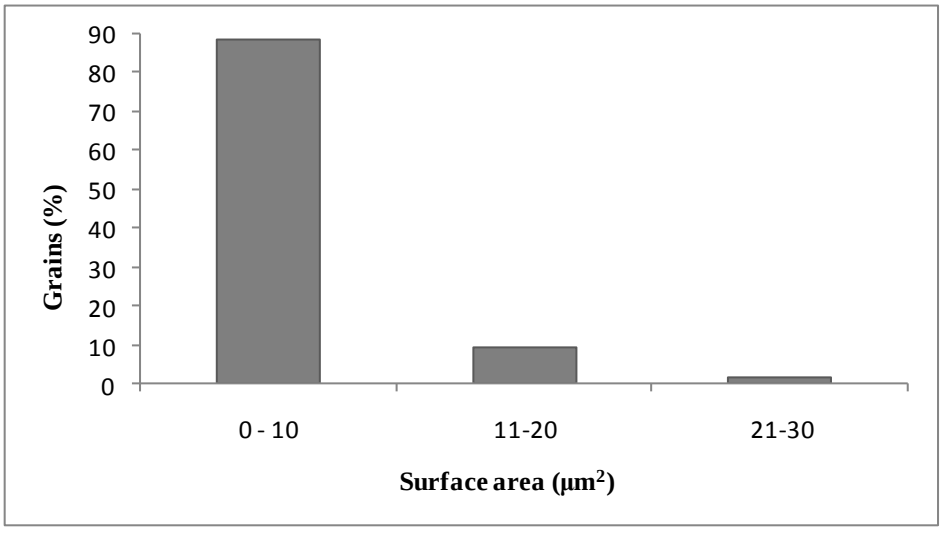


Fig. 4.10: Distribution of surface area of $LiNiVO_4$ by solution evaporation method at sintering temperature of 700 °C

Diameter of the grains concentrate within 2 μm as depicted in Fig 4.11. Around 7.5 % of the grains have diameter 3 μm – 4 μm. The grains with diameter between 5 μm and 6 μm and 7 μm and 8 μm only credits about 2 % respectively.

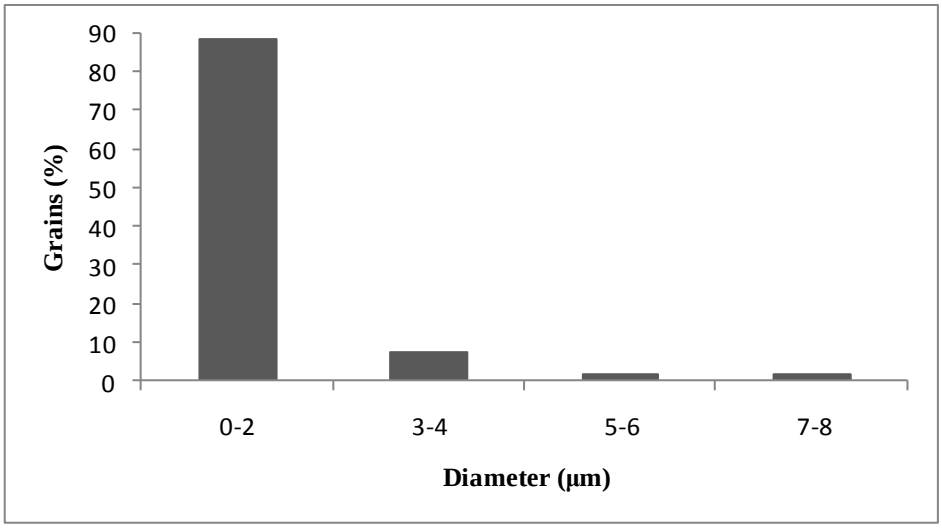


Fig. 4.11: Distribution of diameter of $LiNiVO_4$ by solution evaporation method at sintering temperature of 700 °C

Sintering temperature of 800 °C depicts similar type of image as 700 °C (Fig 4.12). The size of the grains is not uniform which can be explained by the distributions of surface area and diameter.

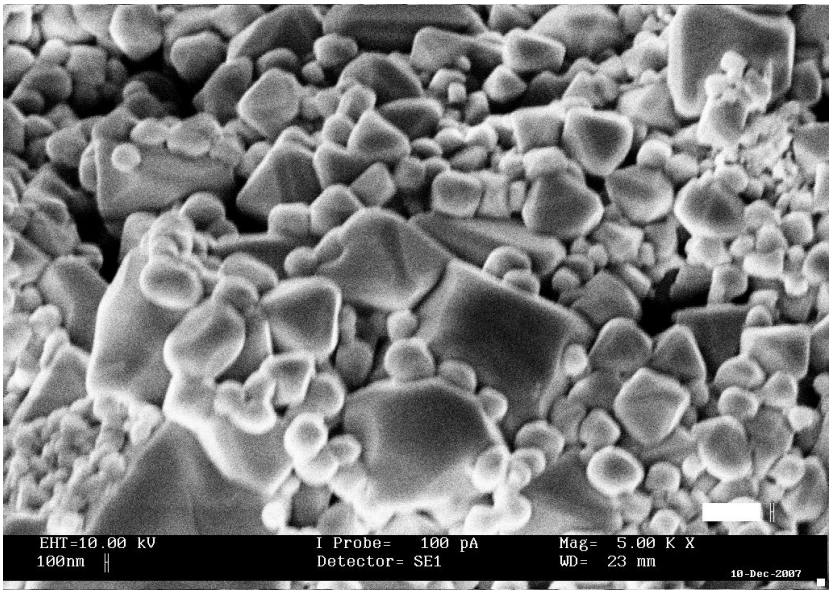


Fig. 4.12: SEM image of $LiNiVO_4$ by solution evaporation method at sintering temperature of 800 °C

The surface areas of 98 % of the grains are within 10 μm^2 as presented by Fig. 4.13. About ~1 % of the grains have surface area between 11 μm^2 and 20 μm^2 and between 21 μm^2 and 30 μm^2 respectively.

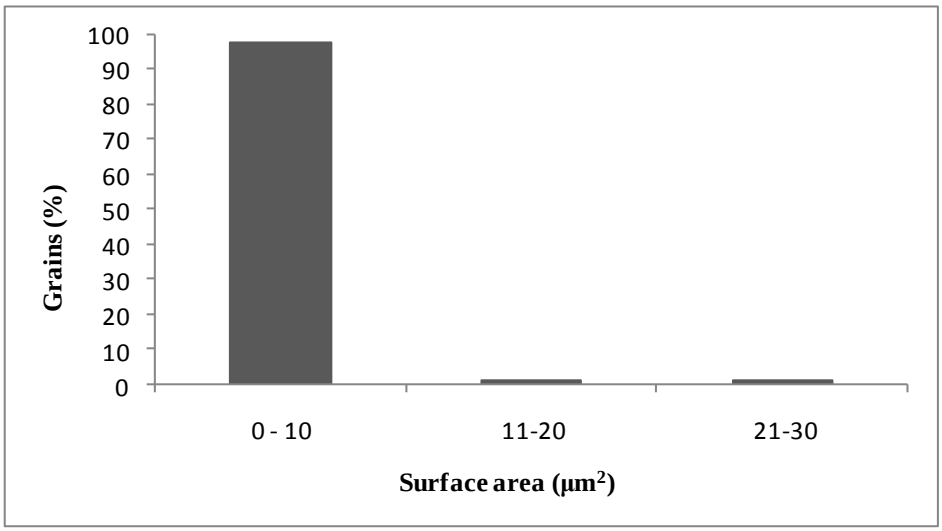


Fig. 4.13: Distribution of surface area of $LiNiVO_4$ by solution evaporation method at sintering temperature of 800 °C

Fig. 4.14 shows distribution of diameter of $LiNiVO_4$ by sol gel method at sintering temperature of 800 °C. 98 % of the grains are within diameter of 2 μm. Another 2 % of the grains cover the diameter of 3 μm to 4 μm.

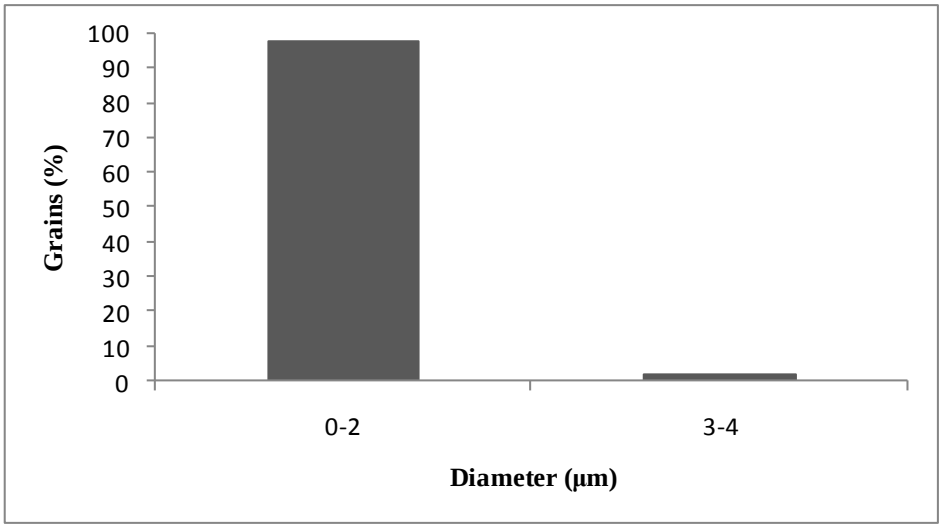
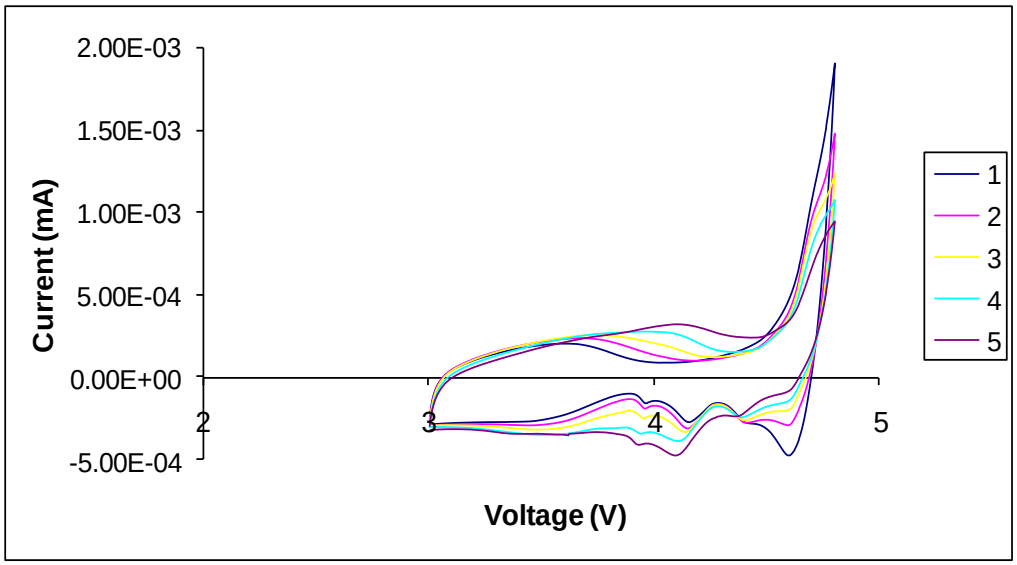


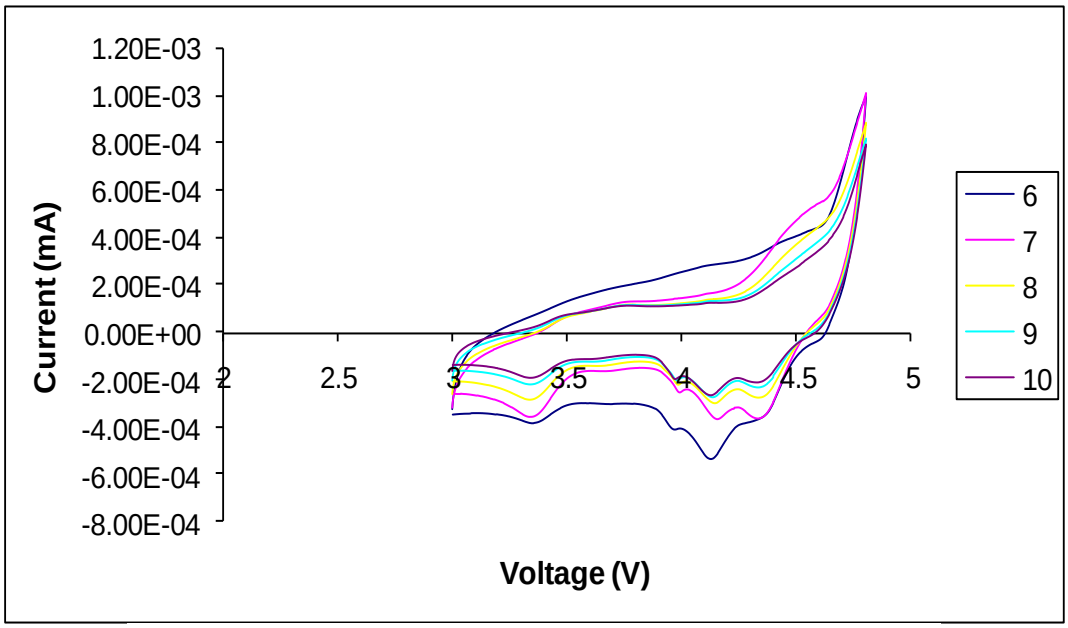
Fig. 4.14: Distribution of diameter of $LiNiVO_4$ by solution evaporation method at sintering temperature of 800 °C

4.5 Cyclic Voltammetry

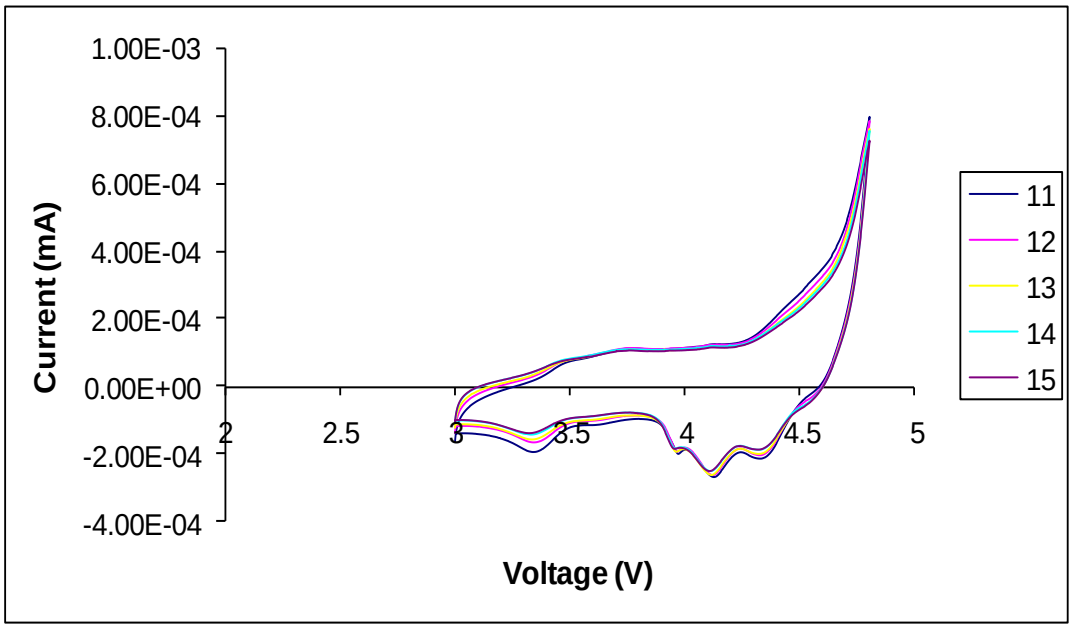
Cyclic voltammetry of $LiNiVO_4$ by sol gel method . The cycles showed instability until the 11^{th} cycle. There are peaks at 4.15 V, 4.36 V and 3.37 V. Scan rate is 0.1 mV s^{-1}.



Cyclic voltammetric of $LiNiVO_4$ (1st-5th cycles)



Cyclic voltammetric of $LiNiVO_4$ (6th-10th cycles)



Cyclic voltammetric of $LiNiVO_4$ (11th-15th cycles)

Fig. 4.15: Cyclic voltammetry of $LiNiVO_4$ by solution evaporation method at sintering temperature of 700 °C

4.6 Charge–Discharge Characteristics

Fig. 4.16 shows charge-discharge studies of $LiNiVO_4$ by solution evaporation method. The plot displays the initial discharge capacity of 10.3 $mAhg^{-1}$ and initial charge capacity of 13.1 $mAhg^{-1}$. However the discharge capacity decreases to 8.1 $mAhg^{-1}$ and charge capacity decreases to 11.3 $mAhg^{-1}$ at the end of 20^{th} cycle.

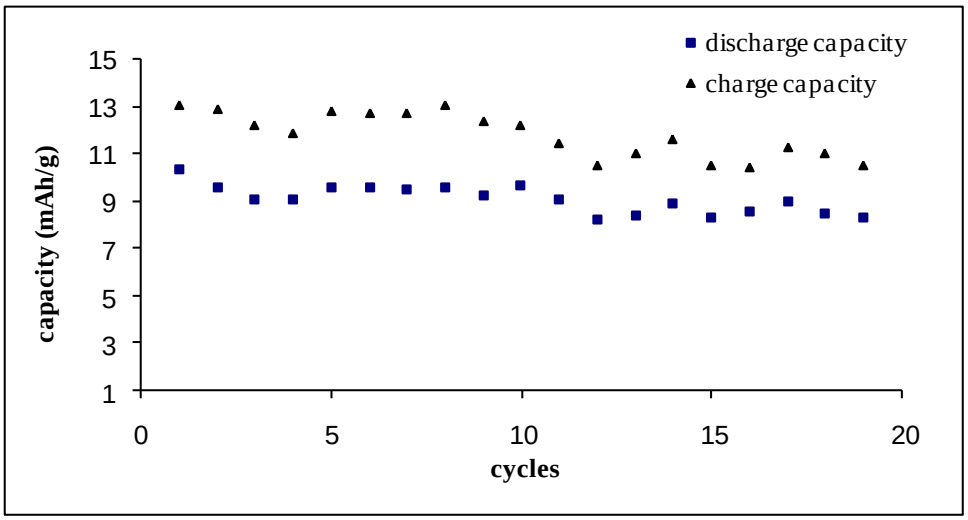


Fig. 4.16: Charge-discharge studies of $LiNiVO_4$ by solution evaporation method

Cycling efficiency from the charge discharge perfomance is plotted against number of cycles as in Fig. 4.17. The cell only exhibits 78.9 % efficiency in first cycle. The efficiency of the cell becomes 73.9 % at second cycle and shows the efficiency of 71.2 % at the end of 20^{th} cycle

Capacity retention of $LiNiVO_4$ by solution evaporation method is represented by Fig. 4.18. The capacity retention is based on initial discharge capacity. The capacity retention reached

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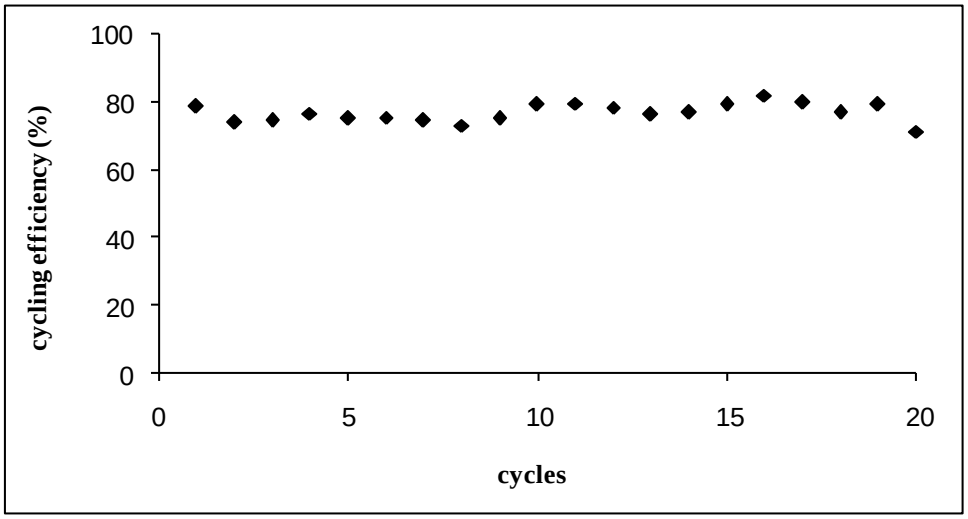

Fig. 4.17: Cycling efficiency of $LiNiVO_4$ by solution evaporation method

92.7 % at 2nd cycle. The capacity retention is also not stable in the following cycles as the discharge capacity is unstable. The cell only retained 78.4 % of its initial discharge capacity at 20th cycle. This record the capacity loss of 21.6 % after the sample is cycled 20 times.

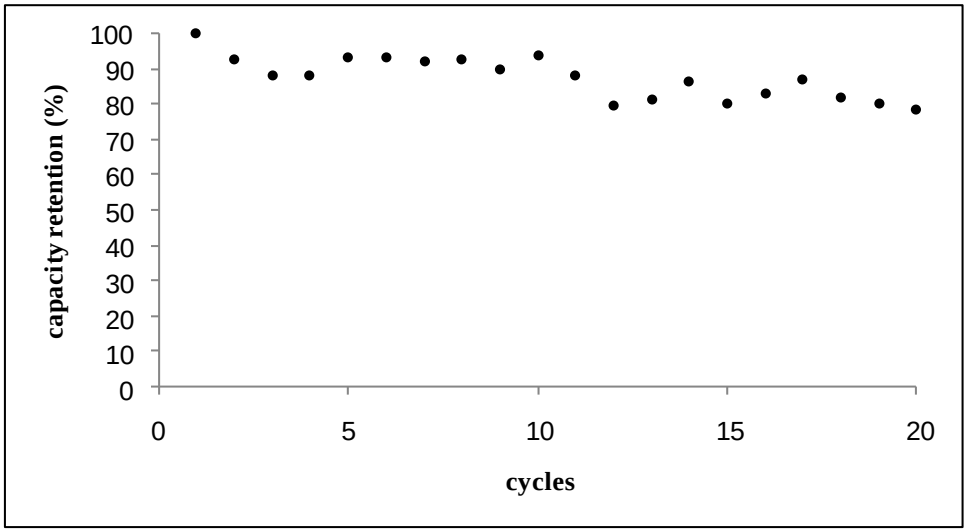

Fig. 4.18: Capacity retention of $LiNiVO_4$ by solution evaporation method

Summary

Solution evaporation method produces $LiNiVO_4$ without any impurities beginning from sintering temperature of 700 °C. SEM micrographs agree well with this statement which shows complete formation of grains at sintering temperature of 700 °C. Crystallite sizes of the samples obtained from this method are in the range of 48.6 nm to 132.6 nm at 500 °C to 800 °C. The cell consisting of $LiNiVO_4$ prepared by solution evaporation method at sintering temperature of 700 °C delivers initial discharge capacity of 10.3 $mAhg^{-1}$.