CHAPTER 6

EFFECT OF ZnO COATING ON $LiNiVO_4$ BY CHITOSAN MODIFIED SOLUTION EVAPORATION METHOD

6.1 Introduction

$LiNiVO_4$ from polymer modified solution evaporation method sintered at 700 °C was chosen as a candidate to prepare coated cathode material. The nanosized crystallite and impurity free characteristics are two reasons for the selection of the sample. Zinc acetate was used as starting material to apply the ZnO coating on $LiNiVO_4$.

6.2 X-ray diffraction (XRD)

Fig. 6.1 presents XRD of bare and ZnO coated $LiNiVO_4$ sintered at 700 °C. $LiNiVO_4$ used was obtained by the chitosan modified solution evaporation method. Different amounts of ZnO was coated on $LiNiVO_4$. All the coated samples were sintered at 700 °C.

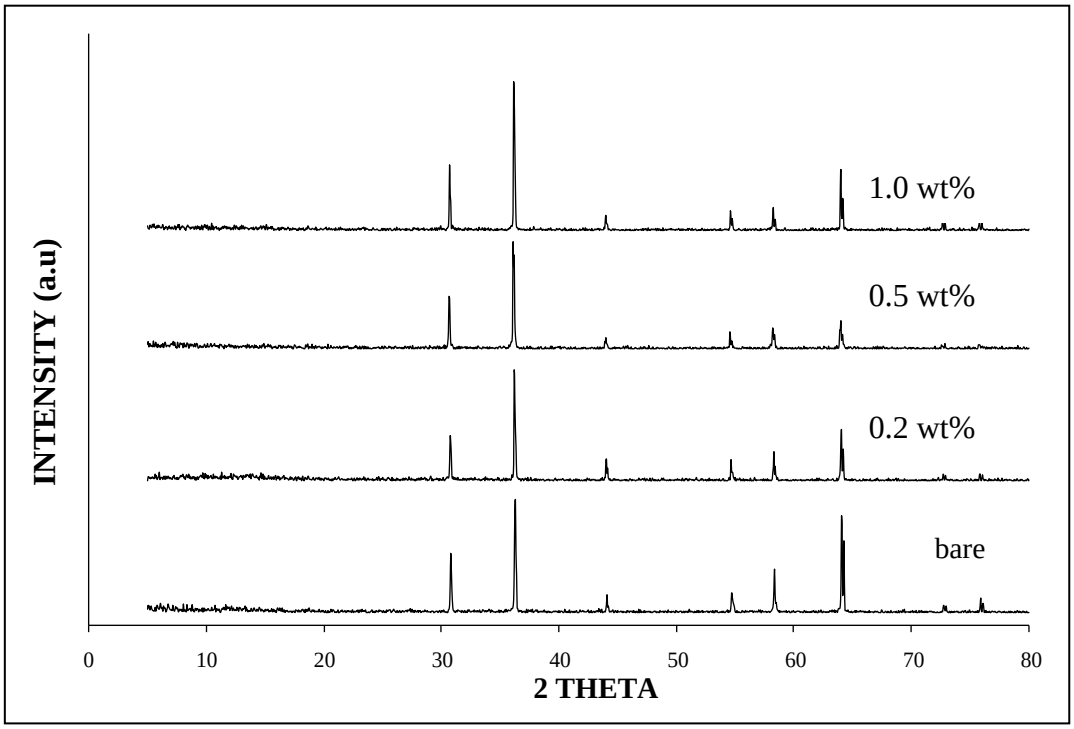


Fig.6.1: XRD of ZnO coated $LiNiVO_4$ at sintering temperature of 700 °C

From the diffractograms, the samples can be indexed as inverse spinel structure of $LiNiVO_4$ with $Fd\bar{3}m$ space group. This confirms that the coating did not change the

structure of the samples and was only coated on the surface of the $LiNiVO_4$. There is no peak corresponding to ZnO indicating that the surface of $LiNiVO_4$ is coated with a thin layer of ZnO. Calculated average lattice parameters of coated samples are given in the Table 6.1 below.

Table 6.1: lattice parameter of ZnO coated $LiNiVO_4$

0.2 wt. %

hkl	**2θ**	**d**	$\mathbf{h^2 + k^2 + l^2}$	$\mathbf{(h^2+k^2+l^2)^{1/2}}$	**a**
220	30.778	2.90274	8	2.8284	8.2102
311	36.214	2.47854	11	3.3166	8.2204
400	44.029	2.05500	16	4.0000	8.2200
422	54.652	1.67801	24	4.8990	8.2205
333	58.295	1.58153	27	5.1962	8.2179
440	64.024	1.45313	32	5.6569	8.2201

Calculated average lattice parameter is 8.218

0.5 wt. %

hkl	**2θ**	**d**	$\mathbf{h^2 + k^2 + l^2}$	$\mathbf{(h^2+k^2+l^2)^{1/2}}$	**a**
220	30.677	2.91204	8	2.8284	8.2365
311	36.152	2.48260	11	3.3166	8.2339
400	44.000	2.05629	16	4.0000	8.2252
422	54.561	1.68061	24	4.8990	8.2333
333	58.205	1.58375	27	5.1962	8.2294
440	63.991	1.45380	32	5.6569	8.2239

Calculated average lattice parameter is 8.230

1.0 wt. %

hkl	**2θ**	**d**	$\mathbf{h^2 + k^2 + l^2}$	$\mathbf{(h^2+k^2+l^2)^{1/2}}$	**a**
220	30.705	2.90942	8	2.8284	8.2291
311	36.186	2.48036	11	3.3166	8.2264
400	43.993	2.05658	16	4.0000	8.2263
422	54.607	1.67928	24	4.8990	8.2268
333	58.24	1.58288	27	5.1962	8.2249
440	63.989	1.45384	32	5.6569	8.2242

Calculated average lattice parameter is 8.226

Lattice parameters of coated samples exhibit values of 8.218, 8.230 and 8.226 at 0.2 wt. %, 0.5 wt. % and 1.0 wt. % of ZnO respectively as shown by Table 6.1.

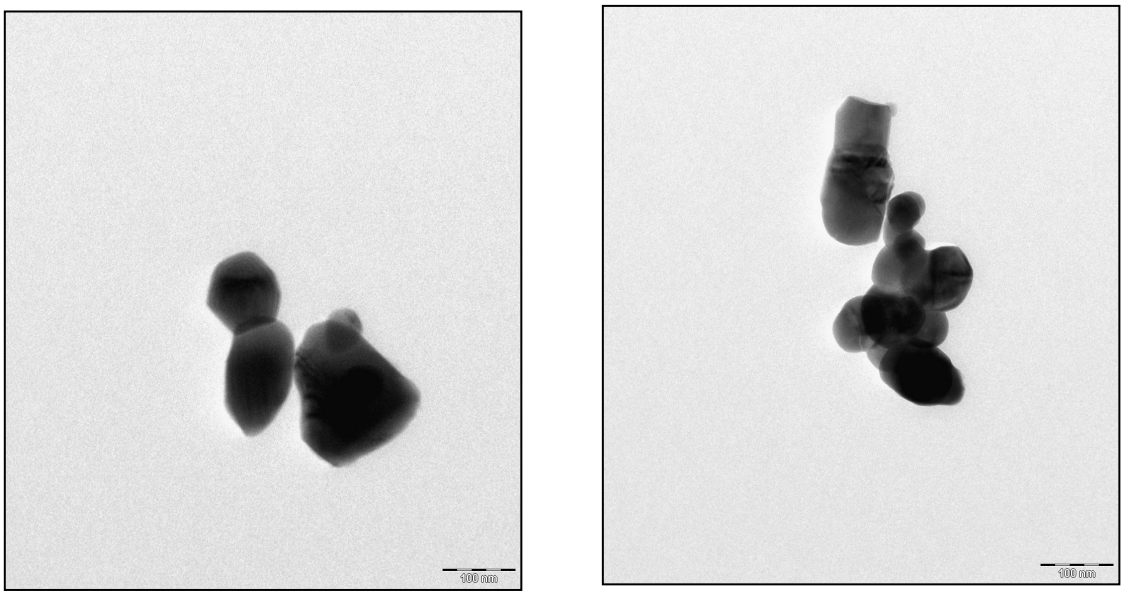
Table 6.2 shows crystallite size of ZnO coated samples at different coating amount. Crystallite size of 0.2 wt.% ZnO coated samples is 70.2 nm. This value is slightly higher than the crystallite size of bare sample which is 60.5 nm. The crystallite size is reduced to 51.6 nm for 0.5 wt.% ZnO coated $LiNiVO_4$ and increases to 59.7 nm for samples coated with 1.0 wt. % ZnO.

Table 6.2: Crystallite size of coated samples

Coating amount (wt.%)	Crystallite size (nm)
0.2	70.2
0.5	51.6
1.0	59.7

6.2 Transmission electron microscopy (TEM)

TEM studies were carried on ZnO coated samples. The following figures show the TEM images of ZnO coated samples at different weight ratios. The diameter of the particles are in the range of 41 nm to 100 nm for 0.2 wt.% ZnO coated cathode materials as shown by Fig 6.2. 61 nm to 80 nm is the range of diameter of most of the particles. 18.2 % of the particles with the diameter between 41 nm to 50 nm. The diameter in the range of 51 nm to 60 nm, 81 nm to 90 nm and 91 nm to 100 nm is represented by 9.1 % particles respectively.



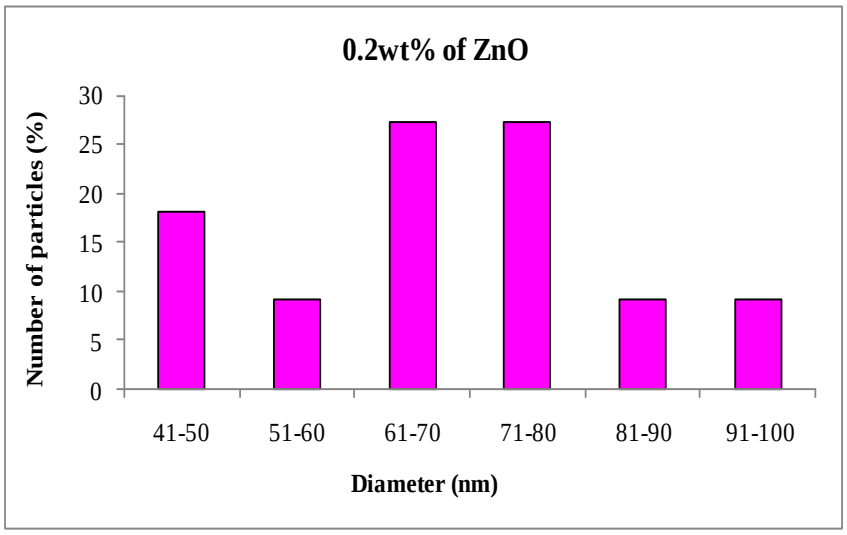


Fig. 6.2: TEM images at 0.2wt.% ZnO

The range of diameters become to 51 nm to 150 nm when the coating level was increased to 0.5 wt.% ZnO as presented by Fig. 6.3. 18.2 % of the particles cover the diameter ranges from 51 nm to 60 nm, 81 nm to 90 nm, 91 nm to 100 nm and 141 nm to 150 nm respectively. Each group in the diameter range from 61 nm to 70 nm, 71 nm to 80 nm and 121 nm to 130 nm consists of 9.1 % of the particles.

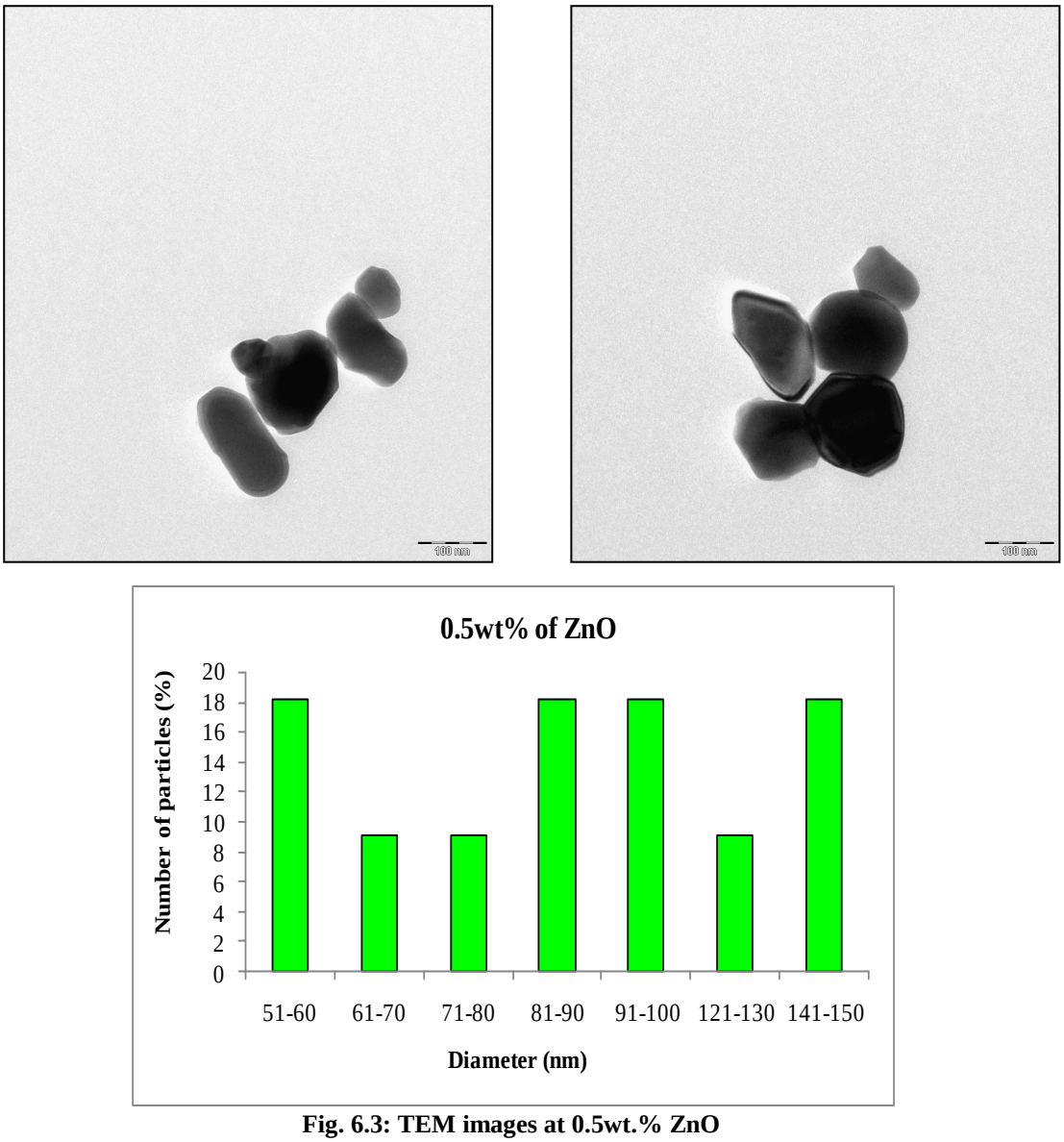
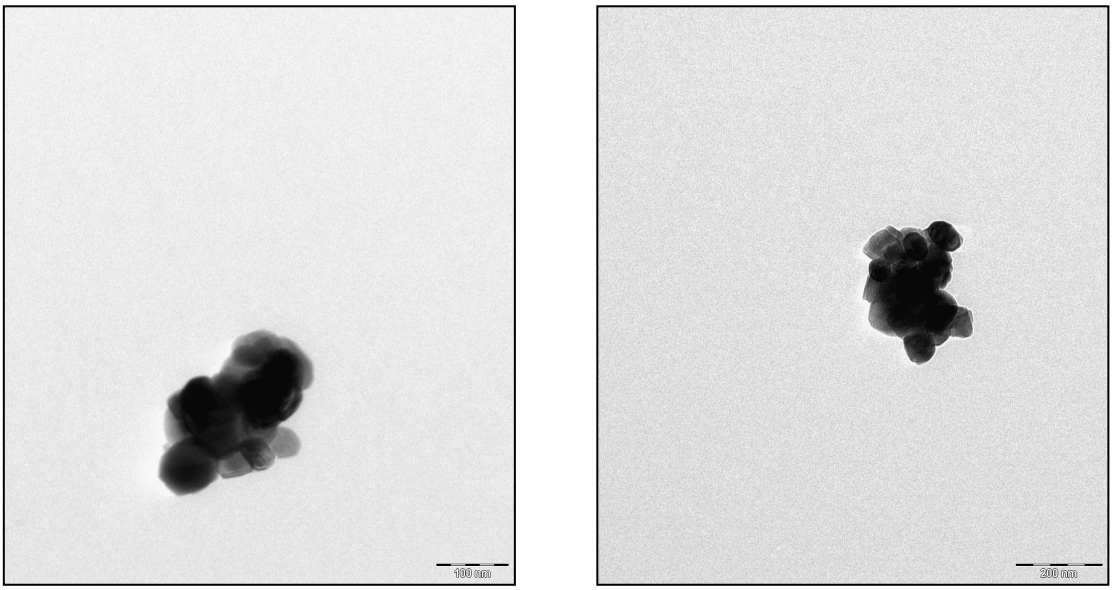


Fig. 6.3: TEM images at 0.5wt.% ZnO

At 1.0 wt.% ZnO coating, the particles exhibit diameter sizes in the range of 41 nm to 90 nm. Even though the diameter of the particles is more concentrated in the range of 71

nm to 80 nm, there are particles uniformly distributed around the range of 41 nm to 70 nm. About 6.7 % of the particles have diameter in the range from 81 nm to 90 nm.



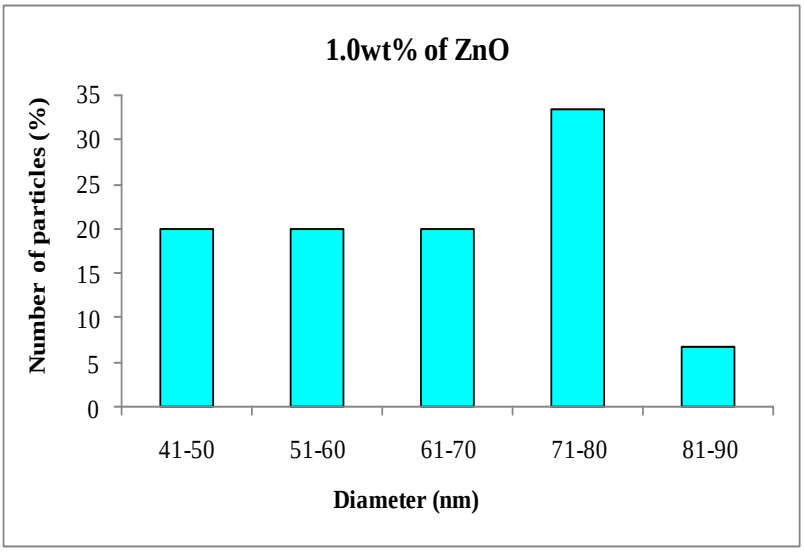


Fig. 6.4: TEM images at 1.0 wt.% ZnO

6.2 Scanning Electron Microscopy (SEM)

SEM images of ZnO coated samples with diffrent coating ratios can be observed in Fig 6.5. 0.2 wt.% ZnO coated samples have smooth surface.

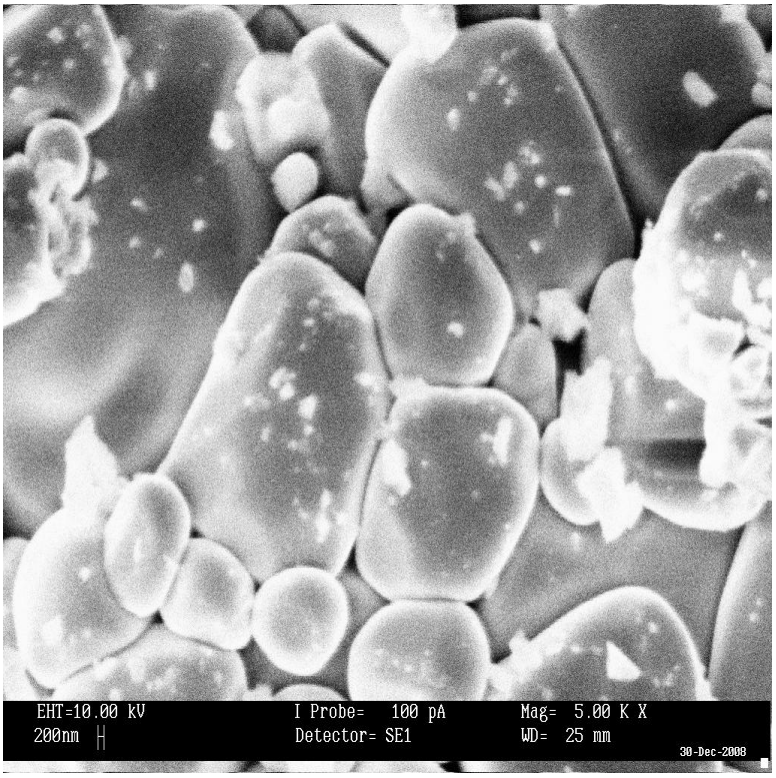


Fig. 6.5: SEM image at 0.2 wt.% ZnO

Fig. 6.6 gives the distribution of surface area of 0.2 wt.% ZnO coated $LiNiVO_4$. 52.0 % of the grains are within surface area of 10 μm^2. 20 % of the grains cover the surface area in the range of 11 μm^2 to 20 μm^2. Surface area in the range of 31 μm^2 to 40 μm^2 contains 16 % of the grains. The range from 21 μm^2 to 30 μm^2 and 41 μm^2 to 50 μm^2 are represented by 8 % and 4 % of the grains respectively.

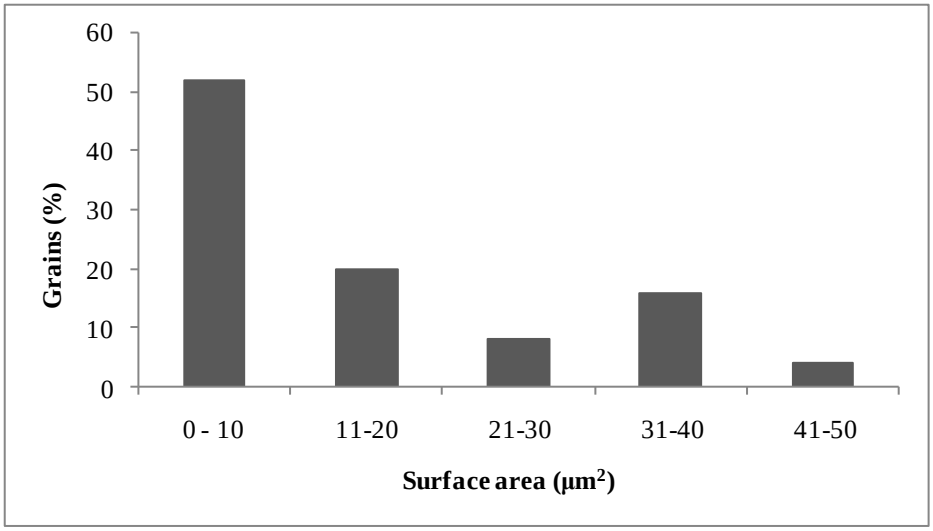


Fig. 6.6: Distribution of surface area of 0.2 wt.% ZnO coated $LiNiVO_4$

Distribution of diameter of 0.2 wt.% ZnO coated $LiNiVO_4$ is shown in Fig. 6.7. 52.0 % of the grains are with diameter in the range of 3 μm to 4 μm. 20 % of the grains has diameter within 2 μm. The diameters range between 5μm to 6 μm are represented by 16 % of grains. 12 % of grains have diameter in the range 7 μm to 8 μm.

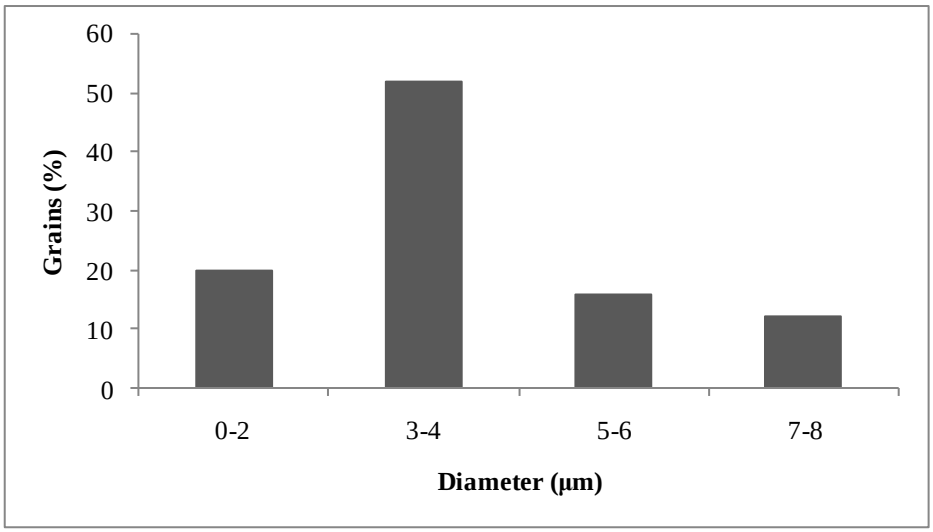


Fig. 6.7: Distribution of diameter of 0.2 wt.% ZnO coated $LiNiVO_4$

The micrograph of 0.5wt.% ZnO coated sample is also similar as that of the previous

sample and is shown in Fig. 6.8.

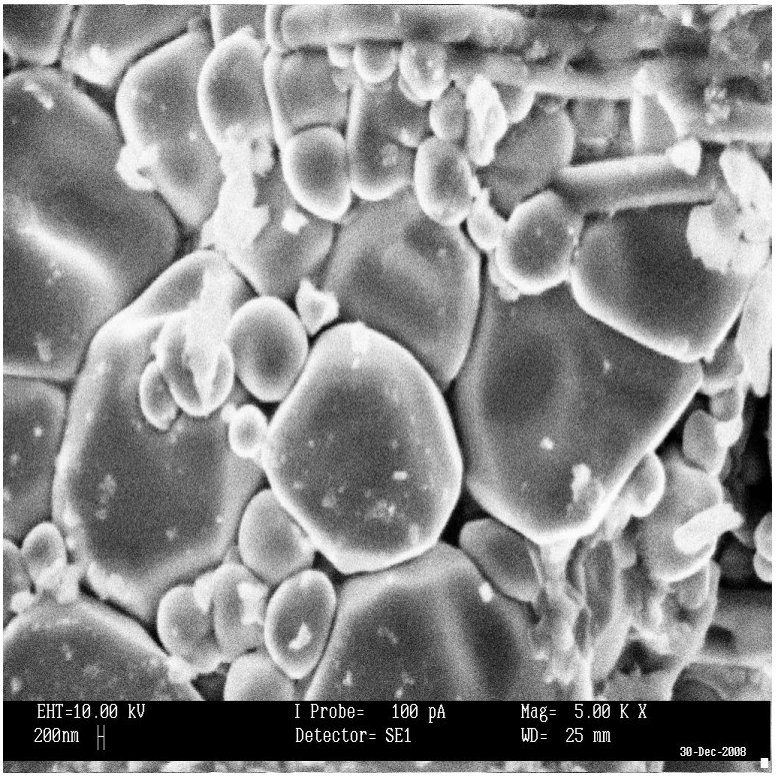


Fig. 6.8: SEM image at 0.5 wt.% ZnO

Fig. 6.9 shows the distribution of surface area of 0.5 wt.% ZnO coated $LiNiVO_4$. 77.4 % of the grains are within surface area of 10 μm^2. About 9.7 % of the grains are in the range of 11 μm^2 to 20 μm^2. Only 6.5 % of the grains with surface area ranging from 21 μm^2 to 30 μm^2 and 31 μm^2 40 μm^2 respectively.

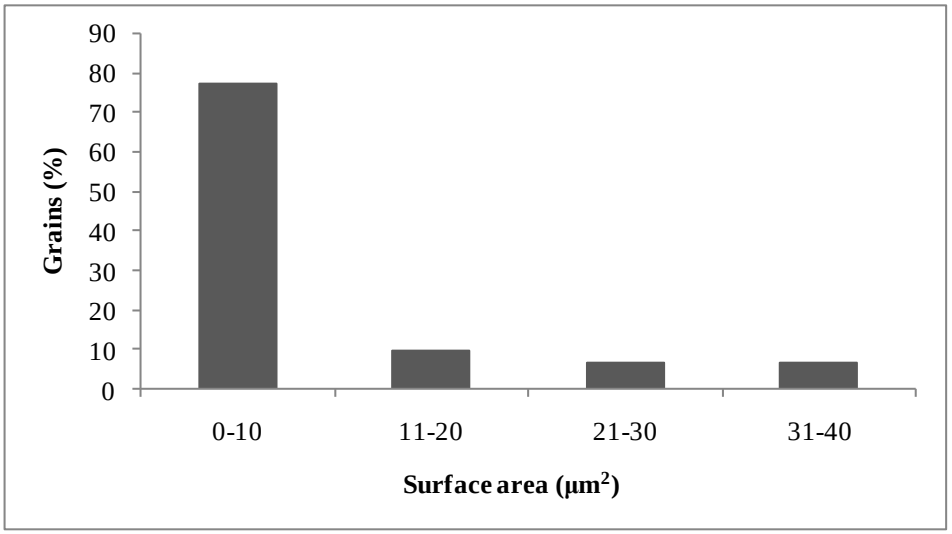


Fig. 6.9: Distribution of surface area of 0.5 wt.% ZnO coated $LiNiVO_4$

Fig. 6.10 shows the diameter distribution for 0.5 wt.% ZnO coated $LiNiVO_4$. 64.5 % of the grains have diameter within 2 μm. The diameter ranging from 3 μm to 4 μm is represented by 22.6 % of the grains. There are 6.5 % of the grains in the diameter ranging from 5 μm to 6 μm and 7 μm to 8 μm respectively.

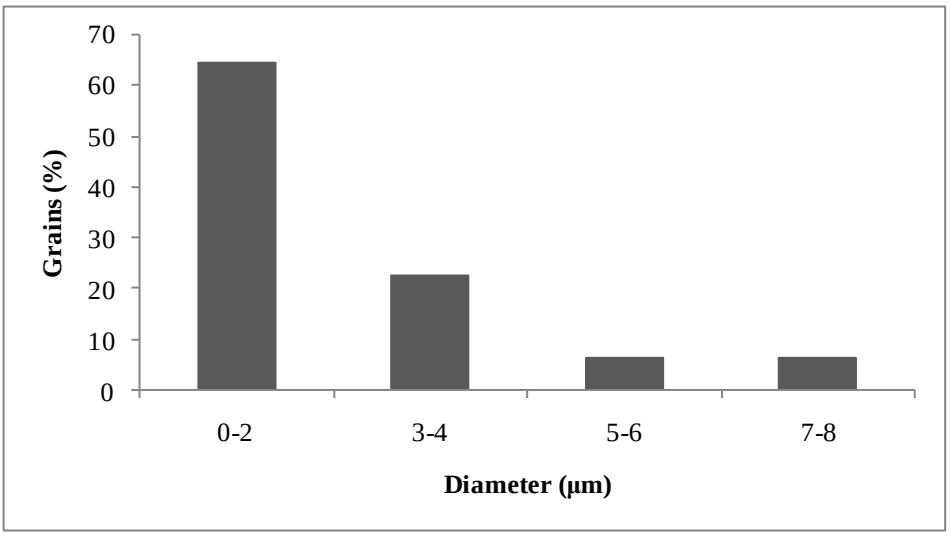


Fig. 6.10: Distribution of diameter of 0.5 wt.% ZnO coated $LiNiVO_4$

Fig. 6.11 depicts micrograph of SEM at 1.0 wt.% ZnO. The grains are bigger in size.

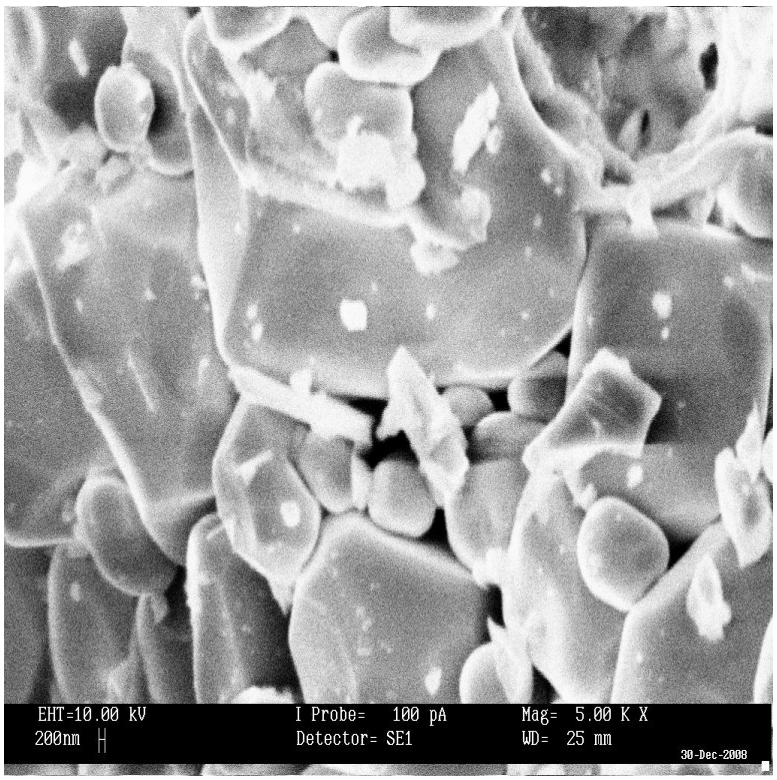


Fig. 6.11: SEM image at 1.0 wt.% ZnO

Fig. 6.12 shows the distribution of surface area of 1.0 wt.% ZnO coated $LiNiVO_4$. Surface areas of 79.2 % of the grains are within 10 μm^2. 8.3 % of the grains are with surface area in the range of 11 μm^2 to 20 μm^2 and 21 μm^2 to 30 μm^2 respectively.

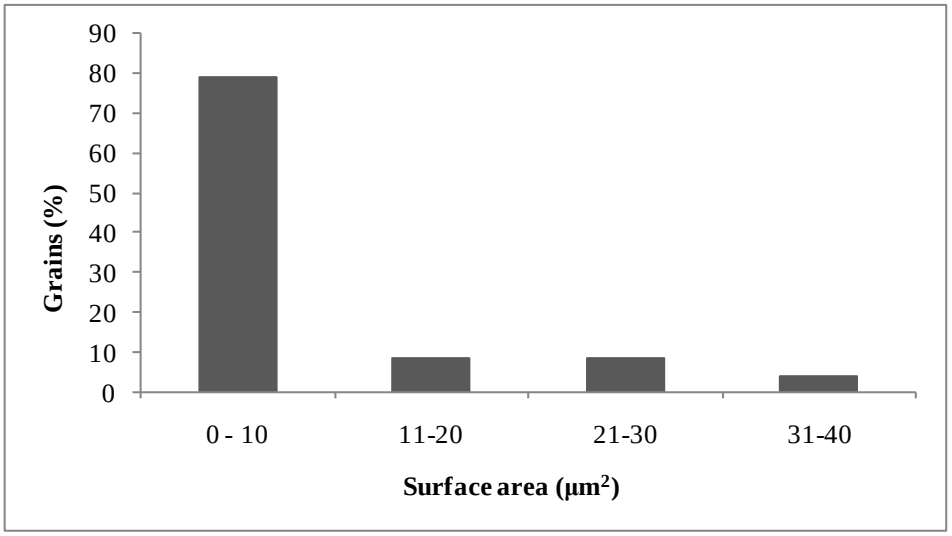


Fig. 6.12: Distribution of surface area of 1.0 wt.% ZnO coated $LiNiVO_4$

Diameter distribution for 1.0 wt.% ZnO coated $LiNiVO_4$ is displayed by Fig. 6.13. Diameters of 50 % of the grains concentrate in the range of 3 μm to 4 μm. 37.5 % of grains is represented by the diameter within 2 μm. 8.3 % of the grains cover the diameter range of 5 μm to 6 μm. Only 4.2 % of grains have diameter in the range of 7 μm to 8 μm.

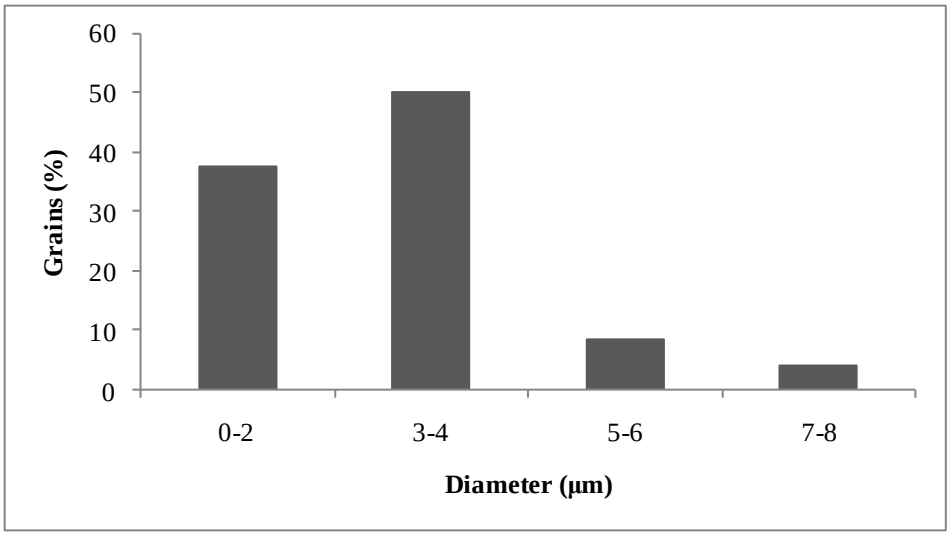
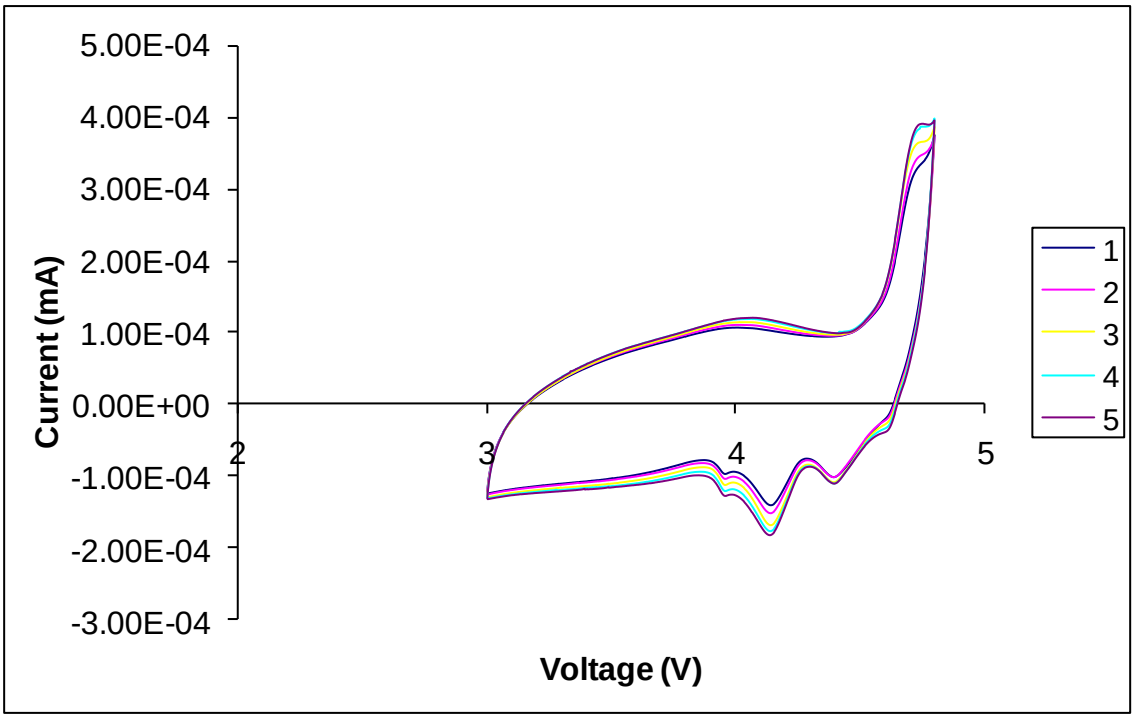


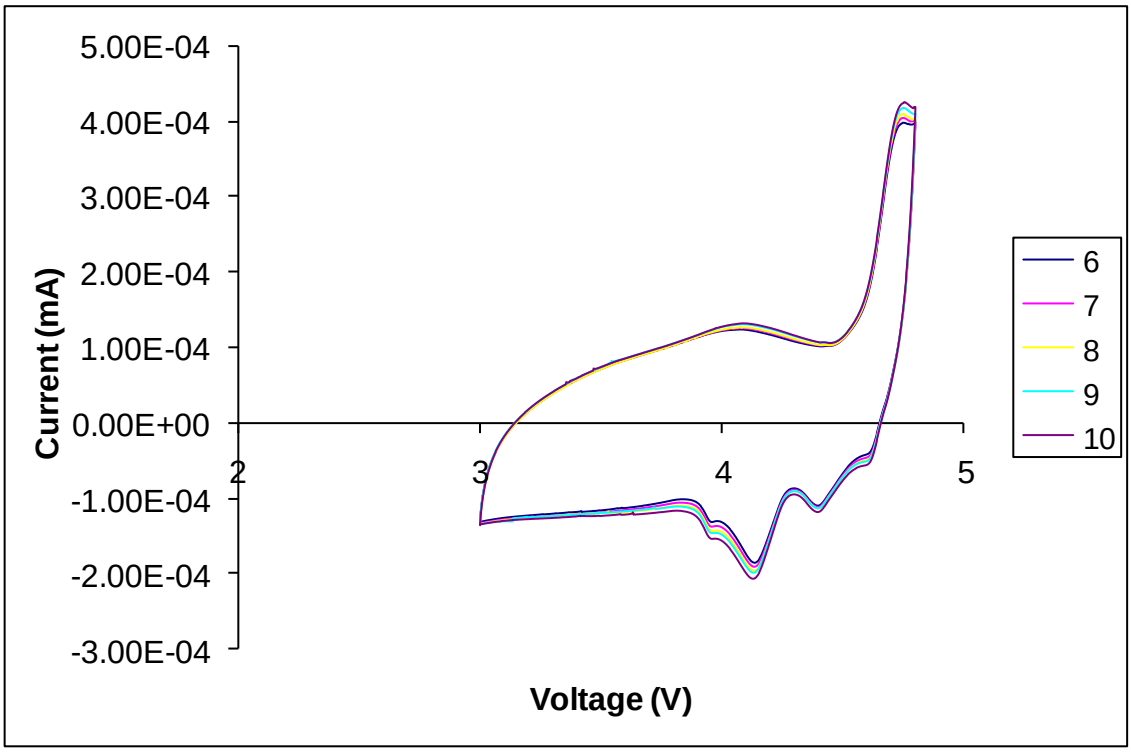
Fig. 6.13: Distribution of diameter of 1.0 wt.% ZnO coated $LiNiVO_4$

6.6 Cyclic voltammetry

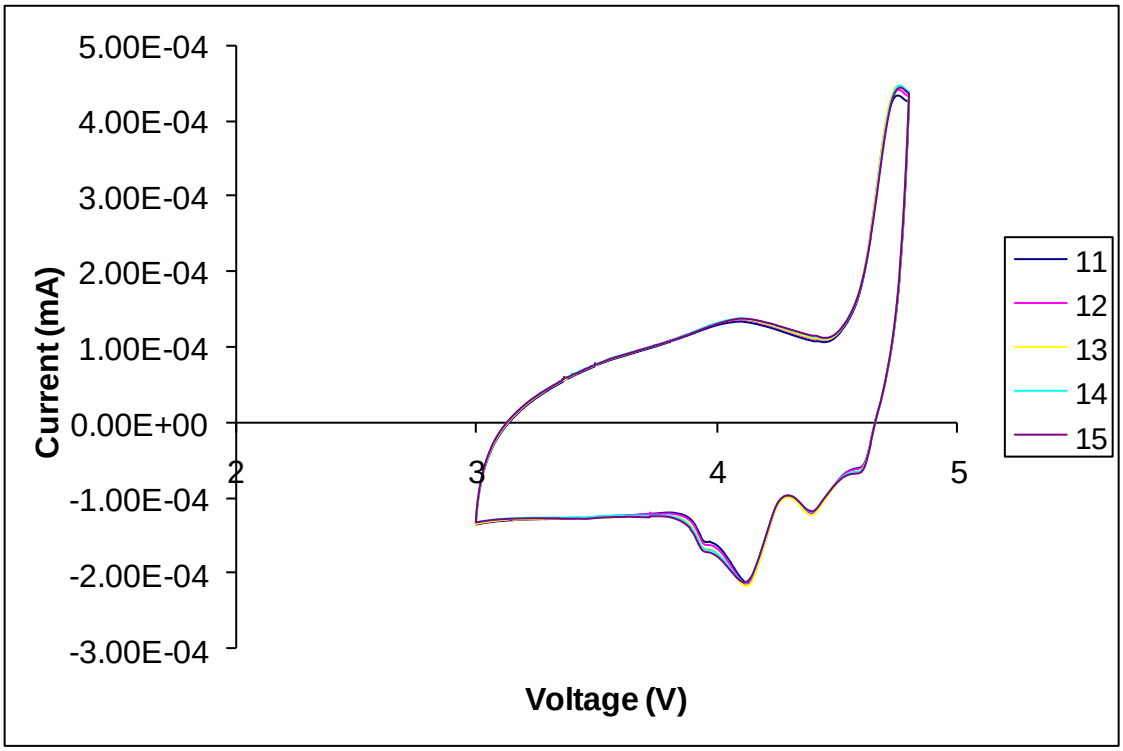
Cyclic voltammetry of 0.2 wt.% ZnO coated $LiNiVO_4$ is shown in Fig. 6.14.



Cyclic voltammetry of 0.2 wt.% of ZnO coated sample (1st-5th cycles)



Cyclic voltammetry of 0.2 wt.% of ZnO coated sample (6th-10th cycles)

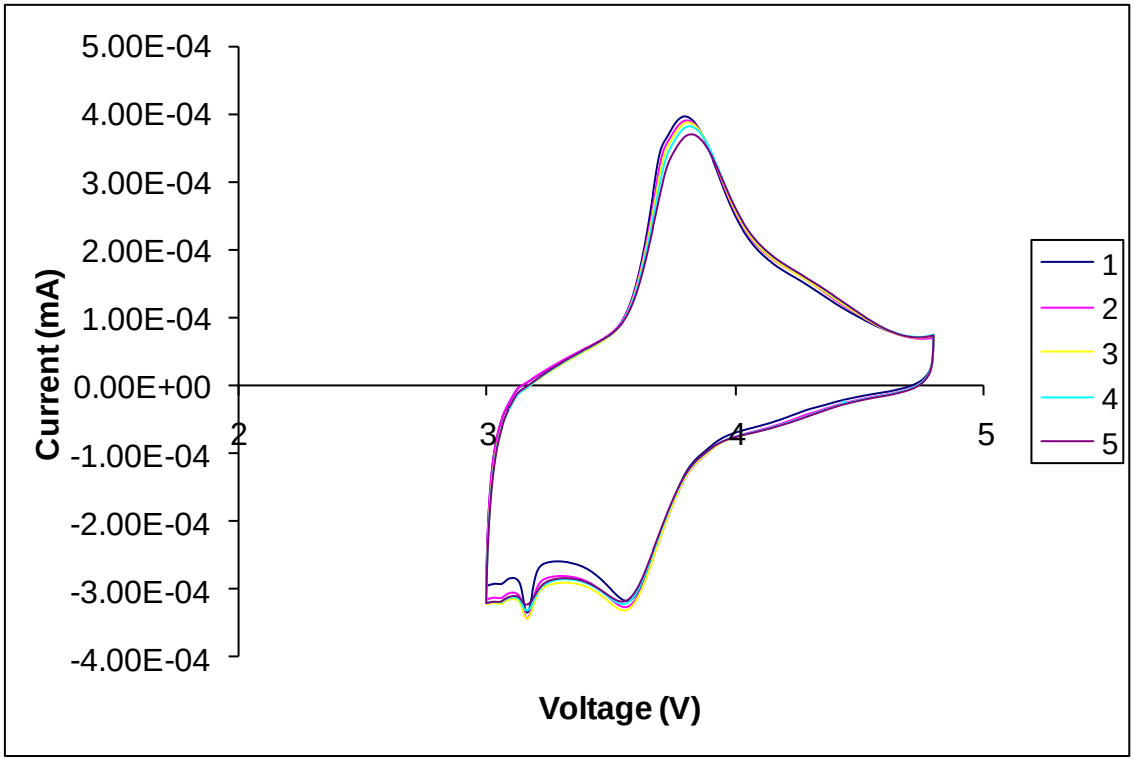


Cyclic voltammetry of 0.2 wt.% of ZnO coated sample (11th-15th cycles)

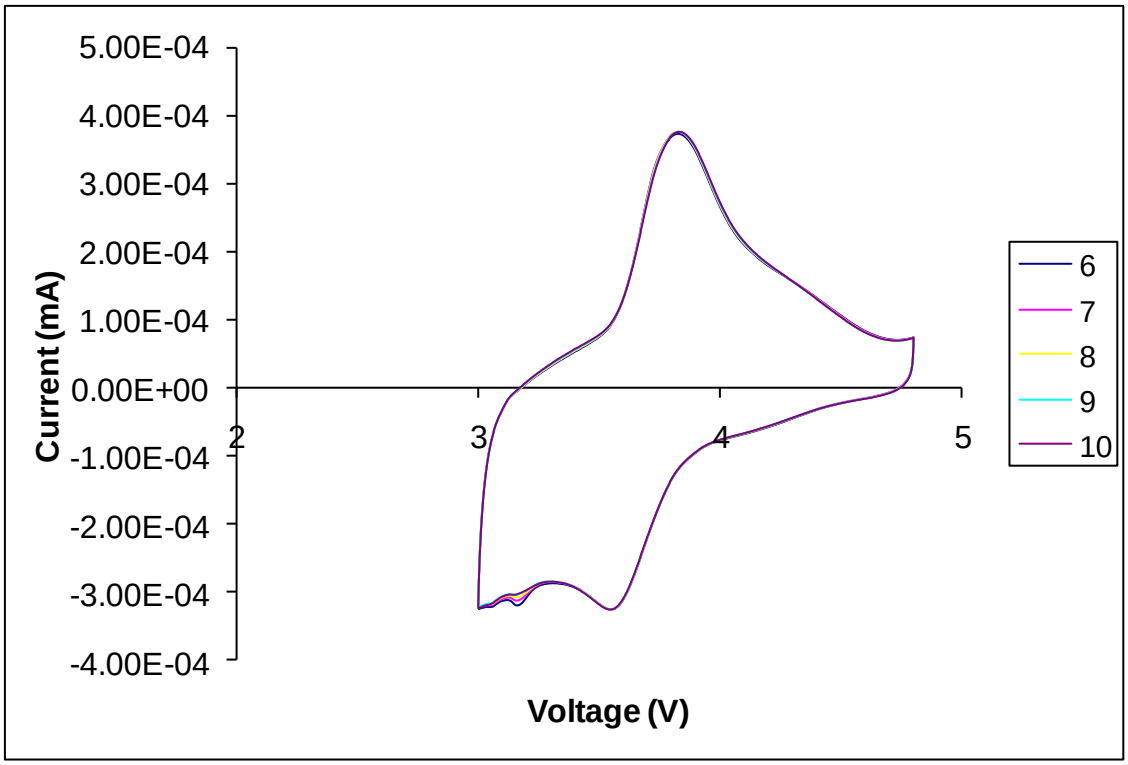
Fig 6.14: Cyclic voltammetry of 0.2 wt.% of ZnO coated sample

The perfomance of the coated cathode materials become more stable with cycling. However the bottom curve exhibits several peaks which could be attributed to changes in the structure.

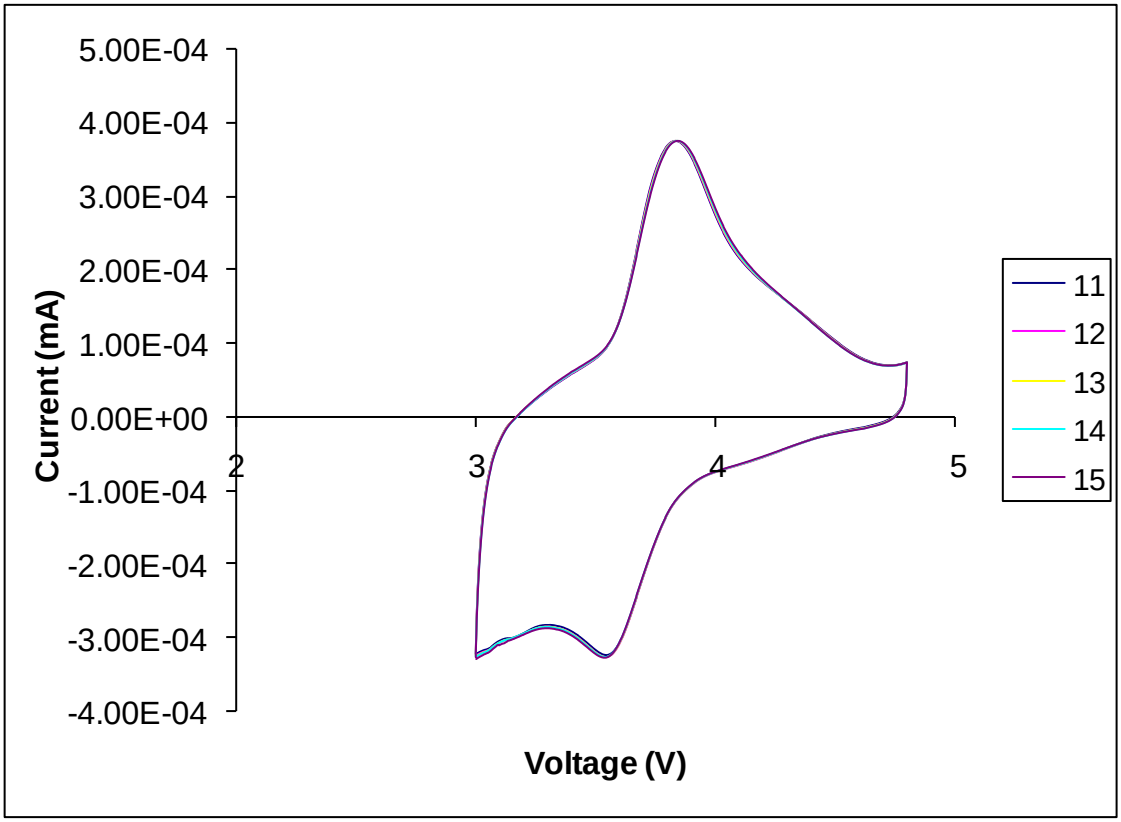
The voltammogram of 0.2 wt. % of ZnO coated $LiNiVO_4$ is shown in Fig. 6.7. The ZnO coating at this concentration seems to stabilize the cycling perfomance. After the 10^{th} cycle only two peaks are observed.



Cyclic voltammetry of 0.5 wt.% of ZnO coated sample (1st-5th cycles)



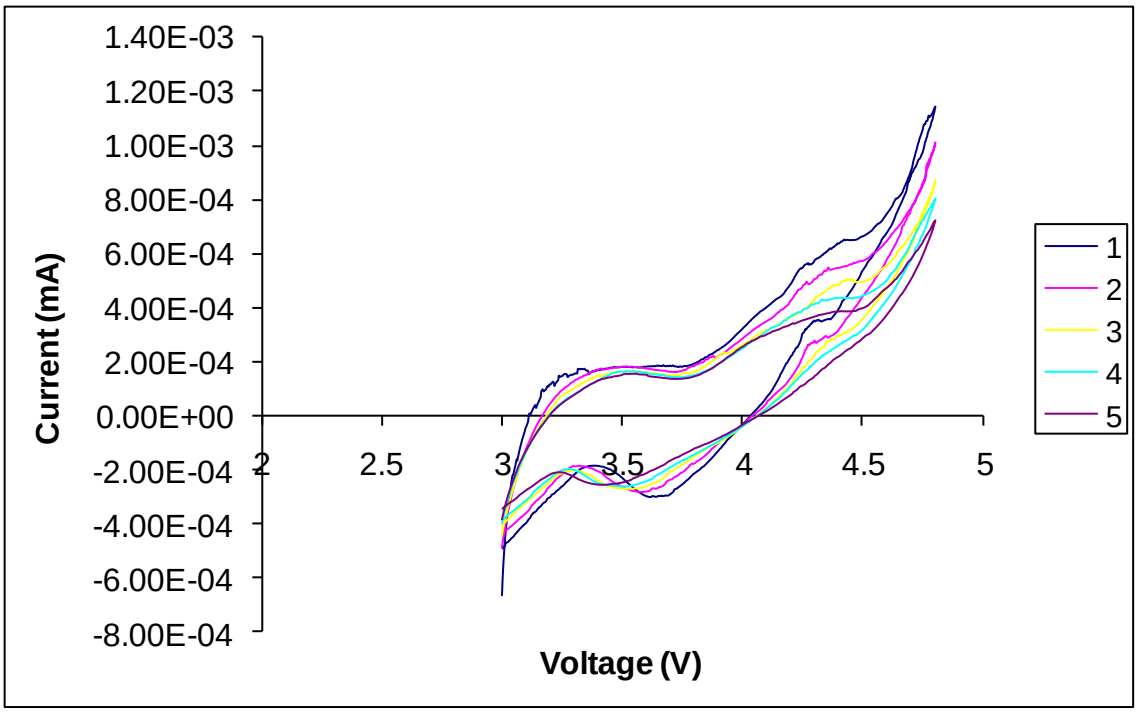
Cyclic voltammetry of 0.5 wt.% of ZnO coated sample (6th-10th cycles)



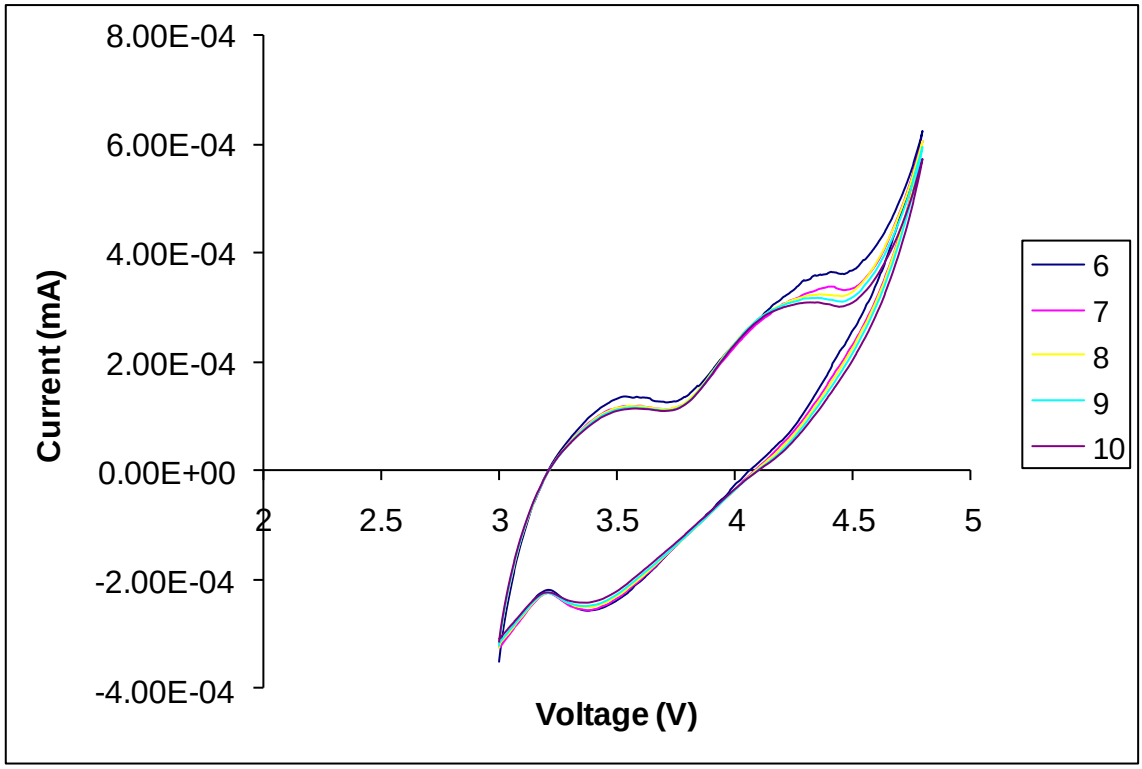
Cyclic voltammetry of 0.5 wt.% of ZnO coated sample (11th-15th cycles)

Fig 6.15: Cyclic voltammetry of 0.5 wt.% of ZnO coated sample

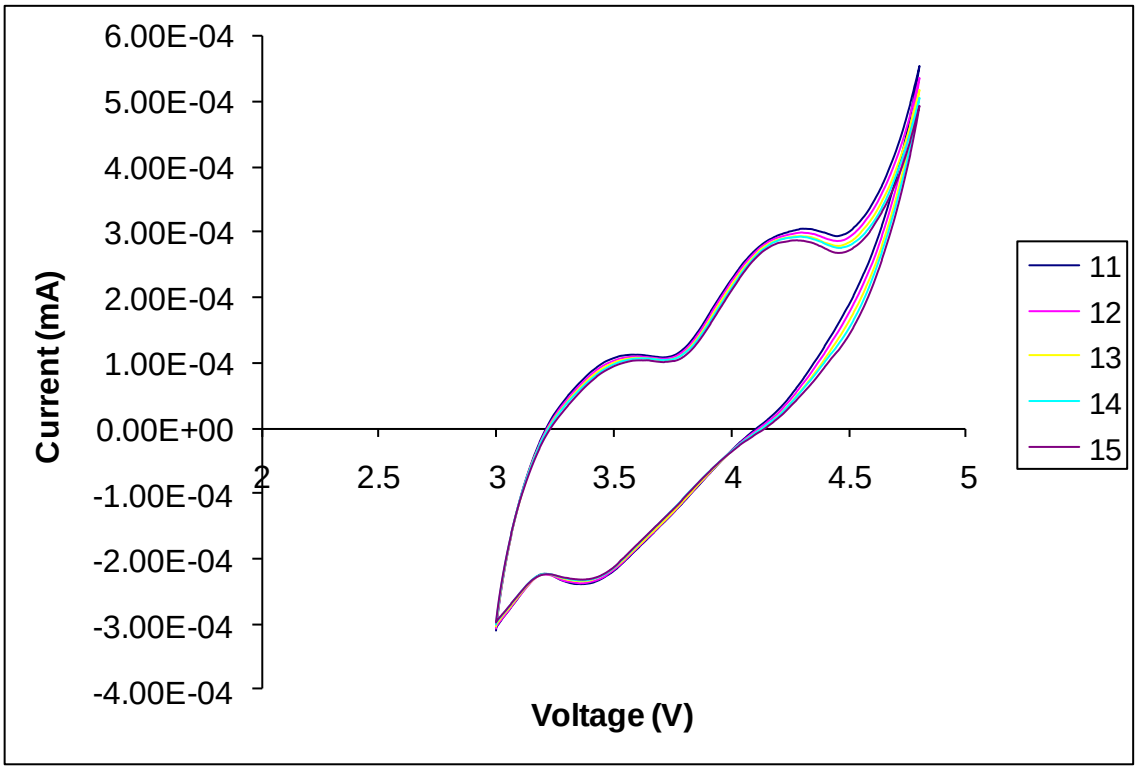
Fig 6.16 displays the voltammogram of 0.5 wt. % of ZnO coated $LiNiVO_4$.



Cyclic voltammetry of 1.0 wt.% of ZnO coated sample (1st-5th cycles)



Cyclic voltammetry of 1.0 wt.% of ZnO coated sample (6th-10th cycles)



Cyclic voltammetry of 1.0 wt.% of ZnO coated sample (11th-15th cycles)

Fig 6.16: Cyclic voltammetry of 1.0 wt.% of ZnO coated sample

6.6 Charge discharge characteristics

Discharge perfomance of fabricated cell using ZnO coated $LiNiVO_4$ is presented in Fig. 6.17 to Fig. 6.19. Initial discharge capacities of 0.2 wt.% ZnO, 0.5 wt.% ZnO and 1.0 wt.% ZnO are 13.96 $mAhg^{-1}$, 13.32 $mAhg^{-1}$ and 18.51 $mAhg^{-1}$ respectively. 1.0 wt.% ZnO coated $LiNiVO_4$ shows high discharge capacity compared with other amounts of coating. However the values of discharge capacity becomes nearly similar with that sample coated with 0.2 wt.% ZnO coated $LiNiVO_4$. At the end of 20^{th} cycle, the discharge capacity reached at 12.3 $mAhg^{-1}$ for 0.2 wt.% ZnO, 11.93 $mAhg^{-1}$ for 0.5 wt.% ZnO and 11.67 $mAhg^{-1}$ 1.0 wt.% ZnO.

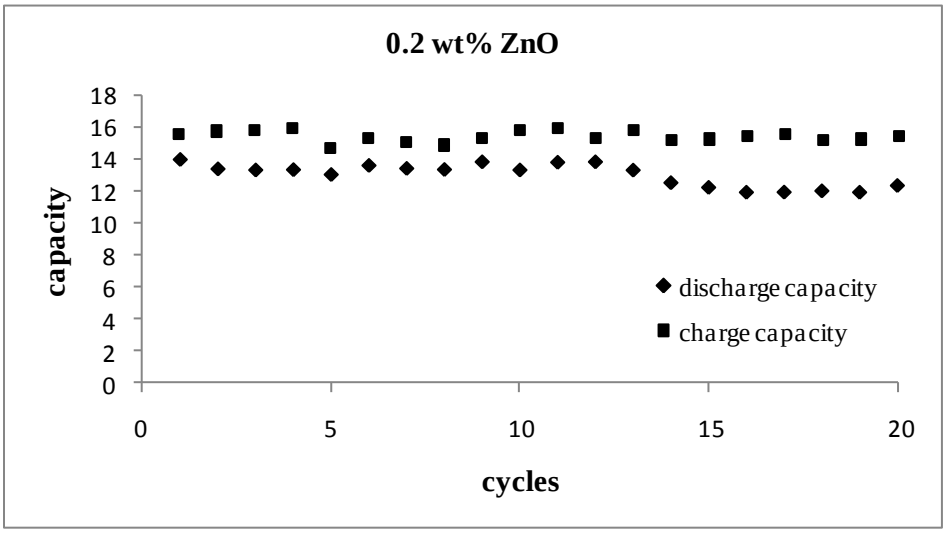


Fig. 6.17: Charge-discharge studies of 0.2 wt% ZnO coated $LiNiVO_4$

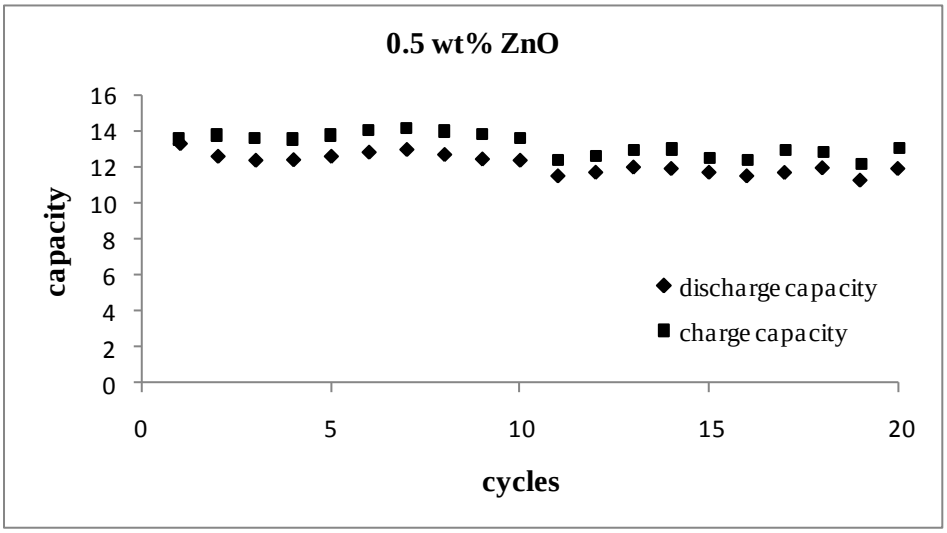


Fig. 6.18: Charge-discharge studies of 0.5 wt% ZnO coated $LiNiVO_4$

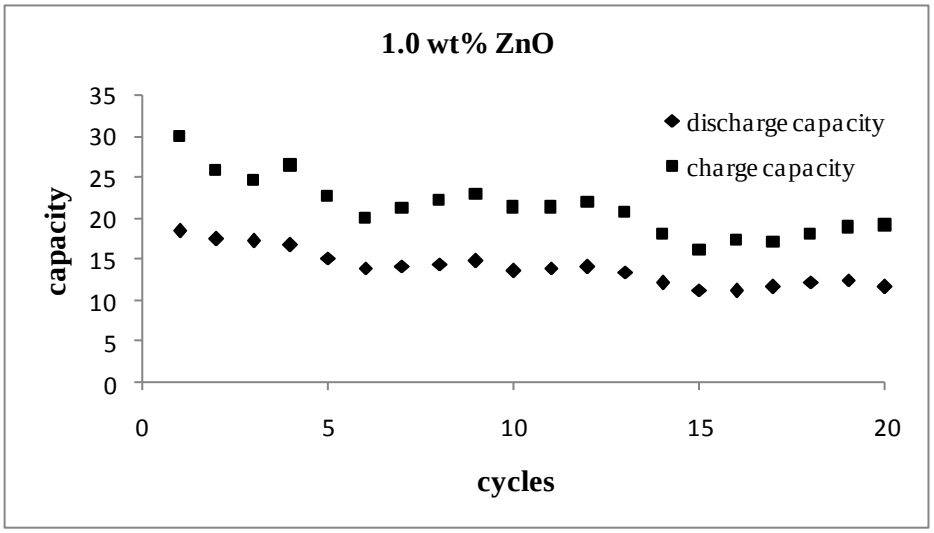


Fig. 6.19: Charge-discharge studies of 1.0 wt% ZnO coated $LiNiVO_4$

Fig. 6.20 shows cycling efficiency of ZnO coated $LiNiVO_4$. From the figure, it can be explained that the 0.5 wt.% ZnO coated $LiNiVO_4$ exhibits better cycling efficiency followed by 0.2 wt.% ZnO coated $LiNiVO_4$. The cycling effiency is in the range of ~90-93 % for 0.5 wt.% ZnO. 0.5 wt.% ZnO showed 89.9% of effiency at first cycle. Eventhough 1.0 wt.% ZnO coated $LiNiVO_4$ only delivered 61.7 % of efficiency in the beginning of the cycling, but it rises in the continuos cycling process. However the value is still not as high as 0.2 wt.% ZnO and 0.5 wt.% ZnO.

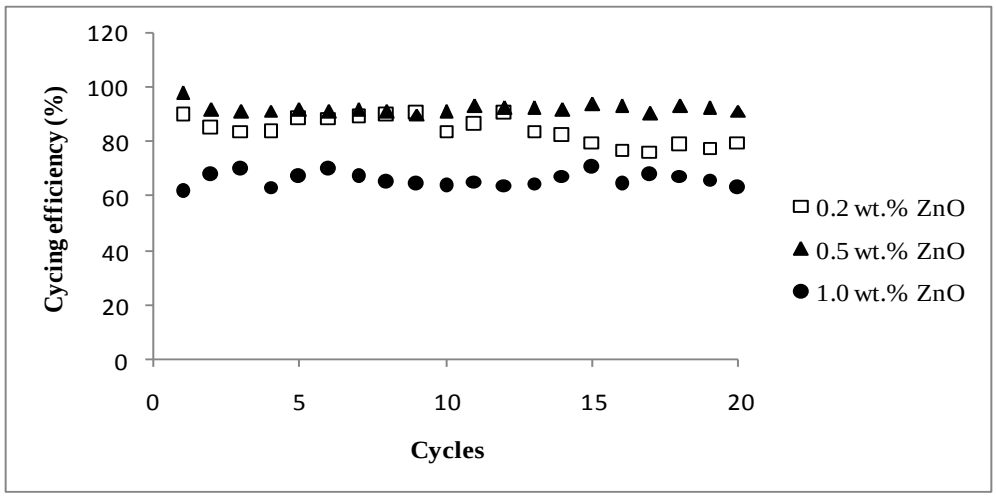


Fig. 6.20: Cycling efficiency of ZnO coated $LiNiVO_4$

Capacity retention of ZnO coated $LiNiVO_4$ is shown Fig. 6.21. Cells occupied with 0.2 wt.% ZnO and 0.5 wt.% ZnO as cathodes retains better capacity during charge-discharge process. The capacity retention of 1.0 wt.% ZnO is better at the first four cycles and decreases from fifth cycle.

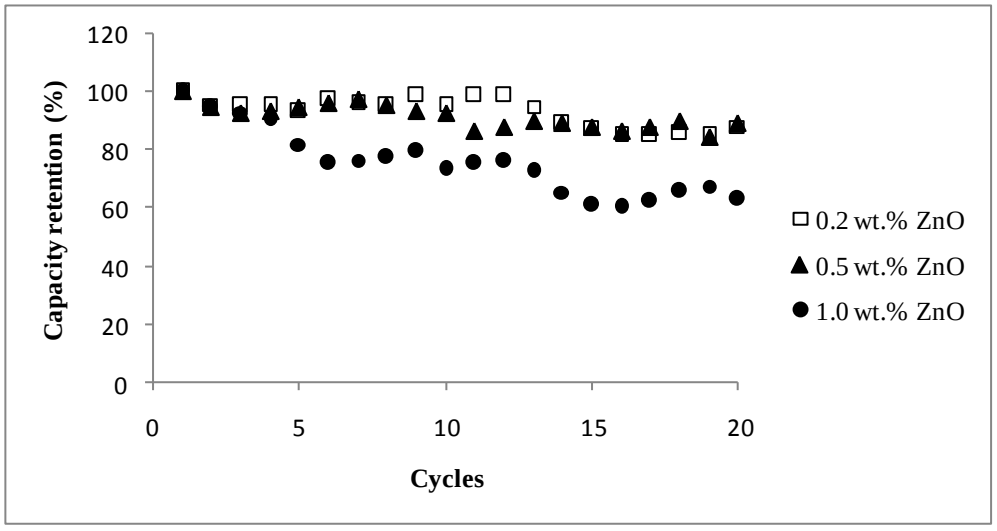


Fig. 6.21: Capacity retention of ZnO coated $LiNiVO_4$

Summary

XRD of ZnO coated samples shows no peaks corresponding to ZnO. This confirms that the ZnO layer only covers the cathode materials and does not merge into the core material. 1.0 wt.% ZnO coated $LiNiVO_4$ delivers high discharge capacity for first five cycles compared with 0.2 wt.% ZnO and 0.5 wt.% ZnO coated $LiNiVO_4$. But $LiNiVO_4$ coated with 0.2 wt.% ZnO and 0.5 wt.% ZnO maintained better cycling efficiency than 1.0 wt.% ZnO. Capacity retention also improved for the cells with 0.2 wt.% ZnO and 0.5 wt.% ZnO.