CHAPTER 7

PREPARATION AND CHARACTERIZATION OF Sn$^{4+}$ SUBSTITUTED NICKEL FERRITE AS ANODES FOR LI ION BATTERIES

7.1 SCOPE OF THE WORK

Li ion batteries are predominantly been manufactured with carbonaceous materials as anodes, despite of its large irreversible capacity loss during extended cycling. Hence the need to identify alternative materials has become mandatory to check the impediments in the Li ion battery market. As a part of this exploration, transition metal oxides have been identified as potential alternative due to its high theoretical capacity when compared to graphite or carbon. In the transition metal oxide series, spinels of general formula AB$_2$O$_4$ are known to be technologically important materials because of their tailorable properties to meet stringent requirements in various applications. Especially ferrites belonging to this class of materials are gaining prominence owing to their efficacious properties such as thermodynamic stability, high electrical conductivity, high corrosion resistance and thus making them suitable for electrochemical, magnetic and metallurgical applications. Nickel ferrite and its derivatives have been evaluated as anodes for Li ion batteries by few research groups (Poizot 2000, Alcantara 2003). It has been reported by many groups that the substitution of A-site (tetrahedral) or B-site (octahedral) of this compound improves its overall properties. Many substitutions like Zn, Pb, Cu, Mn and Co have so far been explored in the Nickel Ferrite to satisfy the requirements for many
applications. But in the case of Li ion battery applications the usage of substituted nickel ferrites as anode is very limited. Few research reports emphasizing the utilization of ferrite/metal oxide composite could be sparingly observed (Kalaiselvan 2006). Hence this chapter focuses on the possibility to deploy substituted nickel ferrite as anodes for Li ion battery applications. In this work, Sn$^{4+}$ has been selected as substituent because of its well known reversible properties experienced from SnO$_2$ and its capacity to store twice the amount of Li$^+$ ions compared to graphite.

In the synthesis of Sn$^{4+}$ substituted Nickel ferrite, self propagating high temperature combustion route has been preferred owing to its potential advantages such as low processing time, low external energy consumption, self sustaining instantaneous reaction and high yield of nano sized particles. The influences of Synthesis methodology and dopants in the structural, morphological, electrical and electrochemical properties have been envisaged in detail. The extent of coulombic efficiency amelioration due to the Sn$^{4+}$ doping has been presented in detail.

7.2 SYNTHESIS METHODOLOGY

The substituted ferrite compounds have been synthesized from the stochiometric quantities of analytical grade Ni(NO$_3$)$_3$.6H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O, SnCl$_2$.2H$_2$O dissolved in minimum quantity of triple distilled water. The stochiometric quantity of urea has been used as the fuelling agent, in order make the reaction self propagating up to high temperature. The reactants have been subjected to 300°C, to initiate a self propagating exothermic reaction evolving large amounts of gases. The gas evolution followed with froth formation has been observed. Further heating, has yielded foamy product in the form of powder. The decomposition reactions of the starting compounds could be presented as
\[
\begin{align*}
\text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} & \rightleftharpoons \text{NiO} + \text{NO}_2 + \text{NO} + 6\text{H}_2\text{O} \quad (7.1) \\
\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} & \rightleftharpoons 0.3\text{Fe}_2\text{O}_3 + 9\text{H}_2\text{O} + 1.5\text{NO} + 1.5\text{NO}_2 + 1.6\text{O}_2 \quad (7.2) \\
\text{CO(NH}_2\text{)}_2 + 1.5\text{O}_2 & \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2 \quad (7.3)
\end{align*}
\]

From the above reactions it has been understood that the decomposition of urea is highly exothermic over other starting compounds and thus aids the decomposition of nitrate salts into desired product at faster rate with low external energy consumption. Hence, urea is identified to be more suited organic fuel over other fuels. The overall synthesis reaction becomes (Balaji 2005).

\[
(1-x)\text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} + 2\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} + \text{SnCl}_2 \cdot 2\text{H}_2\text{O} + \text{CO(NH}_2\text{)}_2 \xrightarrow{\Delta} \text{Ni}_{1-x}\text{Sn}_x\text{Fe}_2\text{O}_4 + 2\text{HCl} + (15 - 4x)\text{H}_2\text{O} + (5 - x)\text{N}_2 + (9.5 - 3x)\text{O}_2 + \text{CO}_2 \quad (7.4)
\]

### 7.3 THERMAL ANALYSIS

The kinetics of the above said reaction has been analyzed by thermo gravimetry studies. The thermo gravimetry curve of the NiFe$_2$O$_4$ has been shown in Figure 7.1. The initial elimination of water molecule from the reactants has been observed around 100°C. The second step in weight loss curve has been observed around 260°C, which could be attributed to the decomposition of urea leaving enormous sufficient energy for the decomposition of Ni and Fe precursors as per equations (7.1) and (7.2) and thus resulting in foamy powder of product. The enormous energy released during urea decomposition as per equation (7.3) could be observed from the exothermic transition in the DTA curves. The compound formation has ceased around 400°C and beyond which the no phase transition has been
observed. This illustrates the compound stability in higher temperature without any oxygen vacancy formation.

Figure 7.1 TG-DTA graph of Urea -Nitrate decomposition in Nickel ferrite synthesis

The TGA curves of the Sn$^{4+}$ Substituted samples have been shown in Figure 7.2. From the figure, it could be observed that for all the samples the dehydration from the reactants has taken place around 100°C and next weight loss has been observed around 250°C corresponding dehydroxylation from the reactants and decomposition of urea -Nitrate precursor. The weight loss while dehydration in the substituted samples has been observed to be higher, which may be attributed to the hygroscopic nature of the ferric nitrate, which absorbs mixture from the atmosphere leading to higher degree of dehydration. The compound formation has been observed to slightly shift to higher temperature while Sn doping. However, for all the samples, the compound formation has been observed to take place within 300°C and after which no appreciable phase transition is observed.
Figure 7.2 TGA graph of Sn$^{4+}$ substituted Nickel Ferrite

The nature of phase transition associated with the dehydration and decomposition of urea nitrate precursor has been analyzed using differential thermal Analysis and shown in Figure 7.3. The DTA graph clearly illustrates the absorption heat from the external source for initial dehydration resulting in endothermic kind of reaction and later once the decomposition temperature of the urea is reached, the enormous amount of heat has been generated in the system itself and which results in the decomposition of the other nitrate precursors to form the compound. Thus the system remains self sustaining in
the low temperature itself. This kind of insitu heat generation could be observed by the exothermic nature of the decomposition profile observed around temperature 250°C.

![DTA-DTG curve of Sn-Substituted Nickel Ferrite](image)

**Figure 7.3** DTA-DTG curve of Sn-Substituted Nickel Ferrite

### 7.4 STRUCTURAL CHARACTERIZATION

#### 7.4.1 X-ray Analysis

X-ray diffraction patterns of the combustion synthesized Ni_{1-x}Sn_xFe_2O_4 (x = 0.0, 0.2, 0.4, 0.6 and 0.8) have been presented in Figures 7.4 and 7.5. From the Figure 7.4 the peaks corresponding to planes (311), (220), (440) of NiFe_2O_4 with inverse Spinel structure and Fd3m space group
have been observed. The peak positions have been observed to coincide well with JCPDS Standard (file. No. 100325). The absence any intermediate phases or impure phases in XRD spectra reveals the superiority of the synthesis methodology. The lattice parameter, crystallite size and X-ray density calculated from the spectra have been presented in the Table 7.1. The experimental lattice parameter has been observed to match well with earlier reports. The crystallite size has been observed to be around 25 nm, which indicates the feasibility to produce nano crystalline materials with the rapid combustion synthesis.

![XRD pattern of NiFe₂O₄ sintered at 1000°C](image)

**Figure 7.4 XRD pattern of NiFe₂O₄ sintered at 1000°C**

The Figure 7.5 shows the diffraction pattern of the Sn⁴⁺ doped samples. From the figure the presence of SnO₂ and intermediate SnO phase has been observed for all the samples. The presence of SnO₂ phase has been observed to have good coincidence with JCPDS standard with orthorhombic structure. Hence along with the formation of Sn substituted NiFe₂O₄, the
formation of nano composite of NiFe₂O₄/SnO₂ has also been expected to form with Sn substitution. This observation is in good concomitance with the research report of Kalaiselvan et al (2008). The presence of SnO₂ phase has been observed to increase with increasing concentration of Sn⁴⁺ doping. The structural parameters of the substituted samples have been presented in the Table 7.1. From the table it could be observed that the lattice parameters of the substituted samples have remained unchanged with increasing Sn⁴⁺ concentration, this may be attributed to the close proximity in the ionic radii of Ni²⁺ and Sn⁴⁺ cations (0.69 Å). Moreover the X-ray density of the sample has been observed to increase with increasing concentration of Sn⁴⁺ doping in the sample.

Table 7.1 Structural parameters from XRD

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constant a311 (Å)</th>
<th>Crystallite Size (nm)</th>
<th>Cell Volume (x10⁻³⁰ m³)</th>
<th>X-ray density (kg/m³)</th>
<th>Dislocation density (lines/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe₂O₄</td>
<td>8.334</td>
<td>25.7</td>
<td>578.84</td>
<td>5.378</td>
<td>0.001514</td>
</tr>
<tr>
<td>Ni₀.8Sn₀.2Fe₂O₄</td>
<td>8.3545</td>
<td>25.7</td>
<td>583.92</td>
<td>5.299</td>
<td>0.001514</td>
</tr>
<tr>
<td>Ni₀.6Sn₀.4Fe₂O₄</td>
<td>8.3054</td>
<td>43</td>
<td>572.92</td>
<td>5.353</td>
<td>0.000541</td>
</tr>
<tr>
<td>Ni₀.4Sn₀.6Fe₂O₄</td>
<td>8.3413</td>
<td>41</td>
<td>580.36</td>
<td>5.215</td>
<td>0.000595</td>
</tr>
<tr>
<td>Ni₀.2Sn₀.8Fe₂O₄</td>
<td>8.3413</td>
<td>36</td>
<td>580.36</td>
<td>5.205</td>
<td>0.000772</td>
</tr>
</tbody>
</table>
Figure 7.5 XRD spectra of Sn$^{4+}$ substituted Nickel ferrite

The crystal strain and residual stress in the sample due to the Sn$^{4+}$ doping have been depicted in the Figure 7.6. The strain and stress in the samples have been observed to decrease with increase in concentration of Sn. But for the Sn 0.4 sample, the residual stress has been observed to be higher and with pronounced compressive nature. The strain has also been observed to be meagre for the Sn 0.4 substituted sample.
7.5 FT-IR ANALYSIS

The IR spectral studies on NiFe$_2$O$_4$ and substituted ferrite compounds have been recorded from 400 to 1000 cm$^{-1}$ and are shown in Figure 7.7. The spectra elucidate the position of the ions in the crystal structure and their vibrational modes, which represents the various ordering positions on the structural properties of the synthesized compounds. In general the ferrites crystallize in spinel form with space group Fd$ar{3}$m-O$_h$. On the basis of the group theoretical calculations, the spinel ferrites are known to exhibit four fundamentals IR active modes in the vibrational spectra, of which two are higher frequency and two are low frequency bands. In the present study, the absorption bands for the synthesized ferrites are in the expected range. The pure NiFe$_2$O$_4$ shows absorption bands at 667, 603.1 and 411.8 Cm$^{-1}$. According to Waldron and Hafner (1952), the high frequency band $\nu_1$
around 603.1 cm\(^{-1}\) could be attributed to the Fe\(^{3+}\)-O stretching vibration in tetrahedral site and a low intensity band \(\nu_1'\) around 667 cm\(^{-1}\) may be attributed to the bending vibration of the tetrahedral complex. The band around 411.8 cm\(^{-1}\) could be attributed to the bond stretching of octahedral complex.

The FT-IR spectra of Ni\(_{1-x}\)Sn\(_x\)Fe\(_2\)O\(_4\) have been observed to possess three distinct bands at 600 cm\(^{-1}\), 412 cm\(^{-1}\) and 485 cm\(^{-1}\). The band around 600 cm\(^{-1}\) corresponding to stretching mode of atoms in tetrahedral site has been observed to shift to higher frequency for all the compositions of Sn\(^{4+}\) substitution up to Sn \(\leq 0.6\). The band \(\nu_2\) corresponding to octahedral complexes have shown a slight shift towards higher frequency with diminishing transmittance intensity. A new band \(\nu_3\) around 485 cm\(^{-1}\) appears on tin substitution which gets more pronounced with increase in tin concentration. This may be due to the vibration mode corresponding to Sn\(^{4+}\)-O\(^2-\) complex (Josyulu 1981). The spectrum for Sn\(_{0.8}\)Ni\(_{0.2}\)Fe\(_2\)O\(_4\) has shown a deviation from other compounds with respect to the band positions. The band \(\nu_1\) corresponding to tetrahedral complex and band \(\nu_2\) corresponding to octahedral complex has shifted to lower frequency values. Hence, the overlapping of high intense \(\nu_3\) band and low intense \(\nu_2\) band has taken place resulting in a single broad band around 490 cm\(^{-1}\). The diminishing octahedral vibrational intensity and increasing intensity of Sn\(^{4+}\)-O reveals the formation of multiphase structure as evidenced from the XRD analysis.
Figure 7.7 FTIR spectra of Sn$^{4+}$ substituted Nickel Ferrite

7.6 PHYSICAL CHARACTERIZATION

The influences of Sn substitution and Sintering in the density of the samples have been presented in Figure 7.8. The synthesized ferrite samples have been tapped in a measuring Jar and from which the initial tap density has been ascertained. The tap density of the samples has been observed to increase with increasing concentration of Sn. The maximum density of around 1.739 g/cm$^3$ has been observed for Sn-0.8 sample. The powers after compaction under 3.5 tons/cm$^2$ in to pellets of diameter 1 cm have been subjected to sintering at 1000°C. The sintered pellets have been suspended in
p-xylene solution to ascertain the density. The pellets have been observed to gain appreciable density after sintering. Similar to the powders, the densities of the pellets have been observed to increase with increase in concentration of Sn. The maximum density around 2.35 g/cm$^3$ has been observed for Sn-0.8 sample.

![Graph showing density variation with Sn$^{4+}$ concentration](image)

**Figure 7.8** Density variation with Sn$^{4+}$ concentration

### 7.7 ELECTRICAL CHARACTERIZATION

The specific conductivity relationship with temperature for all the samples measured in the temperature ranging from room temperature to 1000°C has been presented in Figure 7.9. The results enumerates that the measuring temperature has a decisive effect on the conductivity. This may be explained that at high temperatures, the hopping of polorons gets increases which results in high conductivity. Mean while similar observations made to ascertain the influences of Sn doping on the specific conductivity values shows the decrease in conductivity up to 0.6M concentration of Sn. This may
be due to the strong preference of the Sn$^{4+}$ for B-site and it has a tendency to replace some Fe$^{3+}$ ions from B-site to A-site (Balaji.S, 2005). Hence the decrease in number of Fe$^{3+}$ ions in octahedral site decreases the electronic transition between Fe$^{2+}$ and Fe$^{3+}$ ions, which results in a decrease in conductivity (Singh.M, 1998). Since the Ni$^{2+}$ and Sn$^{4+}$ have preferentially occupied strong B-site position, the following cation distribution could be assigned to the Sn$^{4+}$ substituted NiFe$_2$O$_4$.

$$\text{(Fe}^{3+})[\text{Ni}_{1-x}^{2+}\text{Sn}^{4+}_{x}\text{Fe}^{3+}_x]O_4$$

On the other hand, the behaviour of Sn$_{0.8}$Ni$_{0.2}$Fe$_2$O$_4$ compound has been observed to be quite different from other compositions. The conductivity value of the above compound increases abnormally, which is an anomalous behaviour. This may be explained that when an ion with variable valency enters the structure, charged vacancies are produced in order to maintain the local charge neutrality. Since Ni$^{2+}$ ions are substituted by Sn$^{4+}$ ions, negative ion vacancies or oxygen vacancies are created which result in high conductivity according to the following mechanism.

$$\text{Ni}^{2+} \rightarrow \text{Sn}^{4+} + 2e^-$$

Hence the following redox reactions may be suggested for the competing conducting mechanism

$$\text{Fe}^{2+} \Leftrightarrow \text{Fe}^{3+} + e^-$$

$$\text{Ni}^{3+} \Leftrightarrow \text{Ni}^{2+} + e^-$$
The activation energies calculated using the Arrhenius equation are tabulated in Table 7.2. The Arrhenius plots of the samples (Figure 7.10) have shown three distinct regions with different slopes. Generally, the change in slope is attributed to a change in conduction mechanism. The conduction at low temperature is due to the hopping of electrons between Fe\(^{2+}\) and Fe\(^{3+}\) ions, whereas at high temperatures, it is due to polaron hopping (Ravinder 2003). The activation energies show direct response to the changes in concentration of tin substitution in nickel ferrite because the substitution could change the energy band structure of the compound. The activation energy for pure nickel ferrite at higher temperature is found to be 0.575 eV, which is in agreement with the earlier reported value (Nai Sheng Chen 2000). The equation (7.6 and 7.7) infers that the current carriers are generally electrons originated from Fe\(^{2+}\) center, which act as electron donors (Rosenberg 1966). At higher temperatures the concentration of Fe\(^{2+}\) ions is
found to increase along with increased hopping of holes generated from Ni$^{3+}$ to Ni$^{2+}$ ions transition, thus resulting in increased polaron conductivity.

![Graph](image)

**Figure 7.10** Arrhenius plot of Ni$_{1-x}$Sn$_x$Fe$_2$O$_4$

**Table 7.2** Electrical band gap values Ni$_{1-x}$Sn$_x$Fe$_2$O$_4$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Energy gap (eV)</th>
<th>Region-I</th>
<th>Region-II</th>
<th>Region-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe$_2$O$_4$</td>
<td></td>
<td>0.396</td>
<td>0.793</td>
<td>0.529</td>
</tr>
<tr>
<td>Ni$<em>{0.8}$Sn$</em>{0.2}$Fe$_2$O$_4$</td>
<td></td>
<td>0.833</td>
<td>0.793</td>
<td>0.634</td>
</tr>
<tr>
<td>Ni$<em>{0.6}$Sn$</em>{0.4}$Fe$_2$O$_4$</td>
<td></td>
<td>0.872</td>
<td>0.991</td>
<td>0.872</td>
</tr>
<tr>
<td>Ni$<em>{0.4}$Sn$</em>{0.6}$Fe$_2$O$_4$</td>
<td></td>
<td>0.624</td>
<td>1.16</td>
<td>0.922</td>
</tr>
<tr>
<td>Ni$<em>{0.2}$Sn$</em>{0.8}$Fe$_2$O$_4$</td>
<td></td>
<td>0.495</td>
<td>0.656</td>
<td>0.515</td>
</tr>
</tbody>
</table>
7.8 MORPHOLOGICAL ANALYSIS

The morphological analysis of the samples has been performed using scanning electron microscopy and the resultant micrographs have been presented in Figure 7.11. The uniform distribution of grains throughout the samples has been observed and the absence of coarse aggregates could be attributed to the merit of the adopted synthesis method. The formation of SnO$_2$ has been observed to be predominant in the Sn 0.6 and Sn 0.8 sample. The SnO$_2$ has been observed in the form of small nano rods over the surface of the NiFe$_2$O$_4$ matrix. Thus the formation of NiFe$_2$O$_4$/SnO$_2$ Nano composite could be observed. Since both the NiFe$_2$O$_4$ and SnO$_2$ are being elucidated as best alternative anode materials for Li ion battery instead of graphite, the formation of Nano composite oxide of both could be expected to possess better electrochemical property. The morphological parameters such as porosity, surface roughness and grain size have been ascertained through Image J analysis and presented in the Table 7.3. From the table, it could be observed that the porosity values remains almost constant for all the samples except for Sn-0.6 sample, whose porosity is slightly higher around 50.65%. Similarly surface roughness decreases with increasing concentration of Sn. The grain size variation with Sn concentration has been observed to follow the same trend of porosity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean grain size (microns)</th>
<th>Pore aspect ratio</th>
<th>Porosity (%)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>1.7</td>
<td>1.613</td>
<td>45.2</td>
<td>133.9</td>
</tr>
<tr>
<td>Ni$<em>{0.8}$Sn$</em>{0.2}$Fe$_2$O$_4$</td>
<td>2.3</td>
<td>1.712</td>
<td>44.2</td>
<td>132.3</td>
</tr>
<tr>
<td>Ni$<em>{0.6}$Sn$</em>{0.4}$Fe$_2$O$_4$</td>
<td>2.5</td>
<td>1.562</td>
<td>45.4</td>
<td>130.6</td>
</tr>
<tr>
<td>Ni$<em>{0.4}$Sn$</em>{0.6}$Fe$_2$O$_4$</td>
<td>3.5</td>
<td>1.633</td>
<td>50.6</td>
<td>129.4</td>
</tr>
<tr>
<td>Ni$<em>{0.2}$Sn$</em>{0.8}$Fe$_2$O$_4$</td>
<td>2.1</td>
<td>1.607</td>
<td>44.4</td>
<td>128.5</td>
</tr>
</tbody>
</table>

Table 7.3 Morphological parameters of Ni$_{1-x}$Sn$_x$Fe$_2$O$_4$
Figure 7.11 (Continued)
Figure 7.11 SEM Micrograph and 3D topography of the samples
(a) NiFe$_2$O$_4$, (b) Ni$_{0.8}$Sn$_{0.2}$Fe$_2$O$_4$, (c) Ni$_{0.6}$Sn$_{0.4}$Fe$_2$O$_4$,
(d) Ni$_{0.4}$Sn$_{0.6}$Fe$_2$O$_4$ and (e) Ni$_{0.2}$Sn$_{0.8}$Fe$_2$O$_4$

7.9 ELECTROCHEMICAL ANALYSIS

The chrono potentiometry analysis results of the electrochemical
cell with NiFe$_2$O$_4$, Ni$_{0.8}$Sn$_{0.2}$Fe$_2$O$_4$ and Ni$_{0.4}$Sn$_{0.6}$Fe$_2$O$_4$ as anodes Vs Li/Li$^+$ in
the current density of 50 $\mu$/A/Cm$^2$ have been presented in Figure 7.12. The
initial discharge capacity of the NiFe$_2$O$_4$ sample has been observed to be
around 1178 mAh/g, which is around 2.5 times greater than the graphite or
carbon. In this material, the mechanism of Li interaction during
charging/discharging is highly different from the classical Li
insertion/extraction. While charging and discharging the formation/decomposition of Li$_2$O accompanied with transition metal reduction takes place and hence the plateaus have been observed while charging and discharging in the samples. In advent of this, the theoretical capacity for the formation of 8Li$_2$O is around 915 mAh/g. But the observed capacity of NiFe$_2$O$_4$ is greater than the theoretical capacity, which enumerates the presence of irreversible reaction in the lattice. This may be accounted in two ways (i) large surface area that is facilitated by the smaller particle size and (ii) irreversible reactions of NiFe$_2$O$_4$ nano particles with electrolyte accompanied with the amorphization of nanocrystalline NiFe$_2$O$_4$, when the cell potential approaches to 0V against Li/Li$.^+$ Hence a drastic reduction in the second cycle charge and discharge capacity to 814.6 and 780 mAh/g has been observed. The cell reaction responsible for irreversible capacity loss can be represented as

$$8\text{Li} + \text{NiFe}_2\text{O}_4 \rightarrow \text{Ni} + 2\text{Fe} + 4\text{Li}_2\text{O} \quad (7.9)$$

and the successive charge/discharge cycles can be expressed by the idealized reversible reaction as

$$4\text{Li}_2\text{O} + \text{Ni} + 2\text{Fe} \rightarrow \text{NiO} + \text{Fe}_2\text{O}_3 + 8\text{Li} \quad (7.10)$$
Similarly the first cycle discharge capacities of the Sn0.2Ni0.8Fe2O4 and Sn0.6Ni0.4Fe2O4 have been observed to be around 1080 and 968 mAh/g. The reduction in initial capacity clearly shows the restriction in irreversible reaction with electrolyte and thus the SnO2 has increased the stability of the electrode material in the electrolyte. The reduction in second cycle discharge capacity has also been observed, which may be attributed to the lower electrochemical activity of Sn in SnO2 environment as mentioned by Tirado et al (2003).

The difference between 1st and 2nd cycle discharge capacity of Sn substituted NiFe2O4 is lower than that of the NiFe2O4. Thus the coulombic efficiency has increased with Sn doping. The influence of Sn doping in the cycle life of NiFe2O4 has been presented in Figure 7.13. The capacity has been observed to reduce drastically for the NiFe2O4 sample. The reduction in capacity may be because, while lithium insertion the transfer of atoms from

Figure 7.12 Chrono potentiometry of Sn substituted Nickel Ferrite

![Chrono potentiometry of Sn substituted Nickel Ferrite](image)
octahedral to tetrahedral site may occur, which may distort the whole crystal structure leading to amorphization (Tirado 2003). Whereas with the Sn doping the improvement in the capacity retention could readily be observed from the figure and the capacity retention of the Ni$_{0.8}$Sn$_{0.2}$Fe$_2$O$_4$ and Ni$_{0.2}$Sn$_{0.8}$Fe$_2$O$_4$ after 50 cycles have been observed to be 85% and 91% respectively.

![Figure 7.13 Cycle Life of Sn substituted Nickel Ferrite](image)

7.10 **ELECTROCHEMICAL ANALYSIS OF LiNd$_{0.1}$Mn$_{1.9}$O$_4$/LiPF$_6$ in EC:DMC/Ni$_{0.8}$Sn$_{0.2}$Fe$_2$O$_4$ CELL**

The results of electrochemical chrono potentiometry performed at C/5 rate of the LiNd$_{0.1}$Mn$_{1.9}$O$_4$ cathode coated over Al foil and Ni$_{0.8}$Sn$_{0.2}$Fe$_2$O$_4$ anode coated over copper foil separated by a celgard separator in 1M LiPF$_6$ electrolyte in 1:1 ratio EC:DMC has been presented in Figure 7.14. The initial cycle charging capacity has been observed to be in the range 232 mAh/g and the discharge capacity has been observed to be in the range 138.2 mAh/g. The
difference in charge and discharge capacity may be because of the excessive delithiation from the cathode during charging due to the formation of Li$_2$O as per equation 7.9. The difference may also be attributed to the amorphization due to the reduction of Ni$^{2+}$ into metallic Nickel in the Ni$_{0.8}$Sn$_{0.2}$Fe$_2$O$_4$ lattice, which is partially irreversible phase transformation. From the figure no specific plateaus have been observed, this may be due to the successive reactions like Mn$^{3+}$ oxidation, Li$_2$O formation, Nickel reduction in the investigated potential window.

Figure 7.14 Chrono potentiometry of LiNd$_{0.1}$Mn$_{1.9}$O$_4$ Vs. Ni$_{0.8}$Sn$_{0.2}$Fe$_2$O$_4$
7.10.1 Cycle Life Testing

The cycle life analysis of the battery carried it under same condition has been presented in the Figure 7.15. As per the figure a drastic reduction in the performance after first cycle is noticed and this may be attributed to the limitation in delithiation of anode as a result of irreversible phase transformation. But, after first cycle the capacity has experienced a meagre capacity loss and the capacity retention is also appreciable.

Figure 7.15 Cycle life testing of LiNd$_{0.1}$Mn$_{1.9}$O$_4$ Vs. Ni$_{0.8}$Sn$_{0.2}$Fe$_2$O$_4$