Synthesis and characterization of LiNi$_x$Co$_{(1-x)}$VO$_4$ ($x = 0.2, 0.8$) cathode materials
CHAPTER – V

Synthesis and characterization of LiNi<sub>x</sub>Co<sub>(1-x)</sub>VO<sub>4</sub> (x = 0.2, 0.8) cathode materials

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Synthesis and characterization of LiNi$_x$Co$_{(1-x)}$VO$_4$ (x = 0.2, 0.8) cathode materials

5.1 Introduction

Secondary electrochemical lithium devices are a promising response to the present demand of power sources for electronic portable devices. The development of future generations of rechargeable Li-ion batteries depends critically on the advances in the field of cathode materials [1]. LiNiVO$_4$ is the first material with inverse spinel structure that has been patented as a potential cathode material for rechargeable lithium cell [2, 3]. The insertion potential of the LiNiVO$_4$ compound is around 4.8 V versus Li and this high potential clearly demonstrates that the lithium is relatively tightly bound to the host lattice. Both materials have an inverse spinel structure with Li and Ni or Co atoms occupying the octahedrally coordinated interstices and the V atoms occupying the tetrahedrally coordinated interstices [4, 5]. At the beginning little attention had been directed towards battery applications because of insufficient structural understanding and the lack of high-voltage resistance electrolyte. In order to develop cells using LiNiVO$_4$ as cathode material, electrolytes must be developed with an oxidation resistance of at least 5 V. LiCoVO$_4$ exhibit a lower voltage of 4.2 V, which makes it more suitable for some oxidation-resistant electrolytes below 4.8 V. In the previous chapter, it has noted that both LiNiVO$_4$ and LiCoVO$_4$ are poor conductors and when used as electrodes it is necessary to mix them with some good electrical conductor such as carbon black to ensure that the electrodes have sufficient electrical conductivity; this leads however to lowering material’s energy density [6, 7].

To overcome the fading problems with these electrode materials a lot of work has been done on the preparation and characterization of a mixed inverse spinel with the general
formula LiNi₅Co₁₋ₓVO₄ (x = 0.2 and 0.8) [8-11]. Some researchers extended this work with the replacement of V for other 5+ elements such as Sb [8]. Panero et al. [11] carried out a detailed study on these mixed inverse spinels prepared via a solid-state reaction at 800 °C. Their main findings were that Ni²⁺ tend to be coordinated preferentially at the tetrahedral sites and the Co²⁺ on the octahedral sites and that this distribution increases with increasing temperature. Solid state reaction is widely used to prepare cathode materials but it is a disadvantage method because of high calcination, bigger particle sizes, impurity and long reaction time [12-13]. Therefore, the wet chemical routes such as sol-gel [14], co-precipitate [15] and hydrothermal [16] is the way to synthesized good physical and chemical properties of cathode material. They are advantage because they have the ability to control homogeneity, particle sizes and economy. In this chapter, sol-gel method has been used to synthesize lithium nickel cobalt vandate powder at low temperature.

5.2 Sol-gel synthesis of LiNi₅Co₁₋ₓVO₄

LiNi₅Co₁₋ₓVO₄ powder was synthesized by sol-gel method, which is schematically represented in Fig. 5.1. In sol-gel method, stoichiometric amounts of lithium nitrate (98 %, Merck), nickel nitrate (99 %, Loba chemie), cobalt nitrate (97 %, Merck) and ammonium metavanadate (99 %, Qualigens fine chemicals) were mixed thoroughly and dissolved in de-ionized water. The solution was stirred continuously with gentle heating till a homogeneous solution was obtained. The solution of citric acid was added to the solution as a complexing agent followed by the addition of ethylene glycol. Herein, ethylene glycol acts as a gelling agent. The process of stirring and heating were continued to get thick gel. The formed gel was dried at 110 °C for removing moisture and to get dried mass. The final product was ground and calcined at 700 °C for 6 hour to get the homogeneous product of crystalline LiNi₅Co₁₋ₓVO₄ powder.
5.3 Thermal analysis

The thermogravimetric (TG) curves obtained for the as prepared powders corresponding to LiNi$_{x}$Co$_{(1-x)}$VO$_4$ ($x = 0.2, 0.8$) are shown in Figure 5.2. The thermal behavior is similar for the two samples. The TG plots show three discrete weight-loss steps, and no more weight loss above 700 °C. The observed initial weight loss is attributed to the evaporation of residual water. The weight loss in the second temperature range 200 to 350 °C is due to the decomposition of NH$_3$ and NO$_3$. The weight loss in the third temperature range 350 to 700 °C can be attributed to the release of oxides of carbon during the pyrolysis of citric acid. No significant weight loss is observed above 700 °C. The weight loss stops at 700 °C, which confirms the formation temperature of both compounds. Hence the powders were calcined at 700 °C for 6h in air atmosphere.
5.4 Structural analysis

The phase identification of the product was carried out by powder X-ray diffractometer. Figure 5.3 shows the powder X-ray diffraction patterns of samples LiNi$_{0.8}$Co$_{0.2}$VO$_4$ (a) and LiNi$_{0.2}$Co$_{0.8}$VO$_4$ (b). All the diffraction lines are well indexed in the cubic system with $Fd\bar{3}m$ (227) space group. Both XRD patterns display a single-phase structure without any impurity phase. In addition, the integrated intensity ratio of (3 1 1) to (2 2 0) peaks, $I_{3\,1\,1}/I_{2\,2\,0}$, also reported in Table 5.1, is considered as a sensitive parameter to determine the cationic distribution in the lattice. The smaller $I_{3\,1\,1}/I_{2\,2\,0}$ is, the higher structural deviation is from hexagonal to cubic symmetry. A value less than 1.2 means that undesirable cation mixing would appear. For our synthesized powders by the sol-gel method, we find $I_{3\,1\,1}/I_{2\,2\,0} = 1.537$ and 1.708 for LiNi$_{0.8}$Co$_{0.2}$VO$_4$ (a) and LiNi$_{0.2}$Co$_{0.8}$VO$_4$ (b) cathode materials respectively, which suggest a homogeneous distribution of the cations within the structure of both samples.
The narrow profile of the diffraction lines indicates a high crystallinity of the synthesized powders and suggests homogeneous distribution of cations within the structure. The mean lattice coherence length $L$ was calculated from XRD patterns, using Scherrer’s formula [17],

$$L = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$$

where $\beta$ is the full width at half maximum of any Bragg line in radians, the constant $K = 0.9$, $\lambda$ is the wavelength of the X-ray, $\theta$ is the corresponding Bragg angle. The Scherrer’s formula has been applied to predominant XRD lines, namely $(2 \ 2 \ 0)$, $(3 \ 1 \ 1)$, $(4 \ 0 \ 0)$, $(3 \ 3 \ 3)$ and $(4 \ 4 \ 0)$. The coherence length was found different for the lines considered with the hierarchy: $L_{2 \ 2 \ 0} > L_{3 \ 1 \ 1} > L_{4 \ 0 \ 0} > L_{3 \ 3 \ 3} > L_{4 \ 4 \ 0}$. The mean values of $L$ are listed in Table 5.1.

Figure 5.4a and 5.4b shows the results of the refinement pattern for LiNi$_{0.8}$Co$_{0.2}$VO$_4$ and LiNi$_{0.2}$Co$_{0.8}$VO$_4$ at room temperature, where good agreement between the observed and calculated patterns were obtained. The refinement was carried out such that Li, V and O is fully occupied, and the other site occupancies are variable. The weighted factor $R_{wp}$ is 2.12 %
and 1.55 %. The cell parameters with \( a = 8.2269 \ \text{Å} \) and \( 8.2698 \ \text{Å} \) can be obtained from the result of the Rietveld refinement. The reasonably small \( R_{wp} \) factors suggest that both samples were single-phase compounds can be obtained under our experimental process, and no impurity phases can be detected under the resolution of our X-ray diffractometer. The refined structure and structural parameters of both compounds are given in Table 5.1. It can be seen that the structure of the sample is highly dependent on the synthesis temperature.

![Graph of experimental, calculated, and difference patterns for the Rietveld refinement of LiNi_{0.8}Co_{0.2}VO_4.](image)

Fig. 5.4a Experimental (X), calculated (solid line) and difference (lower line) patterns for the Rietveld refinement of LiNi_{0.8}Co_{0.2}VO_4. Reflection positions are marked by small vertical bars and crystallographic representation of LiNi_{0.8}Co_{0.2}VO_4 structure.
Fig. 5.4b Experimental (X), calculated (solid line) and difference (lower line) patterns for the Rietveld refinement of LiNi_{0.2}Co_{0.8}VO_{4}. Reflection positions are marked by small vertical bars and crystallographic representation of LiNi_{0.2}Co_{0.8}VO_{4} structure.
Table 5.1  Structural parameters obtained from Rietveld refinement of the XRD data for LiNi\textsubscript{x}Co\textsubscript{1-x}VO\textsubscript{4} (x = 0.2, 0.8) cathode materials.

<table>
<thead>
<tr>
<th>Formula: LiNi\textsubscript{0.8}Co\textsubscript{0.2}VO\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>a=b=c= 8.2269 Å, Rp = 0.0406, Rwp = 0.0212, χ^2 = 11.55; I\textsubscript{311}/I\textsubscript{220} = 1.537; L = 2.54 nm</td>
</tr>
<tr>
<td><strong>Atom</strong></td>
</tr>
<tr>
<td>Li</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Co</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula: LiNi\textsubscript{0.2}Co\textsubscript{0.8}VO\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>a=b=c= 8.2698 Å, Rp = 0.0301, Rwp = 0.0155, χ^2 = 4.64; I\textsubscript{311}/I\textsubscript{220} = 1.708; L = 2.17 nm</td>
</tr>
<tr>
<td><strong>Atom</strong></td>
</tr>
<tr>
<td>Li</td>
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<td>Ni</td>
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<tr>
<td>Ni</td>
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</table>
5.5 FESEM analysis

The FESEM images of synthesized cathode materials showed that the particles have controlled morphology generally are submicron in size, and also the particles are interconnected well, which would facilitate good transport properties. Figure 5.5(b) and (d) of FESEM microphotographs of both compounds clearly reveal a dramatic increase of the dimension of the crystallites and large agglomerated clusters with dimension in the order of hundred nanometers.

![FESEM images](image)

Fig. 5.5 FESEM images of (a, b) LiNi0.8Co0.2VO4 and (c, d) LiNi0.2Co0.8VO4 samples.

5.6 TEM studies

Figure 5.6 shows the particle morphology of LiNi_{x}Co_{1-x}VO_{4} (x = 0.2, 0.8) powders obtained using transmission electron microscopy (TEM). One can clearly observe that there were irregular etch pits on the particle surface and the edge of the particle was blurry and zigzag
layer particle in Figure 5.6(c). On the contrary, etch pits were not present and smooth lines appeared in Figure 5.6(a). These results show that agglomeration of the particles can effectively reduced in the materials. The average particle size is estimated to be 70-80 nm. The selected area electron diffraction patterns shown in Fig. 5.6 (b, d) were indexed and the pattern shows several blurry concentric rings of bright spots with different intensities. The values of d-spacing corresponding to the diffraction planes of crystalline product and compared with those of the JCPDS standard. It was found that the diffraction rings of the product and that the diffraction pattern agrees well that of LiNi_{x}Co_{(1-x)}VO_{4} (x = 0.2, 0.8).

Fig. 5.6 TEM and SAED pattern of (a, b) LiNi_{0.8}Co_{0.2}VO_{4} and (c, d) LiNi_{0.2}Co_{0.8}VO_{4} particles.
5.7 FTIR analysis

Figure 5.7 shows the FTIR spectra for LiNi$_{0.2}$Co$_{0.8}$VO$_4$ and LiNi$_{0.8}$Co$_{0.2}$VO$_4$ cathode materials heat treated at 700 °C for 6h. There is a broad strong band in the region 900-500 cm$^{-1}$ that can be assigned to a stretching vibration between the oxygen and V$^{5+}$ ions of the VO$_4$ tetrahedron, which has A$_1$ symmetry. The sub band observed in the region 900 – 500 cm$^{-1}$, which were shifted slightly compared with the reported values of LiNiVO$_4$ [18] and LiCoVO$_4$ [19]. This shift in band positions is attributed to substitution of Co ion in the lattice. The broadness of the 900-500 cm$^{-1}$ region could be tentatively explained in terms of the asymmetrical bonding of the VO$_4$ tetrahedron, in which the cations, namely Li, Ni and Co, may be bonded with each oxygen atom of a VO$_4$ tetrahedron. As a result, some symmetry is introduced into the VO$_4$ unit without disturbing the overall cubic symmetry of the elementary unit cell.

![FTIR spectra of the products prepared by sol-gel method.](image)
5.8 Micro Raman spectra analysis

Raman spectroscopy is very sensitive in differentiating various kinds of crystal symmetries whose atomic arrangements are closely related to one another [20, 21]. Figure 5.8(a) and (b) shows the Raman spectra of LiNi$_{0.8}$Co$_{0.2}$VO$_4$ and LiNi$_{0.2}$Co$_{0.8}$VO$_4$ cathode materials synthesized by sol-gel method at 700 °C. It shows bands of the stretching (A$_{1g}$ symmetry) and bending (E$_g$ symmetry) V-O modes in VO$_4$ tetrahedra. The stretching and bending modes were respectively detected at 813 and 323 cm$^{-1}$ for LiNiVO$_4$, and at 803 and 304 cm$^{-1}$ for LiCoVO$_4$ [18]. The bands of LiNiVO$_4$ appear at higher wavenumbers than those of LiCoVO$_4$. The stretching and bending bands of LiNi$_{0.8}$Co$_{0.2}$VO$_4$ and LiNi$_{0.2}$Co$_{0.8}$VO$_4$ are between those of LiNiVO$_4$ and LiCoVO$_4$.

![Raman spectra](image)

Fig. 5.8 Laser Raman spectra of (a) LiNi$_{0.8}$Co$_{0.2}$VO$_4$ and (b) LiNi$_{0.2}$Co$_{0.8}$VO$_4$ cathode materials.
The substitution of Ni in LiNiVO$_4$ by Co makes the vibration bands of all metal-oxygen in the solid solution weaker by shifting the bands from higher to lower wavenumbers [21].

5.9 XPS studies

X-ray photoelectron spectroscopy (XPS) is a well established, non-destructive technique for evaluation of valence states of the metals/ions in solids and is extensively applied in the characterization of our cathode materials [22]. Fig 5.9(a) and (b) shows the Ni, Co, V and O XPS core level spectra for LiNi$_{0.8}$Co$_{0.2}$VO$_4$ and LiNi$_{0.2}$Co$_{0.8}$VO$_4$ prepared at 700 °C (7 h; sol-gel method). The binding energies of the Li 1s core levels emission peak for the two compounds was located at 54.5 eV and appeared as a broadened signal. This value is close to that for Li$_2$O [23].

The Ni 2p$_{3/2}$ XPS spectra show the characteristic satellite peak with the binding energy (BE) at 861.7 eV. Such satellite peaks are also observed in NiO, LiNiO$_2$, Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ and in the spinel, Li(Mn$_{1.5}$Ni$_{0.5}$)O$_4$ [24-26]. The reason for such satellite peak is explained as due to the multiple splitting in the energy levels of the Ni-oxides [24, 25]. The best fit for the Ni 2p$_{3/2}$ spectrum gives two BE values. The major peak with a BE of 852.7 eV corresponds to the Ni$^{2+}$, containing compounds, such as NiO and the less prominent one at 855.8 eV corresponds to Ni$^{3+}$, as observed in Ni$^{3+}$ containing compounds such as LiNiO$_2$. The shift indicates an increase in the positive interaction between the electrons of 2p$_{3/2}$ and the nucleus increases resulting in higher energy needed to pull the electron from Ni$^{3+}$ level (Ni$^{3+}$ has fewer electrons). The XPS results showed that the predominant state of Ni in the synthesized material is 2+ [27].

The Co 2p core level spectra show that Co 2p$_{3/2}$ peaks are in the 778-782 eV range and Co 2p$_{1/2}$ peaks are in the 792-797 eV range. The spectrum also has weak satellite peaks. The Co 2p$_{3/2}$ peaks was fit into a single peak with the binding energy of 780.7 and 780.6 eV.
which matches with the binding energy reported for Co$^{3+}$ in LiCoO$_2$. The binding energy of Co is indicative of Co$^{3+}$ in low spin configuration. The peaks at 795.3 and 796.6 eV corresponding to Co 2p$_{1/2}$ is assigned to high spin Co$^{2+}$ ions [28].

The binding energies of V are located at 522.3 and 515.5 eV for 2p$_{1/2}$ and 2p$_{3/2}$ splits, respectively, and the difference is round about 6.8 eV, which is closer with binding energies of V$^{5+}$ ions [29]. So this can be concluded that the oxidation state of V in the compound is 5+.

The O 1s spectra shows, which has a main peak around 530 eV and another peak at 531.2 eV that can be deconvoluted to two individual contributions [30]. The peak at 530 eV can be assigned to O$^{2-}$ ions, and the shoulder peak could represent a degree of oxidation more than O$^{2-}$ due to transition metal-oxygen covalent bonds. Accordingly, the binding energies observed at 530 eV and 531.2 eV could be assigned as contributions from the Co-O and Ni-O bonds, respectively, implying the influence of the covalent nature of their bonds. In summary, the XPS results showed that the predominant oxidation states of Ni, Co and V are 2+, 3+, and 5+ respectively.
Fig. 5.9a XPS spectra of LiNi$_{0.8}$Co$_{0.2}$VO$_4$ cathode material. Deconvolution of the peaks is shown.
Fig. 5.9b XPS spectra of LiNi$_{0.2}$Co$_{0.8}$VO$_4$ cathode material. Deconvolution of the peaks is shown.
5.10 Conductivity studies

Electrical properties of the compound were determined using impedance spectroscopy.

Fig. 5.10 Nyquist impedance spectra of (a) LiNi_{0.8}Co_{0.2}VO_4 and (b) LiNi_{0.2}Co_{0.8}VO_4 at different temperatures.

Figure 5.10 shows the Nyquist plots relative to LiNi_{x}Co_{(1-x)}VO_4 at different x values from x = 0.2 and x = 0.8. As shown in both figures, the semicircles have a high frequency intercept on the Z' that represents the bulk resistance of the compound. At lower frequencies, the resistance related to the charge transfer between the electrolyte and the active material of the compound. A very low frequency region of the straight line is attributed to the diffusion of the lithium ions into the bulk of the electrode material or the so-called Warburg diffusion. The value of bulk resistance (R_b) was determined from the intersection of the arc with real axis of the impedance Z'. The magnitude of dc conductivity (\(\sigma\)) value has been calculated from R_b by using the following relation [31],

\[
\sigma = \frac{l}{R_b A} \text{ S cm}^{-1}
\]

where, \(R_b\) is bulk resistance of the sample,

\(l\) is the thickness of the pellet, and
\( A \) is the area if the sample.

The small increase in dc conductivity with temperature is due to the increase in the thermally activated drift mobility of ions according to hopping conduction mechanism. As temperature increases, the radius of the arc corresponding to the bulk resistance of the sample decreases indicating as activated conduction mechanism. The conductivity values are calculated from the above relation and it has been given in Table 5.2.

Table 5.2 Conductivity values of LiNi\(_x\)Co\(_{1-x}\)VO\(_4\) (\( x = 0.2, 0.8 \)) at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>LiNi(_0.8)Co(_0.2)VO(_4)</th>
<th>LiNi(_0.2)Co(_0.8)VO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \sigma_{dc} ) (S cm(^{-1}))</td>
<td>( \sigma_{dc} ) (S cm(^{-1}))</td>
</tr>
<tr>
<td>30</td>
<td>( 3.9 \times 10^{-4} )</td>
<td>( 7.7 \times 10^{-5} )</td>
</tr>
<tr>
<td>60</td>
<td>( 2.1 \times 10^{-4} )</td>
<td>( 8.1 \times 10^{-5} )</td>
</tr>
<tr>
<td>80</td>
<td>( 2.2 \times 10^{-4} )</td>
<td>( 8.9 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

Fig. 5.11 Arrhenius plot of dc conductivity from complex impedance plot.

Generally, conductivity in this kind of materials obeys the Arrhenius law, which can be expressed as follows:

\[
\sigma_{dc} T = \sigma_0 \exp(-\frac{E_a}{k_B T})
\]
where $\sigma_{dc}$ is the dc conductivity, $\sigma_0$ is the pre-exponential factor, $T$ is the temperature in K, $E_\sigma$ is the dc conductivity activation energy and $k_B$ is the Boltzmann’s constant. Arrhenius plots of the LiNi$_x$Co$_{(1-x)}$VO$_4$ ($x = 0.2, 0.8$) shown in Fig. 5.11. The activation energy $E_\sigma$ for the conduction process was extracted from the slope of the straight line plot of $\log (\sigma_{dc} \cdot T)$ against reciprocal temperature $1000/T$ in each case the magnitude of Li$^+$ ion conductivity is at higher temperature. The maximum value of conductivity in LiNi$_x$Co$_{(1-x)}$VO$_4$ ($x = 0.2, 0.8$) was found to be $2.2 \times 10^{-4}$ and $8.9 \times 10^{-5}$ S cm$^{-1}$ at 80 °C.

5.11 Dielectric spectra analysis

The measured impedance and phase angle data were used to calculate the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the complex dielectric permittivity as,

$$\varepsilon^* = \frac{1}{j\omega C_0 Z^*}$$

where $Z^*$ is the complex impedance, $C_0 = \varepsilon_0 A/d$, $A$ is the area of the sample, $d$ is thickness of the samples and $\varepsilon_0$ is the permittivity of the free space. Figure 5.12 shows the frequency dependent of real and imaginary part of complex permittivity $\varepsilon^*$ respectively for the LiNi$_x$Co$_{(1-x)}$VO$_4$ ($x = 0.2, 0.8$) compound. The observed variation in $\varepsilon'$ with frequency is ascribed to the formation of a space charge region at the electrode/sample interface, which is familiarly known as $\omega^{-1}$ variation or the non-Debye type of behavior. The dispersion in $\varepsilon^*$ is attributed to the lack of translational invariance in the free energy barriers for ion diffusion. The increase of $\varepsilon'$ in lower frequencies can be attributed to the contribution from polarization of charges. In the low frequency region, the ions jump in the field direction and pile up at sites with high free energy barrier in the field direction after successfully hopping sites with low free energy barrier. This piling of charges leads to a net polarization of the ionic medium.
and hence a large contribution to the low frequency value of $\varepsilon'$. At high frequencies the periodic reversal of the field takes place so rapidly that there are no excess ion jumps in the field direction. The $\varepsilon'$ remains nearly constant at the high frequency which is probably the result of rapid polarization process with no ionic movement contribution. At this frequency the ions can only oscillate without reaching the sample electrode interface [32].

Fig. 5.12 Real and imaginary part dielectric spectra of (a, b) LiNi$_{0.8}$Co$_{0.2}$VO$_4$ and (c, d) LiNi$_{0.2}$Co$_{0.8}$VO$_4$ cathode materials.

Typical variation of imaginary part of permittivity with frequency is shown in Fig. 5.12 (b, d). In the present case, an upward trend in $\varepsilon''$ at low frequencies, is attributed to dc conductivity with electrode polarization, i.e., the conductivity losses predominate and hence
at all temperatures the imaginary part of permittivity $\varepsilon''$ shows $1/\omega$ dependence on frequency. Also $\varepsilon''$ is found to increase with increase temperature and dielectric loss peak has not been observed. However, the data were converted into electric modulus where the contributions from electrode effects are minimized [33].

5.12 Modulus spectra analysis

An alternative approach to investigate the electrical response of materials is the complex electric modulus. The electrode polarization [34, 35] effect is minimized in this representation. The complex electric modulus can be represented by the following equation [36, 37].

![Modulus spectra](image)

Fig. 5.13 Real and imaginary part modulus spectra of (a, b) LiNi$_{0.8}$Co$_{0.2}$VO$_4$ and (c, d) LiNi$_{0.2}$Co$_{0.8}$VO$_4$ cathode materials.
\[ M' = \frac{1}{\varepsilon'} = j\omega C_0 Z' \]

where \( C_0 \) is the vacuum capacitance of the cell. Fig. shows the variation of real and imaginary part of electric modulus as function of frequency at different temperatures.

In the variation of real part of electric modulus, at lower frequencies \( M' \) trends to be very small, confirming that the electrode effects make a negligible contribution and hence may be ignored when the data are analyzed in modulus formalism [38]. In the figure, \( M' \) reaches to constant value \( M_\infty (M_\infty = 1/\varepsilon_\infty) \) at high frequencies for all temperatures and this is due to relaxation processes, which are spread over a range of frequencies. The variation of \( M'' \) with frequency is shown in Fig. 5.13 (b, d) at different temperatures. In the \( M'' \) plot, shows an asymmetric behavior with respect to \( M'' \) peak at all measured temperatures. The peak in the \( M'' \) plot shifts toward peak higher frequencies with increase in temperature. Two apparent relaxation regions appear, the region towards left of the peak is associated to the conduction process where the charge carriers are mobile over a long distance. The region towards right of the peak associated to the relaxation polarization process where the charge carriers are spatially confined to the potential wells. Similar behavior was observed for the other samples also.

5.13 Electrochemical performance

Figure 5.14 shows the charge-discharge cycling of LiNi\(_x\)Co\(_{1-x}\)VO\(_4\) (\( x = 0.2 \) and 0.8) cathode material were carried out up to 30 cycles at ambient temperature. For LiNi\(_x\)Co\(_{1-x}\)VO\(_4\) (\( x = 0.2 \) and 0.8) cathode materials prepared at 700 °C, cycling was performed with upper cut-off voltages 4.3 and 4.4 V. In both cases, the lower cut-off voltage was 3.0 V. For clarity, only selected cycles are shown. The initial charge capacities of the LiNi\(_x\)Co\(_{1-x}\)VO\(_4\) (\( x = 0.2 \) and 0.8) cathode were 96 and 51 mA h/g and discharge capacities were 84 and 48 mA h/g, respectively. After 30 cycles, the discharge capacities were 58 and 32 mA h/g, respectively.
and are plotted as a function of cycle number. As nickel content $x$ increased to 0.8, the electrolyte oxidation occurred at such a high voltage causing a rapid decline in capacity during the initial cycle. So we were unable to obtain adequate cycling performance for cell with $x = 0.8$. The observed capacity values are smaller and comparing with these compounds we have obtained the better electrochemical performance of $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{VO}_4$ cathode material.

![Charge discharge curves and cyclic performance of (a, b) $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{VO}_4$ and (c, d) $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{VO}_4$ cathode materials.](image)

Fig. 5.14 Charge discharge curves and cyclic performance of (a, b) $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{VO}_4$ and (c, d) $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{VO}_4$ cathode materials.
5.14 Cyclic voltammetry

Cyclic voltammetry (CV) is a useful electrochemical tool wherein the changes taking place in an electrochemical reaction is monitored by measuring the current-potential responses. Fig. 5.15 shows the CV recorded between 2.8 and 4.8 V. It could be seen that the cathodic peaks of LiNi_{0.8}Co_{0.2}VO_{4} and LiNi_{0.8}Co_{0.2}VO_{4} at 4.08 and 4.31 V, respectively. And the corresponding anodic peaks shift from 3.80 to 3.85 V. The difference between cathodic and anodic potential demonstrates the reversibility of the intercalation and deintercalation of lithium ions in the electrode materials, and lower the value of potential difference give better reversibility of the electrode materials [39, 40]. The present results show, the mixed oxides with y = 0.2 and 0.8, a modest result in the discharge capacity but a good performance in cycle life provided the range of charge voltage is limited to 4.6 V to prevent electrolyte decomposition.

![Cyclic voltammogram](image)

Fig. 5.15 Cyclic voltammogram of LiNi_{x}Co_{(1-x)}VO_{4} (x = 0.2, 0.8) compound.
5.15 Conclusions

LiNi$_x$Co$_{1-x}$VO$_4$ (x = 0.2 and 0.8) cathode materials were prepared by sol-gel method at 700 °C in air and characterized by X-ray diffraction, FESEM, laser Raman and XPS measurements. Rietveld refinements show that these cubic structure belong to the inverse-spinel structure with $Fd\bar{3}m$ space group. FESEM and TEM micrograph confirmed the size of the particle formed by the sol-gel process. Analysis of Raman spectra has been carried out using a local environment model including VO$_4$ tetrahedra, (Ni, Co)$_6$O$_6$ and LiO$_6$ octahedra as vibrational local units and the linear relationships between mode frequency and composition confirmed that all the members of the LiNi$_x$Co$_{1-x}$VO$_4$ series in between LiNiVO$_4$ and LiCoVO$_4$. XPS studies indicated that the oxidation states of nickel, cobalt and vanadate are +2, +3 and +5, respectively. Charge-discharge cycling tests carried out in the range 3.0 to 4.6 V showed that better reversible capacity of 58 – 84 mAhg$^{-1}$ for LiNi$_x$Co$_{1-x}$VO$_4$ (x = 0.2) cathode material applicable to lithium battery. Cyclic voltammetry studies revealed the reversibility and structural stability during cycling.
References


