Chapter 4

AC Conductivity of Nanostructured Nickel Oxide
AC CONDUCTIVITY OF NANOSTRUCTURED NICKEL OXIDE

4.1 Introduction

The electrical properties of nanostructured materials are reported to be markedly varied from those of their bulk counterparts. In nanostructured materials, over and above the possible modifications of the electronic band structure, the large volume fraction of the interfacial region and lattice defects play a decisive role in determining the electrical properties.\textsuperscript{1-11}

AC conductivity of single crystalline NiO at room temperature is reported to be less than $\sim 10^{-13}$ ohm$^{-1}$ cm$^{-1}$, which is of the same order as its dc conductivity.\textsuperscript{12-28} Different approaches have been used by different investigators for accounting for the experimentally observed ac electrical response of NiO in the form of single crystals, consolidated coarse-grained polycrystals and thin films.\textsuperscript{12-40} It was observed that the dc conductivity, $\sigma_{dc}$, of nanostructured nickel oxide samples is increased by six to eight orders of magnitude over that of undoped NiO single crystals (Chapter 3). This chapter contains a detailed analysis of the ac conductivity of nanostructured nickel oxide samples consolidated in the form of pellets as a function of temperature, frequency of the applied signal and average grain size.

4.2 Experimental

For the study of ac conductivity, nanostructured nickel oxide samples of five different average grain sizes (same as those of the samples used in the study of
dc conductivity) were used. For reference, sample codes and the average grain sizes are reproduced in Table 4.1.

Table 4.1. Sample codes assigned to nanostructured nickel oxide samples used for the ac conductivity study.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Average grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>2-3</td>
</tr>
<tr>
<td>N2</td>
<td>4-5</td>
</tr>
<tr>
<td>N3</td>
<td>5-7</td>
</tr>
<tr>
<td>N4</td>
<td>12-13</td>
</tr>
<tr>
<td>N5</td>
<td>16-17</td>
</tr>
</tbody>
</table>

AC electrical measurements of the nanostructured nickel oxide samples consolidated in the form of cylindrical pellets were carried out in an evacuated dielectric cell. Before taking the actual measurements, each pellet was subjected to a heat and cool run between 313 and 413 K in vacuum in order to remove any residual strain due to pelletisation. The complex impedance $Z^*$ and the phase angle $\theta$ were measured at different signal frequencies ranging from 50 Hz to 3 MHz using a HIOKI Model 3531 Z-Hi Tester. The temperature of the sample pellets was varied from 313 to 413 K using an in-built heating system and electrical measurements were performed at an interval of 20 K, each temperature being kept constant with an accuracy of ±1 K. The electrical measurements were limited to a maximum temperature of 413 K to avoid any grain growth of the samples and to ensure that the average size of the samples remained the same during the measurements. Sufficient stabilization time was ensured at each particular temperature. The repeatability of the readings was found to be good. Parallel equivalent circuit model was chosen for analyzing the data due to the high dielectric loss exhibited by the samples.$^{41,42}$ The ac conductivity of the samples was determined from the measured values of the
impedance, $Z^*$, and the phase angle, $\theta$, using the equation, $\sigma_m = [(d \cos \theta) / (|Z^*| A)]$, where $d$ and $A$ are respectively the thickness and the area of cross-section of the cylindrical pellet.

4.3 Results

Figures 4.1 to 4.4 shows the variation of the measured ac conductivity, $\sigma_m$, with frequency of the applied ac signal at different temperatures for the nanostructured nickel oxide samples.

Figure 4.1. Frequency dependence of measured ac conductivity, $\sigma_m$, at different temperatures for (a) sample N2 and (b) sample N1.
Figure 4.2. Frequency dependence of measured ac conductivity, $\sigma_m$, at different temperatures for sample N3.

Figure 4.3. Frequency dependence of measured ac conductivity, $\sigma_m$, at different temperatures for sample N4.
The numerical values of ac conductivity of all the five samples are found to be much larger than that for single crystalline nickel oxide, which is much less than about $10^{-13}$ ohm$^{-1}$ cm$^{-1}$ at room temperature. For all the samples, $\sigma_m$ is found to be more or less independent of frequency of the applied ac signal below about 50 kHz, while at higher frequencies, $\sigma_m$ increases with increase in the frequency of the applied signal. Also, for all the samples the measured ac conductivity increases with increase in temperature with the temperature dependence being more pronounced at higher frequencies.

In the following section, a detailed analysis of the observed variation of the ac conductivity of nanostructured nickel oxide samples with frequency of the applied signal, temperature and average grain size is presented.
4.4 Discussion

In the dc conductivity study presented in Chapter 3, it was observed that $\sigma_{\text{DC}}$ of nanostructured nickel oxide samples were enhanced by six to eight orders of magnitude over that of undoped NiO single crystals. This enhancement in dc conductivity was attributed to the high concentration of Ni$^{2+}$ vacancies (of the order of $10^{14}$ to $10^{16}$ cm$^{-3}$) associated with the defective interfacial region of nanostructured nickel oxide samples.

In the present study, the measured ac conductivity $\sigma_m$ of nanostructured nickel oxide samples are found to be larger by six to eight orders of magnitude over that of NiO single crystals. This is as expected since, though the charge transfer mechanisms in presence of dc and an ac fields are distinctly different in NiO, the charge carriers involved in both cases are holes associated with Ni$^{2+}$ vacancies. The high density of Ni$^{2+}$ vacancies explains the large enhancement in the ac conductivity of the order of six to eight in magnitude for the nanostructured samples in comparison with that of NiO single crystals.

Detailed discussion of the possible conductivity mechanisms in NiO have been reported in the literature. As already mentioned in Chapter 3, in undoped NiO, the conductivity is primarily associated with Ni$^{2+}$ vacancies. The Correlated Barrier Hopping Model (CBH Model) has been successfully employed by many workers for analyzing the electrical conductivity data of a number of materials including NiO which exhibit defect dependent conductivity.

According to the CBH model, in NiO, the energy required for the hopping of holes from one Ni$^{3+}$ site to Ni$^{2+}$ or O$^{2-}$ site depends on a number of factors. At a single lattice site, a short range localization energy will arise because of the random fluctuations in site separation or atomic configurations or polaron effects. In addition, associated with each Ni$^{2+}$ vacancy, there exists a long range defect potential well which affects the localization energy within a radius of a few lattice spacing. CBH model proposes two types of charge carrier movements in NiO as follows,
(i) Inter-well hopping involving the hopping of a hole from a Ni$^{3+}$ ion located in one defect potential well to a Ni$^{2+}$ or O$^{2-}$ ion in an adjacent defect potential well.

(ii) The hopping of holes between ions within one defect potential well constituting intra-well hopping.

In presence of a dc electric field, the probability of occurrence of intra-well hopping is zero and all the charge carriers (holes) in the material take part in inter-well hopping.\textsuperscript{28,29} Thus when a dc electrical field is applied, only the inter-well charge transfer process occurs resulting in pure dc conduction. However, in presence of an ac signal, both the aforementioned charge transfer mechanisms do have a finite probability of occurrence, their relative probabilities being dependent on the energy of the charge carriers, frequency of the applied signal, and concentration, mean site separation, depth and extent of percolation of the potential wells associated with Ni$^{2+}$ vacancies.\textsuperscript{28,29} Thus the measured ac conductivity, $\sigma_m$, is constituted by a frequency independent dc component $\sigma_{dc}$ (due to inter-well hopping) and a frequency dependent ac component $\sigma_{ac}$ (due to intra-well hopping) i.e. $\sigma_m = \sigma_{dc} + \sigma_{ac}$.\textsuperscript{28,29} It may be noted that the dc contribution to $\sigma_m$, viz. $\sigma_{dc}$, will be slightly less than the conductivity in presence of a dc field, $\sigma_{DC}$, since, even at very low frequencies of the applied ac signal (frequency $\rightarrow$ 0) the probability of occurrence of intra-well hopping has a finite value and only a portion of the total number of charge carriers in the material take part in inter-well hopping.

In order to find the dc contribution ($\sigma_{dc}$) to the measured ac conductivity a two step curve fitting procedure devised by Jonscher was employed.\textsuperscript{43,44} In the first step nonlinear least square fitting was done on $Y''$ - $\omega$ plots using the equation $Y'' = A_n (\omega)^n$ where $Y'' = \sin \theta / |Z^*|$ is the imaginary part of the complex admittance function, $A_n$ is a constant, $\omega = 2\pi f$ is the angular frequency of the applied ac signal and n (with 0<n<1) is a measure of the deviation of the sample from ideal Debye behavior.\textsuperscript{43,44} In the second step, nonlinear least square fitting was done on $Y'$ - $\omega$ plots using the equation $Y' = [G_v + \omega^n A_n \cot (n\pi / 2)]$ using the values of $A_n$ and n obtained...
from the first curve fitting procedure. Here $Y' = \cos \theta / |Z^*|$ is the real part of the complex admittance function (measured ac conductance) and $G_v$ is the pure dc contribution to $Y'$. From $G_v$ values, $\sigma_{dc}$ values were calculated knowing the dimensions of the pellets for all the samples. The results of curve fitting procedure for the sample N2 at 333 K are shown in Figure 4.5.

![Figure 4.5](image_url)

**Figure 4.5.** Results of curve fitting procedure for sample N2 at 333 K
(a) $Y' - \omega$ plot and (b) $Y'' - \omega$ plot.

Numerical values of the dc contribution ($\sigma_{dc}$) to the measured ac conductivity for the samples at different temperatures estimated from the aforementioned curve fitting procedure are listed in Table 4.2.
Table 4.2. $\sigma_{dc}$ values for nanostructured nickel oxide samples at different temperatures estimated from curve fitting procedure.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$\sigma_{dc}$ (ohm$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>313 K</td>
</tr>
<tr>
<td>N1</td>
<td>$5.15 \times 10^{-6}$</td>
</tr>
<tr>
<td>N2</td>
<td>$8.84 \times 10^{-6}$</td>
</tr>
<tr>
<td>N3</td>
<td>$1.12 \times 10^{-5}$</td>
</tr>
<tr>
<td>N4</td>
<td>$9.43 \times 10^{-7}$</td>
</tr>
<tr>
<td>N5</td>
<td>$7.52 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

The sample pellets used in the present study were dry-pressed and were not sintered and hence some porosity may be present in them. Since, the samples were prepared by thermal decomposition of the carbonate precursor followed by annealing, the possibility of presence of pore fluids and adsorbed water is exceedingly small. The only possible moisture content should be that from air occluded during pelletisation. However, all the pellets were subjected to heat and cool runs between 313 and 413 K in vacuum before the electrical measurements and hence the moisture content and occluded air, if any, might almost completely be removed. In this analysis it is assumed that the contribution of pores to ac conductivity data of the nanostructured nickel oxide samples, if at all any, is minimal.

4.4.1 Frequency dependence

The frequency dependence of the measured ac conductivity $\sigma_{m}$ of the nanostructured nickel oxide samples at different temperatures is shown in Figures 4.1 to 4.4. $\sigma_{m}$ is found to be more or less independent of frequency below $\approx$ 50 kHz. A similar frequency independent response at low frequency region
has earlier been reported for NiO thin films. This low frequency region corresponds to the dc conductivity, $\sigma_{dc}$, where the inter-well hopping responsible for pure dc conduction completely dominates over the intra-well hopping associated with pure ac conduction.\textsuperscript{26,28,29} At still higher frequencies, $\sigma_m$ shows marked increase with frequency. The variation of pure ac conductivity, $\sigma_{ac} = \sigma_m - \sigma_{dc}$, with frequency of the applied signal is shown in Figures 4.6 to 4.9.

![Figure 4.6](image-url)  

Figure 4.6. Frequency dependence of pure ac conductivity, $\sigma_{ac}$, at different temperatures for (a) sample N2 and (b) sample N1.
Figure 4.7. Frequency dependence of pure ac conductivity, $\sigma_{ac}$, at different temperatures for sample N3.

Figure 4.8. Frequency dependence of pure ac conductivity, $\sigma_{ac}$, at different temperatures for sample N4.
A careful analysis of $\sigma_m$ as the sum of $\sigma_{dc}$ and $\sigma_{ac}$ (Figures 4.1 to 4.4 & 4.6 to 4.9) reveals the following general trends;

(i) At lower frequencies and higher temperatures ($> 373K$), $\sigma_m$ is very nearly equal to $\sigma_{dc}$ i.e. $\sigma_{ac} = \sigma_m - \sigma_{dc} \equiv 0$ (Figures 4.6 to 4.9). At lower frequencies and lower temperatures, $\sigma_m$ is slightly higher than $\sigma_{dc}$ and the contribution due to $\sigma_{ac}$ is distinguishable.

(ii) At higher frequencies and higher temperatures, the contribution of $\sigma_{ac}$ to $\sigma_m$ is more, though the contribution of $\sigma_{dc}$ cannot be neglected. At higher frequencies and lower temperatures, $\sigma_{ac}$ contribution to $\sigma_m$ completely predominates over that due to $\sigma_{dc}$.
At low frequencies, the probability for inter-well hopping predominates over that due to intra-well hopping and $\sigma_m \approx \sigma_{dc}$.\textsuperscript{28,29} The probability for inter-well charge transfer by hopping over the barrier (HOB) and hopping through the barrier (HTB) are given by\textsuperscript{46}

$$W = W_0 \exp\left(-\frac{E_0}{kT}\right) \quad \text{(4.1)}$$

where $E_0$ is the activation energy for hopping, $k$ the Boltzmann constant and $T$ the absolute temperature. The frequency factor, $W_0$, is given by

$$W_0 = \left(\frac{\pi}{4kTE_0}\right)^{\frac{1}{2}} J^2 \frac{\hbar}{2\pi},$$

for hopping through the barrier.

$$= \omega_0 / 2\pi,$$

for hopping over the barrier.

where $J$ is the matrix element of the perturbing potential between hole wavefunctions centered at neighboring Ni\textsuperscript{2+} ions, $\hbar$ is the Plank's constant and $\omega_0$ is the longitudinal optical phonon frequency.\textsuperscript{46} From Equation (4.1), it is clear that the probability for both HOB and HTB increase as temperature is increased. Thus at higher temperatures and lower frequencies $\sigma_m$ is dominated by inter-well hopping and $\sigma_{ac}$ does not contribute to $\sigma_m$. However, as the signal frequency is increased to higher values, the probability of occurrence of intra-well hopping does increase and $\sigma_{ac}$ contribute to $\sigma_m$.\textsuperscript{28,29} At lower temperatures the probability of occurrence of the inter-well charge transfer decreases according to Equation (4.1) and even at low frequencies $\sigma_{ac}$ contributes markedly to $\sigma_m$. At these lower temperatures, as the frequency of the applied signal is increased, the probability of occurrence of the intra-well hopping completely dominates over $\sigma_{dc}$ (Figures 4.1 to 4.4 & 4.6 to 4.9). However, even at room temperature and in the MHz frequency range, $\sigma_{dc}$ contributes markedly to $\sigma_m$ which may be attributed to the percolation of the potential wells associated with Ni\textsuperscript{2+} vacancies.\textsuperscript{28,29} This is justifiable owing to the very high density of Ni\textsuperscript{2+} vacancies concentrated at the highly disordered and defective grain boundaries of the nanostructured nickel oxide.\textsuperscript{46,47}
An analysis of the frequency dependence of the pure ac conductivity, \( \sigma_{ac} \), in the form \( \sigma_{ac} = A (\omega)^s \) was carried out. It was observed that 's' values are always less than 1 for all the samples at all temperatures. It was found that for all the five samples 's' values increased from 0.3 to 0.9 as the frequency increased from kHz to MHz range. In an earlier study by Lunkenheimer and Loidl on NiO thin films 's' values show some distribution (from 0.75 to 1.0) with frequency at temperatures above room temperature.²⁶ The wide distribution for 's' values with frequency observed in the present study of nanophase nickel oxide samples might be a result of the random distribution of hoping distances and localization energies in the nanoparticle samples as discussed in section 4.4.2 below.

4.4.2 Temperature dependence

The temperature dependence of \( \sigma_m \) of the samples at two selected frequencies are shown in Figures 4.10 (a) and (b) while this dependence for the sample N2 at different frequencies are shown in Figure 4.11 (a). Arrhenius plots for the sample N2 at different frequencies is shown in Figure 4.11 (b).

![Figure 4.10](image)

**Figure 4.10.** Temperature dependence of the measured ac conductivity, \( \sigma_m \), for the samples at (a) 3 MHz and (b) 50 kHz.
Figure 4.11. (a) Temperature dependence of the measured ac conductivity, $\sigma_m$, for the sample N2 at different frequencies and (b) corresponding Arrhenius plots.

Figures 4.12 (a) and (b) show the temperature dependence of pure ac conductivity, $\sigma_{ac}$ of the samples at selected frequencies. Figure 4.13 (a) depicts the temperature dependence of $\sigma_{ac}$ for the sample N2 at different frequencies and the corresponding Arrhenius plots are shown in Figure 4.13 (b).
Figure 4.12. Temperature dependence of pure ac conductivity, $\sigma_{ac}$, for the samples at (a) 1 MHz and (b) 500 kHz.

Figure 4.13. (a) Temperature dependence of pure ac conductivity, $\sigma_{ac}$, for the sample N2 at different frequencies and (b) corresponding Arrhenius plots.
An analysis of the results reveal that $\sigma_m$ and $\sigma_{ac}$ differ conspicuously in their temperature dependence, which is expected on the basis of the difference in the temperature dependence of the intra-well and inter-well charge transfer mechanisms.\textsuperscript{28,29} The activation energies for $\sigma_m$ and $\sigma_{ac}$ of the samples at different frequencies were calculated from Arrhenius plots and are listed in Table 4.3. For comparison the activation energies for conductivity in presence of a dc electric field $\sigma_{DC}$ from Chapter 3 is also included in the table. It may be noted from Table 4.3 that the activation energy for $\sigma_m$ is nearly equal to that for $\sigma_{ac}$ in the MHz range, while at lower frequencies it is very close to that for $\sigma_{DC}$. This supports the inference that at MHz range $\sigma_m$ is mostly contributed by intra-well hopping of charge carriers and at lower frequencies the major contribution to $\sigma_m$ arises from inter-well hopping.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$\sigma_{DC}$ (eV)</th>
<th>$\sigma_m$ (eV)</th>
<th>$\sigma_{ac}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kHz</td>
<td>kHz MHz MHz MHz kHz kHz MHz MHz MHz MHz</td>
<td>kHz MHz MHz MHz MHz MHz</td>
</tr>
<tr>
<td>N1</td>
<td>0.30 0.24 0.23</td>
<td>0.23 0.21 0.20</td>
<td>0.14 0.18 0.18 0.15 0.16</td>
</tr>
<tr>
<td>N2</td>
<td>0.30 0.21 0.26</td>
<td>0.28 0.28 0.28</td>
<td>0.10 0.25 0.27 0.27 0.28</td>
</tr>
<tr>
<td>N3</td>
<td>0.30 0.29 0.28</td>
<td>0.28 0.26 0.26</td>
<td>0.18 0.19 0.18 0.15 0.17</td>
</tr>
<tr>
<td>N4</td>
<td>0.38 0.40 0.36</td>
<td>0.36 0.31 0.31</td>
<td>0.17 0.15 0.17 0.18 0.19</td>
</tr>
<tr>
<td>N5</td>
<td>0.40 0.39 0.33</td>
<td>0.33 0.27 0.27</td>
<td>0.14 0.14 0.14 0.16 0.16</td>
</tr>
</tbody>
</table>

The activation energy for the intra-well charge transfer ($\sigma_{ac}$) is determined by the short range localization energy, $\Delta$, arising from the random fluctuations in the site separation of hopping sites and an energy $E(r)$ which depends on the position of the ions within the long range potential well associated with the Ni\textsuperscript{2+} vacancies.\textsuperscript{28,29} For intra-well hopping the average hopping distance is one lattice spacing.\textsuperscript{28,29} In the case of nanostructured materials, due to the high values for surface to volume ratio, a large
percentage of the atoms reside in the grain boundary environment where the lattice parameter ‘a’ and hence the average hopping distance for intra-well hopping will have a distribution in value. The activation energies calculated from Arrhenius plots represent only an average value of this quantity associated with the average hopping distance. The actual spread of lattice parameters in the samples will depend on a number of factors like the average grain size, ionic radii of the constituent ions, and shape of the grains. Qualitatively, we can say that the average hopping distance in the nanoparticles having different average particle sizes are nearly the same giving rise to nearly equal values for the activation energies obtained from Arrhenius plots. The diffused nature of the electron diffraction pattern (Chapter 2, Figure 2.5) is an indication of the structural disorder within the grain boundary of the nanoparticle sample. It may be inferred that the observed spread in ‘s’ values for the samples in the present study also possibly arises from the spread in the hopping distance (lattice parameter) for the nanoparticle samples. According to Pollak and Pike $\sigma_{ac} \propto \omega^s$; $s \leq 1$ dependence occurs when the primitive relaxation times are exponential functions of one or more random variables with a reasonably smooth and wide distribution. In the present case of nanostructured nickel oxide, the random variables involved could be the hopping distance and the associated random fluctuations in the localization energy. It may be concluded that the observed spread in the ‘s’ values and activation energies stem from the distribution in the numerical value of lattice parameter ‘a’, which is associated with the structure of the grain boundaries of the nanoparticle samples.

From Table 4.3, it may be noted that the activation energies for $\sigma_{ac}$ are smaller than those for $\sigma_{DC}$. This is attributable to the fact that for inter-well hopping corresponding to dc conduction, in addition to the short range localization energy, the long range localization energy associated with the $\text{Ni}^{2+}$ vacancies is to be overcome. The activation energy for $\sigma_m$ should be the weighed average of the activation energies for intra-well and inter-well, weighed according to their relative probability of occurrence. From Table 4.3, activation energy for $\sigma_m$ falls in between that for $\sigma_{ac}$ and $\sigma_{DC}$; at lower frequencies it is closer to that for $\sigma_{DC}$ while at MHz range it approaches that for $\sigma_{ac}$. Also it may be noted that the activation energies for all the five samples in
the present study are slightly less than that for NiO single crystals. This can be attributed to the possible screening of charge carriers by the very high density of quadrupole complexes associated with the Ni\textsuperscript{2+} vacancies.

4.4.3 Size dependence

Figures 4.14 (a) and (b) show the variation of measured ac conductivity $\sigma_m$ with average particle size at different frequencies and different temperatures. It may be noted that $\sigma_m$ increases as the average particle size increases from 2-3 nm for sample N1 to 4-5 nm for sample N2, tend to saturate and then falls off attaining a somewhat steady value for the samples N4 and N5 with larger average particle sizes. The variation has the same general form at different temperatures and frequencies.

![Figure 4.14. Variation of $\sigma_m$ with average grain size (a) for different frequencies of the applied signal at 313 K and (b) for 1 MHz at different temperatures.](image)
It may be noted from Figure 4.14 that the variation pattern of the measured ac conductivity, $\sigma_m$, of nanostructured nickel oxide samples with average grain size is identical with that for dc conductivity (Chapter 3, Figure 3.2). Hence the explanation for the observed side dependence of dc conductivity is valid for the case of ac conductivity also (Chapter 3, Figure 3.3). Thus it is concluded that triple junctions form an important component of the interface along with grain boundaries in determining the transport properties of nanostructured materials as the grain size becomes smaller than about 10 nm.

4.5 Conclusion

The ac conductivity of nanostructured nickel oxide samples consolidated in the form of pellets were studied as a function of frequency of the applied signal, temperature and average particle size. The observed enhancement in conductivity by six to eight orders of magnitude over that of NiO single crystals is attributed to the high defect density in nanostructured nickel oxide. The measured ac conductivity $\sigma_m$ was analyzed as the sum of pure ac component $\sigma_{ac}$ and dc component $\sigma_{dc}$. The variation of $\sigma_m$ and $\sigma_{ac}$ with temperature and frequency of the applied signal and temperature are discussed on the basis of the Correlated Barrier Hopping (CBH) model. The variation of $\sigma_m$ with average particle size can be semi-quantitatively explained on the basis of the important role played by the triple junctions in determining the transport properties of nanostructured materials when the average grain sizes becomes smaller that about 10 nm.

4.6 References