Effect of Sr doping on structural, electrical and electrochemical properties of Nd$_{2-x}$Sr$_x$NiO$_{4+\delta}$ mixed ionic-electronic conductors

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The Nd$_{2-x}$Sr$_x$NiO$_{4+\delta}$(x = 0.2 and 0.4) solid solutions prepared by combustion synthesis are of submicron/superfine crystallites size. The linear variation in dc conductivity with oxygen partial pressure around Nd$_{1.6}$Sr$_{0.4}$NiO$_{4+\delta}$ is understood on the basis of defect chemistry. The electrochemical properties of the cathode material, studied using electrochemical impedance spectroscopy, reveal area specific resistance (ASR) = 0.84 ohm cm$^2$ at 973 K. The charge transfer process in cathode and across cathode-electrolyte interface is the rate limiting reaction.

Keywords: Cathode, Mixed ionic-electronic conductor, Electrochemical impedance spectroscopy, Area specific resistance

1 Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) have been gaining much importance due to high efficiency and low pollution. Since the cathode material (one of the important components of IT-SOFCs) decides the efficiency, development of new and efficient cathode material has posed a great challenge before scientists and engineers. The K$_2$NiF$_4$-type mixed ionic-electronic conductors (MIECs) have attracted great attention because of interesting structure, transport and catalytic performance$^{1-3}$. The thermochemical stability of K$_2$NiF$_4$-type manganates, ferrates, cuprates and nickelates reported higher than those of the corresponding perovskite-type oxides$^1$. Additionally, oxygen diffusivity and surface reaction rate in Ni-based K$_2$NiF$_4$-type oxides found higher as compared to in perovskite-type mixed conductors$^{4,5}$. The Co- and Fe-containing K$_2$NiF$_4$-type compounds studied extensively in near recent past$^{6,7}$. Different kinds of oxygen defects can be formed in K$_2$NiF$_4$-type compounds depending on Sr-doping, oxygen partial pressure and preparation temperature$^{8,9,10,11}$. A close scrutiny of the literature revealed that the Nd$_{2-x}$Sr$_x$NiO$_{4+\delta}$ has been less attended as cathode for IT-SOFCs application. The preparation and characterization of Nd$_{2-x}$Sr$_x$NiO$_{4+\delta}$ (x = 0.2 and 0.4) solid solutions following combustion (without fuel) synthesis have been studied in the present paper. The samples were characterized with the help of X-ray powder diffraction, scanning electron microscopy and four-probe dc conductivity. Additionally, electrochemical impedance spectroscopy (EIS) studies were carried out on the symmetric cell of configuration as given below:

Nd$_{1.6}$Sr$_{0.4}$NiO$_{4+\delta}$/ GDC / Nd$_{1.6}$Sr$_{0.4}$NiO$_{4+\delta}$

2 Experimental Details

All the reagents in the form of acetates with purity ≥ 99.9%, procured from Aldrich Chemicals, USA, were dried at 393 K for 6 h so as to remove the traces of moisture. The solid solutions Nd$_{2-x}$Sr$_x$NiO$_{4+\delta}$ (x = 0.2 and 0.4) were prepared using combustion technique as discussed earlier$^{11}$. The pellets of 10 mm diameter and 2 mm thickness were finally sintered at 1273 K for 4 h.

All the sintered samples were characterized using X-ray powder diffraction (XRD), PANalytical X’pert PRO, Philips, Netherlands. The density of the sintered pellets was measured following Archimedes principle with the help of Mettler XS105 dual range monopan balance with density kit attachment and built in density measurement software. Microhardness number was measured by the Vickers indentation technique (HMV-2 microhardness tester, Shimadzu, Japan). The dc conductivity of solid solutions was measured at 973, 923 and 873 K as a function of oxygen partial pressure (0-21%) during cooling cycle using four-probe technique$^{11}$. Details of procedure
followed for the preparation of symmetric cells [configuration given below (A)] and the characterization were similar to those discussed in earlier work\textsuperscript{11}.

\[
\text{Nd}_{1.6}\text{Sr}_{0.4}\text{NiO}_{4+\delta}/\text{GDC} / \text{Nd}_{1.6}\text{Sr}_{0.4}\text{NiO}_{4+\delta} \quad (A)
\]

3 Results and Discussion

The formation of \(\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}\) (\(x = 0.2\) and 0.4) solid solutions is confirmed from X-ray powder diffraction data analyses similar to that as described in previous work\textsuperscript{11}. Crystallite size of all compositions under study as compared in Table 1, is determined using X’pert Highscore plus software based on the following expression:

\[
C_s = \frac{0.9\lambda}{\beta \cos \theta_b}
\]

where \(C_s\), \(\lambda\), and \(\theta_b\) are thickness of crystallite, X-ray wavelength and Bragg’s angle, respectively. Here, \(\beta\) was determined by:

\[
\beta^2 = \beta_m^2 - \beta_i^2,
\]

where \(\beta_m\) and \(\beta_i\) are the measured and the standard full width of half maximum, FWHM, of diffracted line, respectively. The value of \(\beta\) is estimated from the XRD pattern obtained by running the experiment on a standard silicon sample\textsuperscript{11} provided by PANalytical, Netherlands. The effective crystallite sizes (Table 1) for \(\text{Nd}_{1.8}\text{Sr}_{0.2}\text{NiO}_{4+\delta}\) and \(\text{Nd}_{1.6}\text{Sr}_{0.4}\text{NiO}_{4+\delta}\) are 260 and 216 nm, respectively.

From the Table 1, it is also evident that the lattice strain \((S_l)\) increases with decrease in crystallite size. Furthermore, partial substitution of \(\text{Sr}^{2+}\) for \(\text{Nd}^{3+}\) reduces the sintered density, which in turn reduces micro-hardness number \((HV)\) commensurately.

The SEM photographs of cathode of symmetric Cell-A and its fractured surface across the electrode-electrolyte interface are shown in Fig. 1 (a and b), respectively. A close look at the Fig. 1 (a) reveals agglomerated submicron crystallites of \(\text{Nd}_{1.6}\text{Sr}_{0.4}\text{NiO}_{4+\delta}\) leading to formation of porous electrode layer. The electrolyte, however, is nonporous, i.e. highly dense [Fig. 1 (b)]. The electrode and electrolyte form homogeneous intimate contact all along the interface [Fig. 1 (b)]. In spite of heating and cooling thermal cycles four times in the temperature range 973-293 K, there are no crack(s) or separation between electrode and electrolyte at the interface. The electrode layer thickness is \(\approx 20\) µm.

The variation of \(dc\) conductivity with oxygen partial pressure for \(\text{Nd}_{1.6}\text{Sr}_{0.4}\text{NiO}_{4+\delta}\) under study is shown in Fig. 2. As seen, conductivity changes linearly with changing oxygen partial pressure in the entire temperature range of measurement. The conductivity variation with oxygen partial pressure is, however, insignificant. Similar results for MIECs have been reported in the literature\textsuperscript{11,12}.

As a matter of fact, the conductivity due to electron holes \((h^+)\) is proportional to charge \((e)\), concentration \((c_p)\) and mobility \((\mu_p)\) according to the expression given below:

\[
\sigma_p = c_p \mu_p e,
\]

Table 1 — Comparison of crystallite size \((C_s)\), lattice strain \((S_l)\), sintered density \((\rho)\) and microhardness number \((HV)\) of \(\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}\) \((x = 0.2\) and 0.4)

<table>
<thead>
<tr>
<th>Composition Code</th>
<th>(C_s) (nm)</th>
<th>(S_l) (%)</th>
<th>(\rho) (%)</th>
<th>(HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSNO-0.2</td>
<td>260.9</td>
<td>0.127</td>
<td>69.34</td>
<td>338</td>
</tr>
<tr>
<td>NSNO-0.4</td>
<td>216.5</td>
<td>0.157</td>
<td>57.95</td>
<td>118</td>
</tr>
</tbody>
</table>

Fig. 1 — Scanning electron microphotographs of Cell-A (a) cathode surface and (b) electrode-electrolyte interface
Intrinsically, electrons and holes can be produced in Nd$_2$NiO$_4$ lattice according to two-point defect equilibria:

\[
O_2 \leftrightarrow V^{**} + 2e' + \frac{1}{2}O_2 \tag{4}
\]

\[
\frac{1}{2}O_2 \leftrightarrow O'_{e} + 2h' \tag{5}
\]

coupled with intrinsic ionization

\[
nil \leftrightarrow e' + h' \tag{6}
\]

In Nd$_{2-x}$Sr$_x$NiO$_{4+\delta}$, Sr$_{2+}$ occupies the neodymium regular lattice sites (Nd$_{Sr}$) with one effective negative charge, resulting in interstitial oxygen ion (O$_i^-$) with double negative effective charge; and Ni$_{2+}$ oxidizes to Ni$_{3+}$ and occupy regular lattice site o Ni with one effective positive charge (Ni$_{Ni}$). Thus, the partial substitution of Sr$_{2+}$ for Nd$_{3+}$ introduces extrinsic defects according to quasi-chemical reaction:

\[
Nd_{Nd} + Sr + 2Ni_{Ni} + \frac{1}{2}O_2 \leftrightarrow Sr_{Nd} + 2Ni_{Ni} + O' \tag{7}
\]

where Ni$_{Ni}$ and Ni$_{Nd}$ are Ni$_{2+}$ and Ni$_{3+}$ at Ni regular lattice site, respectively. Alternatively, for Nd$_{2-x}$Sr$_x$NiO$_{4+\delta}$ with $\delta > 0$, the electroneutrality condition may be written as:

\[
2[O'_e]+[Sr_{Nd}] = [Ni_{Ni}] = [h^+] \tag{8}
\]

The corresponding defect equilibrium may be represented by Eq. (5). Thus, in accordance with relations given in Eqs (4-6) the charge carrier density increases with an increasing oxygen concentration and correlatively the conductivity as per relation given in Eq. (3).
electrolyte. The CPE takes care of the depression in high frequency semicircle. The values of $L$ and $R_l$ in the equivalent circuit represent the inductance and lead resistance, respectively. Since the impedance data are accurately modeled with the Gerischer element, a chemical-electrochemical-chemical type reaction is proposed at the mixed ionic-electronic conducting cathode. Similar electrical equivalent circuit model has been proposed in case of Nd$_{1.8}$Ce$_{0.2}$O$_{4+\delta}$ MIEC cathode.

The dependence of log(ASR) on log($P_{O_2}$) at 923 K is shown in the inset of Fig. 4. The ASR of the electrode varies with $P_{O_2}$ in accordance with the law:

$$\text{ASR} = \text{ASR}_0 \left( P_{O_2} \right)^n$$  \hspace{1cm} \ldots(9)

The value of $n$ provides useful information on the type of species involved in reactions that occur at the electrode:

$$n = \frac{1}{4}, \quad O_2 (g) + 2e^- + V_0^- \leftrightarrow O_0^+$$  \hspace{1cm} \ldots(12)

The $n = 0.249$ obtained in the present study allows to infer that the charge transfer reaction is rate-limiting in the entire range of $P_{O_2}$ measurement. A number of researchers have analyzed the $P_{O_2}$ dependent ASR behaviour in MIECs based on the Eqs (9-12).

4 Conclusions

The crystallites are of submicron/superfine size when Nd$_{2-x}$Sr$_x$NiO$_{4+\delta}$ ($x = 0.2$ and $0.4$) solid solutions are prepared by combustion synthesis. The slight increase in dc conductivity with increasing oxygen concentration is attributed to enhancement in charge carrier density. Nd$_{1.6}$Sr$_{0.4}$NiO$_{4+\delta}$ cathode exhibits area specific resistance (ASR) = 0.84 ohm cm$^2$ at 973 K. Oxygen ion transfer from Nd$_{1.6}$Sr$_{0.4}$NiO$_{4+\delta}$ cathode to GDC electrolyte is the rate-limiting step. Nd$_{1.6}$Sr$_{0.4}$NiO$_{4+\delta}$ may be a potential cathode material for IT-SOFC applications.

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References