Cathode materials for intermediate temperature solid oxide fuel cells

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The superfine crystallites of Nd1.8Ce0.2CuO4+dare obtained when prepared by mechanochemical reaction using different process control agents. The crystallite size, \( C_i = 34 \text{ nm} \) is the smallest for Nd1.8Ce0.2CuO4+d prepared using salicylic acid process control agent (NCCO(Sa)) as compared to others. The \( dc \) conductivity (1.64 S cm\(^{-1}\)) is the highest for NCCO(Sa) amongst all, which is attributed to the smallest crystallite size and high sintered density. The agglomeration of superfine grains leads to optimal distribution of nano-pores results in low area specific resistance (1.1 ohm cm\(^2\)) for the NCCO(Sa).

The electrochemical performance suggests adsorption of oxygen by cathode as rate-limiting step. The proposed mechanochemical reaction is useful as a technique for the synthesis of materials with submicron-sized crystallites.

**Keywords:** Mixed ionic-electronic conductor, Electrochemical impedance spectroscopy, \( dc \) electrical conductivity

1 Introduction

The new power generating system based on solid oxide fuel cell (SOFC), which converts the chemical energy directly into the electrical energy, has been viewed as the future promise\(^1\). However, the conventional SOFCs exhibit major disadvantages like cell-cracking, formation of non-conducting compound(s) at electrode/electrolyte interfaces, need of expensive non-metallic interconnects, etc. Consequently, intermediate solid oxide fuel cells, intermediate temperature solid oxide fuel cells (IT-SOFCs), have gained increased importance.

The past choice of cathode material LSM (lanthanum strontium manganite) restricted its utility due to chemical reactivity with YSZ (yttria-stabilized-zirconia)\(^2\). Furthermore, it has been reported that its performance reduces rapidly on lowering the operating temperature due to its poor ionic conductivity at such temperature. In the near recent past, the LSCFs (La\(_{1-x}\)Sr\(_x\)Co\(_{1-y}\)Fe\(_y\)O\(_{3-\delta}\)) have been proposed as alternative cathode materials\(^3,4\) for IT-SOFC. However, their utility has been restricted due to both the lack of chemical stability and the incompatible thermal expansion coefficient (TEC) with YSZ.

Mixed ionic-electronic conducting materials have paved the way towards decreasing polarization losses due to enlargement of the electrochemical zone from triple-phase boundary (TPB) to two-phase boundary (2PB) between the gas phase and the mixed ionic-electronic conductors\(^5,7\) (MIECs). Additionally, this has allowed decreasing the operating temperature\(^8\) from 1000\(^\circ\)C to 500\(^\circ\)C-800\(^\circ\)C.

MIECs of the type A\(_2\)BO\(_4\) (A = rare earth, alkaline earth; B = transition metal) with K\(_2\)NiF\(_4\)-type structure have been of considerable interest due to high electronic conductivity, adequate oxygen conduction, strong electrocatalytic activity towards oxygen reduction and thermal expansion coefficient (TEC) comparable with those of the conventional electrolytes\(^8,11\). The K\(_2\)NiF\(_4\)-type structure has an outer intergrowth of alternating perovskite (ABO\(_3\)) and rock-salt (AO) layers stacked along c-axis. Excess oxygen ions can be incorporated in the form of intermediary species into rock-salt layer similar to the transition metal analogs, and not compensated by cation vacancies as observed in the ABO\(_3\) type materials\(^12-15\).

In recent past, significant mixed ionic and electronic conductivities with appreciable electrocatalytic activity have been found in Ln\(_2\)NiO\(_4\) and Ln\(_2\)CuO\(_4\) systems having K\(_2\)NiF\(_4\)-type structure\(^16-21\). In addition to these, the thermochemical stability of K\(_2\)NiF\(_4\)-type manganites, ferrates, cuprates and nickelates has been reported higher than those of the corresponding perovskite-type oxides\(^20\). The Co-and Fe-containing K\(_2\)NiF\(_4\) compounds have been studied from cathode in near recent past\(^22,23\). Although the total conductivity and TEC of La\(_{2-x}\)Sr\(_x\)CuO\(_{4+\delta}\) materials have been fairly satisfactory, they exhibit rather high area specific resistance\(^8,21\) (ASR). On the other hand, the ASR of Nd\(_{1.7}\)Sr\(_{0.3}\)CuO\(_4\) cathode on
smectum-doped ceria (SDC) electrolyte has been found satisfactory.\(^{16}\) Recently, the ASR of La\(_2\)NiO\(_4\), \(\text{Nd}_2\text{NiO}_4\) and Pr\(_2\)NiO\(_4\) has been reported as 5.2, 1.5 and 0.6 ohm cm\(^2\), respectively.\(^{24}\) Ferchaud et al\(^{25}\) have shown improvement in electrochemical properties of Pr\(_2\)NiO\(_{4+δ}\) by optimizing the microstructure of the porous cathode.\(^{22}\) Zhao et al\(^{26}\) reported significant effect of sintering temperature on microstructure of superfine La\(_2\)NiO\(_{4+δ}\) leading to low electrode polarization (0.28 ohm cm\(^2\)). Also, nanoparticles of \(\text{Nd}_2\text{NiO}_{4+δ}\), with controlled crystallinity, size and morphology have been prepared via ultrasonic spray pyrolysis.\(^{27}\)

The preliminary study of the \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}\) \((0 ≤ x ≤ 0.2)\) with both the GDC (Ce\(_{0.2}\)Gd\(_{0.8}\)O\(_{1.5}\)) and the LSGM (La\(_{0.9}\)Sr\(_{0.1}\)Ga\(_{0.8}\)Mg\(_{0.2}\)O\(_{1.5}\)) electrolytes has been reported by Soori et al.\(^{35}\) Furthermore, the solid solubility of Ce in \(\text{Nd}_2\text{CuO}_4\) is established\(^{31,35}\) up to \(x = 0.2\). The improved ASR in combustion derived \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}\) has been reported due to uniform microcrystallinity.\(^{31}\) The sintering temperature of symmetric cell with \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_4\) has been optimized to 1000°C in terms of lowest \(^{28}\) ASR \((1.62\) ohm cm\(^2\)). Sol-gel derived \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}\) offered lower ASR \((0.93\) ohm cm\(^2\) at 700°C) as compared to obtained by solid state sintering\(^{29}\) \((2.03\) ohm cm\(^2\)). Use of different process control agents (PCAs) during preparation of \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}\) via mechanochemical alloying exhibited significant effect on structural and electrical properties.\(^{36}\) Furthermore, superfine crystalline \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}\) obtained by microwave synthesis offered good electrochemical performance.\(^{31}\) The milling time of mechanochemical synthesis\(^{31,33}\) of submicron crystalline \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}\) has been optimized to 36 h at 600 rpm.

The present study was aimed at preparation of \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}\) using mechanochemical reaction. Practically, three different PCAs viz. ethanol, salicylic acid and stearic acid, were used in order to study their effects on electrical and electrochemical properties of \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}\). The prepared samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), \(dc\) electrical conductivity. The electrochemical performance using electrochemical impedance spectroscopy (EIS) was carried out on the symmetric cells with configuration given below:

\[
\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}/\text{GDC}/\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}
\]

The improved electrochemical performance is discussed in the light of microstructural results.

2 Experimental Details

The \(\text{Nd}_2\text{O}_3\), CeO\(_2\) and CuO with purity ≥ 99.9% (Aldrich Chemicals, USA) were used as reagents. The requisite mole fractions of well-dried reagents were mixed with 2 wt% of ethanol (process control agent (PCA)) and ball milled with the help of a Pulverisette-6 planetary monomill (Fristch, Germany) equipped with 80 ml tungsten carbide (WC) bowl containing 35 balls (10 mm diameter). The milling time and speed of the planetary monomill were 12 h and 600 revolutions per minute (rpm), respectively. Similar procedure was followed for the other two PCAs, i.e. salicylic acid and stearic acid. The milled samples were compressed uniaxially (3 tons/cm\(^2\)) to obtain pellets of 10 mm diameter and 1-2 mm thickness using Specac (UK) stainless steel die-punch and hydraulic press. The pellets were finally sintered at 900°C for 9 h. The \(\text{Nd}_{1.8}\text{Ce}_0\text{CuO}_{4+δ}\) prepared using ethanol, salicylic acid and stearic acid as PCA are termed as NCCO(Et), NCCO(Sa) and NCCO(St), respectively.

All the prepared samples were characterized by X-ray powder diffraction, (PANalytical X’pert PRO, Netherlands) and scanning electron microscopy (Jeol JSM 6380). The \(dc\) conductivity as a parametric function of temperatures was measured on sintered pellets using four-probe method as described earlier.\(^{39}\) The symmetric cells, with the configuration NCCO(Sa)/GDC/NCCO(Sa) were obtained by spin coating the NCCO(Sa) cathode ink on both the flat surfaces of sintered GDC pellet as reported elsewhere.\(^{39}\) Electrochemical impedance spectroscopy (EIS) measurements on the sintered symmetric cells were carried out using a computer-controlled Solartron 1255B FRA in combination with a Solartron SI 1287 electrochemical interface as described elsewhere.\(^{39}\)

3 Results and Discussion

3.1 X-ray powder diffraction and scanning electron microscopy

The X-ray powder diffraction patterns of 12 h ball milled sample with ethanol, salicylic acid and stearic acid and subsequently sintered at 900°C for 9 h are shown in Fig. 1(a), (b) and (c), respectively. All the characteristic diffracted lines match with the JCPDS (joint committee for powder diffraction standard) data (File No. 01-084-2177) corresponding to \(\text{Nd}_2\text{CuO}_4\)
with small deviations. The small deviation is attributed to the solid solubility of Ce in Nd$_3$CuO$_4$ lattice. A comparison of Fig. 1 (a),(b) and (c) reveals that the characteristic potential peaks are sharper for Nd$_{1.8}$Ce$_{0.2}$CuO$_4$ prepared using salicylic acid [Fig. 1(b)] and ethanol [Fig. 1(c)] as compared to that for Nd$_{1.8}$Ce$_{0.2}$CuO$_4$ prepared using stearic acid PCA [Fig. 1(a)]. The increase in the sharpness of the characteristic diffraction lines is the manifestation of improvement in the crystallinity. The crystallite size determined following the procedure described earlier is compared along with lattice cell constants, sintered density and micro-hardness number in Table 1. As seen, the lattice cell constants, which matched well with reported one, and are the same irrespective of PCA used during the preparation. Furthermore, the highest sintered density for NCCO(Sa) amongst all is due to smallest crystallite size. The micro-hardness number depends on sintered density i.e. higher the sintered density higher is the micro-hardness number.

The SEM micro-photographs of cathode surface for Cell(NCCO-Sa) and fractured surface across the electrode-electrolyte interface of Cell(NCCO-Sa) are depicted in Fig. 2 (a) and (b). Understandably, the grains of cathode (Cell(NCCO-Sa)) are, in general, of superfine/nano-size [Figs. 2(a)]. Furthermore, the agglomerated nano-size grains [Fig. 2 (a)] form lumps of about 1-2 µm resulting in nano-pores. Moreover, uniform arrangement of these porous lumps gave sufficient number of micron-sized pores thereby forming a highly porous cathode film. A close look at the Fig. 2(b) reveals homogeneous intimate contact between electrode and electrolyte all along the interface. The electrode layer thickness is ≈ 19 µm.

### Table 1 — A comparison of lattice cell constants (a, c and v), crystallite size ($C_s$), density ($\rho$) and hardness number (HV) of Nd$_{1.8}$Ce$_{0.2}$CuO$_4$ prepared by using different PCA

<table>
<thead>
<tr>
<th>PCA</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>v (nm$^3$)</th>
<th>$C_s$ (nm)</th>
<th>$\rho$ (%)</th>
<th>HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.395</td>
<td>1.211</td>
<td>0.189</td>
<td>59</td>
<td>81.24</td>
<td>71.44</td>
</tr>
<tr>
<td>Salicylic Acid</td>
<td>0.395</td>
<td>1.211</td>
<td>0.190</td>
<td>34</td>
<td>93.13</td>
<td>108.8</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>0.395</td>
<td>1.210</td>
<td>0.189</td>
<td>55</td>
<td>84.02</td>
<td>78.06</td>
</tr>
</tbody>
</table>

### 3.2 dc Conductivity

The temperature dependent dc conductivity of NCCO(Et), NCCO(Sa) and NCCO(St) (Fig. 3) exhibits semiconductor to pseudo-metal phase
transition at about 625ºC. Below this transition temperature, they obey the Arrhenius law:

$$\sigma T = (\sigma T)_0 \exp \left( \frac{-E_a}{kT} \right)$$  \(\ldots(1)\)

where \((\sigma T)_0\), \(k\), \(T\) and \(E_a\) are pre-exponential factor, Boltzmann constant, absolute temperature and activation energy, respectively. Oxygen losses above 625ºC reduce the mobile charge carrier density with temperature leading to decrease in conductivity and so semiconductor to pseudo-metallic transition. Similar semiconductor to pseudo-metal transition is reported in the literature\(^{29}\). In our earlier studies on NCCO, a negative temperature coefficient (NTC) to positive temperature coefficient (PTC) at around 625ºC is observed\(^{28,29,31}\). Whereas, the transition temperature \((T_c)\) in Arrhenius plot for NCCO has, however, not been observed in mechanochemically\(^{32}\) derived NCCO. Amongst all samples under study (Fig. 3) NCCO(Sa) exhibits highest conductivity in entire temperature range of measurement which is due to smallest grain/crystallite size and highest sintered density (Table 1).

The electrical conductivity of NCCO prepared by sol-gel\(^{28}\) is found to be very low as compared to present study. The large deviation in conductivity is due to the difference in preparation technique leading to a large difference in crystallite sizes i.e. crystallite size of sol-gel derived NCCO reported 150 nm, which is much larger as compared to present study (= 34 nm). In fact, generally, the conductivity increases with decrease in grain size. Also, the porosity in former case is higher as compared to in latter. Furthermore, very low conductivity is also due to sintering of sol-gel derived sample at relatively higher temperature (1000 °C). We have observed that sintering of the NCCO at relatively higher temperature reduces the conductivity considerably\(^{30}\). All above factors are responsible for very high conductivity in NCCO of present study as compared to earlier report\(^{28}\). It is, however, worth to mention here that a comparable conductivity is reported in NCCO prepared by combustion\(^{11}\), microwave combustion\(^{31}\) and mechanochemical alloying\(^{32}\).

### 3.3 Electrochemical impedance spectroscopy (EIS)

The typical complex impedance plots for Cell(NCCO-Sa) at different temperatures are shown in Fig. 4(a). The presence of two semicircular arcs at each temperature is evident. The semicircular arc in the low frequency region represents electrode polarization. However, the arc in the high frequency region is due to GDC electrolyte. The increasing real axis intercepts of all semicircular arcs with decreasing temperature indicates enhancement in ASR as well as electrolytic bulk resistance. The ASR obeys the Arrhenius law in the entire temperature range of measurement. The low ASR = 1.1 ohm cm\(^2\) for Cell(NCCO-Sa) is due to agglomeration of superfine grains leading to optimal distribution of nano-pores [Fig.2 (a)], which commensurately increases the electrochemically active sites.

The complex impedance plots of Cell(NCCO-Sa) at 650ºC for different values of \(P_o\) are shown in Fig. 5(a). Evidently, the x-axis intercept corresponding to the low frequency semicircular arc (electrode) is dependent on \(P_o\). On the other hand, the electrolytic bulk resistance/conductivity does not change with variation in \(P_o\). The oxygen partial \((P_o)\) dependent ASR at 650 ºC is shown in Fig. 5(b). The variation of ASR [Fig. 5(b)] is represented as follows:

$$\text{ASR} = (\text{ASR})_0 (P_o)^{n^3}$$  \(\ldots(2)\)

The type of species involved in the reactions that occurs at the electrode can be understood from value of \(n\).
Conclusions

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