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Kevin Huang
University of South Carolina - Columbia, huang46@cec.sc.edu

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Sr- and Ni-Doped LaCoO$_3$ and LaFeO$_3$ Perovskites

New Cathode Materials for Solid-Oxide Fuel Cells

Keqin Huang,* Hee Y. Lee, and John B. Goodenough

Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, USA

ABSTRACT

An improved cathode material for a solid-oxide fuel cell (SOFC) must perform three functions: (i) provide a mechanism for breaking the covalent bond of the O$_2$ oxidant molecule, (ii) accept electrons from the external circuit and distribute them to the reaction sites for the reduction of the oxidant, and (iii) allow passage of the reduced O$^-$ ions to the electrolyte for transfer to the anode where they combine with the fuel to form H$_2$O and CO$_2$ with the release of electrons to the external circuit. These three functions can be realized in a transition-metal oxide that is both an electronic and an oxide-ion conductor at the operating temperature $T_{op} \geq 700^\circ$C of the fuel cell.

Numerous transition-metal oxides are metallic, but few of them are also good oxide-ion conductors in the oxidizing atmosphere at the cathode of an SOFC. Any oxide that remains electronically conducting in an O$_2$ atmosphere can perform the first two functions. At $T_{op}$, the loss of bound water from the surface of an oxide creates surface-oxygen vacancies, which we denote by $\square$. If the oxide is an electronic conductor, the covalent bond of the dioxygen molecule may be broken by the reactions

$$O_2 + \square + 2e^- \rightarrow (O_2)^{2-}$$

[1]

$$\square + 2e^- \rightarrow 2O$$

[2]

However, unless the surface oxygen contacts an interconnected oxide-ion subarray that also contains oxygen vacancies, conduction of O$^-$ ions across the electrode to the electrolyte is blocked. A representative electronic conductor that is not an oxide-ion conductor is the Sr-doped perovskite La$_{1-x}$Sr$_x$MnO$_3$, that has been used extensively as a cathode in ZrO$_2$-based SOFCs. It remains a good electronic conductor, but the lack of oxide-ion vacancies, and hence of oxide-ion conduction, at $T_{op}$ forces the use of thick, porous electrodes containing an extensive array of triple-phase boundaries where gas, electrolyte, and electrode meet. The performance of such a cathode depends sensitively on its microstructure, which may change under operating conditions. Depending on the microstructure, cathode overpotentials have been reported to vary from a few tens to a few hundreds of millivolts. On the other hand, the perovskite system La$_{1-x}$Sr$_x$CoO$_3$, contains oxide-ion vacancies in the bulk even in an oxidizing atmosphere; this mixed electronic and oxide-ion conductor has been demonstrated to give an excellent cathode performance with very low overpotential even at high current densities when present as a film on the electrolyte.$^5$-$^7$

Unfortunately, the thermal expansion of the La$_{1-x}$Sr$_x$CoO$_3$ system is exceptionally high as a result of oxygen loss and a smooth change with increasing temperature from itinerant to polaronic conduction and/or a low spin to high-spin transition at Co$^{3+}$ ions even where an intermediate-spin state has been stabilized over most of the Co$_3$O$_4$ matrix.$^8$ The thermal-expansion mismatch between the electrode and the electrolyte and interconnect makes this system unsuitable as a cathode material for an SOFC subject to repeated thermal cycling. In this paper we report exploration of other mixed-valent perovskite systems that are designed to have a thermal expansion better matched to that of the electrolyte and interconnect and also to be good mixed electronic and oxide-ion conductors in an oxidizing atmosphere at 700 $\leq T_{op} \leq 1000^\circ$C. For this purpose, we have used the Ni$^{2+}$/Ni$^{3+}$ redox couple in association with the Fe$^{3+}$/Fe$^{2+}$ and the low-spin/intermediate-spin Co$^{3+}$/Co$^{4+}$ couples in the perovskite structure. It was anticipated that the presence of the Ni$^{2+}$/Ni$^{3+}$ redox couple would suppress low-spin-to-high-spin and/or itinerant-to-polaron transitions so as to reduce the thermal expansion without loss of electrical conductivity.

The early observations of metallic conductivity in the Na$_2$WO$_4$, La$_{1.5}$Mn$_{0.5}$O$_3$, and La$_{1.5}$Sr$_{0.5}$MnO$_3$ mixed-valent perovskite systems became clarified with the prediction by Goodenough and demonstration by Ramesh that the metallic conductivity and Pauli paramagnetism of stoichiometric LaNiO$_3$ containing low-spin Ni$^{2+}$.$^9$ The metallic conductivity is due to strong Ni$^{2+}$-O covalent bonding, which causes the $\sigma$-bonding e orbitals of octahedral-site, low-spin Ni$^{2+}$ to be transformed into itinerant $\sigma^*$-band states as a result of (180°-) Ni—O—Ni interactions in the NiO$_2$ array. Subsequently, the system La$_{1.6}$M$_x$Ni$_{0.4}$O$_3$, M = Ca, Sr, and Ba, 0.05 $\leq x \leq$ 0.05, were studied extensively by several groups.$^{10-12}$ However, these nickelates are thermally unstable at temperatures $T \leq 1100^\circ$C where they lose oxygen to form Ruddlesden-Popper intergrowth structures (La$_{2}$Sr$_{2}$)$_{1-x}$Ni$_{x}$O$_{3+\delta}$. Below 1100°C, the Ni$^{2+}$ ions retain their low-spin configuration, and LaNiO$_3$ has a relatively small thermal-expansion coefficient of 10.0 $\times 10^{-5}$ K$^{-1}$. By contrast, the low-spin Co$^{3+}$, $t_{2g}^6$ configuration makes LaCoO$_3$, a diamagnetic insulator at the lowest temperatures; but it becomes more metallic at the highest temperature where an intermediate-spin state $t_{2g}^4\delta t_{2g}^{4+\delta}$ is stabilized at the Co$^{3+}$ ions.$^{13}$ In the system La$_{1-x}$Sr$_x$CoO$_3$, the intermediate-spin state Co$^{3+}$ becomes stabilized at lower temperatures,$^{14}$ but then is a ferrimagnetic state with a $t_{2g}^4$ ferromagnetic polar phase coexisting with a Co$^{3+}$-rich paramagnetic phase that undergoes a low-spin to high-spin transition. In addition, the larger Sr$^{2+}$ ion may induce a change from itinerant to polaronic behavior above the Curie temperature in the fer-
romagnetic phase. These electronic transitions give La_{1-x}Sr_xCoO_3 a large thermal expansion coefficient (TEC = 22.0 x 10^{-5} K^{-1}), but the stability of the Co^{3+}/Co^{4+} couple makes it difficult to oxidize fully the Co^{3+} array and therefore introduces oxygen vacancies into this array while retaining itinerant spin-density states in the ferrimagnetic phase.\(^8\) Substitution of Ni\(^{II}\) for Co\(^{III}\) in La_{1-x}Sr_xCoO_3 is designed to retain mixed-valent polaronic conductivity at temperatures T > 300 K while eliminating the Co\(^{III}\)-rich phase and with it the low-spin to high-spin transitions that contribute to the large TEC in La_{1-x}Sr_xCoO_3. At the same time, operation on the Co\(^{III}/Co^{IV}\) and/or Ni\(^{II}/Ni^{IV}\) redox couples should retain oxygen reduction in the Co\(^{III}/Co^{IV}\) array. Undoped LaFeO_3 contains high-spin Fe\(^{III}\)-t^6 localized-electron configurations; it is an antiferromagnetic insulator with a Néel temperature T\(_{N}\) = 750 K.\(^{1,11}\) In the La_{1-x}Sr_xFeO_3 system, a thermally activated hopping of small polarons between Fe ions appears to describe the transport properties. Abbate et al.\(^{18}\) have shown, with soft X-ray absorption spectroscopy, that the initial substitution of Sr\(^{II}\) for La\(^{III}\) in La_{1-x}Sr_xFeO_3 oxidizes primarily the oxygen rather than the iron atoms of the FeO array; the holes occupy molecular antibonding states of an FeO complex in which the dominant component of the ground state is 3d^5L, where L denotes a ligand hole. However, as the Sr\(^{II}\)-ion concentration increases, the spectral weight shifts to an increasing Fe-5d component in the hole ground state. The nickel substituting La\(^{II}\) for Sr\(^{II}\) in La_{1-x}Sr_xNiO_3 oxidizes primarily the oxygen rather than the nickel atoms of the NiO array; the holes occupy molecular antibonding states of an FeO complex in which the dominant component of the ground state is 3d^5L, where L denotes a ligand hole. However, as the Sr\(^{II}\)-ion concentration increases, the spectral weight shifts to an increasing Fe-5d component in the hole ground state. The La\(^{II}\)-substituting La\(^{II}\) for Sr\(^{II}\) in La_{1-x}Sr_xNiO_3 oxidizes primarily the oxygen rather than the nickel atoms of the NiO array; the holes occupy molecular antibonding states of an FeO complex in which the dominant component of the ground state is 3d^5L, where L denotes a ligand hole. However, as the Sr\(^{II}\)-ion concentration increases, the spectral weight shifts to an increasing Fe-5d component in the hole ground state.

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In this paper we report a study of the La—Sr—Co—Ni—O system, a thermally activated hopping of small polarons between Fe ions appears to describe the transport properties. Abbate et al.\(^{18}\) have shown, with soft X-ray absorption spectroscopy, that the initial substitution of Sr\(^{II}\) for La\(^{III}\) in La_{1-x}Sr_xFeO_3 oxidizes primarily the oxygen rather than the iron atoms of the FeO array; the holes occupy molecular antibonding states of an FeO complex in which the dominant component of the ground state is 3d^5L, where L denotes a ligand hole. However, as the Sr\(^{II}\)-ion concentration increases, the spectral weight shifts to an increasing Fe-5d component in the hole ground state. The nickel substituting La\(^{II}\) for Sr\(^{II}\) in La_{1-x}Sr_xNiO_3 oxidizes primarily the oxygen rather than the nickel atoms of the NiO array; the holes occupy molecular antibonding states of an FeO complex in which the dominant component of the ground state is 3d^5L, where L denotes a ligand hole. However, as the Sr\(^{II}\)-ion concentration increases, the spectral weight shifts to an increasing Fe-5d component in the hole ground state. The La\(^{II}\)-substituting La\(^{II}\) for Sr\(^{II}\) in La_{1-x}Sr_xNiO_3 oxidizes primarily the oxygen rather than the nickel atoms of the NiO array; the holes occupy molecular antibonding states of an FeO complex in which the dominant component of the ground state is 3d^5L, where L denotes a ligand hole. However, as the Sr\(^{II}\)-ion concentration increases, the spectral weight shifts to an increasing Fe-5d component in the hole ground state.

Thermoelectric power.—Seebeck coefficients of sintered electrodes were measured with a Keithley 224 current source and a HP 3478A multimeter, respectively. A computer was used to control the furnace temperature and to communicate data from the current source and multimeter. The validity of Ohm’s law was checked by measuring the conductivity at different currents. Since the density of the polycrystalline samples has a significant effect on the conductivity, the densities of all sintered pellets prepared in this study were determined with a Micromeritics Accupyc 1330 pycnometer.

Thermoelectric power.—Seebeck coefficients of sintered pellets were measured in open air from room temperature to 700°C, both heating and cooling, with a home-made device described elsewhere.\(^{14}\)

Impedance spectroscopy with prepared electrodes LSCO and LSMN.—Impedance spectroscopy of the La_{1-x}Sr_xGa_{1-x}Mg_xO_3 (LSGM) electrolyte with HSO_3, Li_2SO_3, and LSMN gaskets was performed with an HP4192A LF impedance analyzer from 800 to 320°C in open air. The frequencies of the measurements range from 5 Hz to 13 MHz with an ac amplitude of 40 mV, measurements were taken at a total of 25 temperatures. The impedance spectroscopy of the well-known perovskite electrodes La_{1-x}Sr_xCoO_3 (LSCO) and La_{1-x}Sr_xMnO_3 (LSM) were also measured and compared with the investigated electrodes.
The structure of the undoped perovskite LaCoO$_3$ is rhombohedral at room temperature with space group $R3m$ (no. 166) having six formula units per unit cell. Sr and Ni doping at La and Co sites, respectively, do not change the structure of the parent perovskite, as shown in Table I (rhombohedral settings transformed from hexagonal settings), but lattice parameters do change with composition as expected. For all compositions, the $\alpha$ parameter is essentially invariant within experimental error. However, comparison of the distortion angles $\alpha$ at the same Ni doping reveals a decrease with Sr doping, which is consistent with the finding that $\alpha$ becomes $90^\circ$ (cubic) when the Sr doping becomes $x > 0.5$. In contrast, at the same Sr concentration, $\alpha$ increases with Ni content, since Ni favors the rhombohedral structure.

All the LSCN compositions $0 \leq x \leq 0.3$, $0 \leq y \leq 0.2$ shown in Table I were found to be single phase. A small, unidentified peak at 28 = 38° is evident in Fig. 1 as well as in some of our studies of other perovskite systems. It does not match any component oxide; it matches the main peak observed for the first run, but not in an immediately following second run. This observation definitely implies a desorption of adsorbed species.

The structure of LaFeO$_3$ is orthorhombic at room temperature with space group $Pnma$ (no. 62) and parameters $a = 5.5647(1)$, $b = 7.8551(1)$, and $c = 5.5560(1) \, \text{Å}$. There are four formula units per unit cell. At lower Sr and Ni doping levels, the perovskite structure remains orthorhombic; it changes to rhombohedral with an increase of both Sr and Ni content, as shown in Table II (rhombohedral settings transformed from hexagonal settings). Table II lists all single-phase LSFN compositions studied; they fall in the region $0 \leq x \leq 0.3$, $0 \leq y \leq 0.2$. Similar to the LSCN system, a primary unwanted impurity, La$_7$Ni$_2$O$_{19}$, was formed outside the above compositional range. In solely Sr-doped LaFeO$_3$, the orthorhombic lattice parameters $a$, $b$, and $c$ were found to decrease with increasing Sr content (JCPDS 35-1478). Accordingly, the orthorhombic lattice parameters $a$, $b$, and $c$ decrease with both Sr and Ni doping, a trend also reported previously. In the rhombohedral LSFN phases, unlike in the LSCN system, Sr doping at the same Ni doping increases slightly the $\alpha$ parameter while decreasing $\alpha$; the larger Sr$^{2+}$ favors the cubic structure. Ni doping at a given Sr doping does not alter the $\alpha$ parameter, but it decreases $\alpha$ as the smaller Ni$_{2+}$ ion, like the larger Sr$^{2+}$ ion, increases the geometric tolerance factor.

### Table I. Lattice parameters of the La$_{1-x}$Sr$_x$Co$_{1-y}$Ni$_y$O$_3$ system.*

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a(h)$ ($\AA$)</th>
<th>$b(h)$ ($\AA$)</th>
<th>$c(h)$ ($\AA$)</th>
<th>$\alpha(h)$</th>
<th>$\beta(h)$</th>
<th>$\gamma(h)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCoO$_3$</td>
<td>5.5647(1)</td>
<td>7.8551(1)</td>
<td>5.5560(1)</td>
<td>90°</td>
<td>120°</td>
<td>90°</td>
<td>17, 18</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$_x$Ni$_2$O$_3$</td>
<td>5.5560(1)</td>
<td>7.82(1)</td>
<td>5.5560(1)</td>
<td>90°</td>
<td>120°</td>
<td>90°</td>
<td>17, 18</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$<em>x$Fe$</em>{1-y}$Ni$_y$O$_3$</td>
<td>5.534(1)</td>
<td>7.82(1)</td>
<td>5.534(1)</td>
<td>90°</td>
<td>120°</td>
<td>90°</td>
<td>17, 18</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$<em>x$Fe$</em>{1-y}$Ni$_y$O$_3$</td>
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<td>5.534(1)</td>
<td>7.82(1)</td>
<td>5.534(1)</td>
<td>90°</td>
<td>120°</td>
<td>90°</td>
<td>17, 18</td>
</tr>
</tbody>
</table>

* $\alpha(r)$: rhombohedral lattice parameter; $a(h)$ and $c(h)$ are hexagonal parameters.

### Table II. Lattice parameters of the La$_{1-x}$Sr$_x$Fe$_{1-y}$Ni$_y$O$_3$ system.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a(r)$ ($\AA$)</th>
<th>$b(r)$ ($\AA$)</th>
<th>$c(r)$ ($\AA$)</th>
<th>Angles (°)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFeO$_3$</td>
<td>5.5647(1)</td>
<td>7.8551(1)</td>
<td>5.5560(1)</td>
<td>$\alpha = \beta = \gamma = 90°$</td>
<td>17, 18</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$<em>x$Fe$</em>{1-y}$Ni$_y$O$_3$</td>
<td>5.5560(1)</td>
<td>7.82(1)</td>
<td>5.5560(1)</td>
<td>$\alpha = \beta = \gamma = 90°$</td>
<td>This work</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$<em>x$Fe$</em>{1-y}$Ni$_y$O$_3$</td>
<td>5.534(1)</td>
<td>7.82(1)</td>
<td>5.534(1)</td>
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<tr>
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<td>5.534(1)</td>
<td>7.82(1)</td>
<td>5.534(1)</td>
<td>$\alpha = \beta = \gamma = 90°$</td>
<td>This work</td>
</tr>
</tbody>
</table>

The structure of LaFeO$_3$ is orthorhombic at room temperature with space group $Pnma$ (no. 62) and parameters $a = 5.5647(1)$, $b = 7.8551(1)$, and $c = 5.5560(1) \, \text{Å}$, having four formula units per unit cell. At lower Sr and Ni doping levels, the perovskite structure remains orthorhombic; it changes to rhombohedral with an increase of both Sr and Ni content, as shown in Table II (rhombohedral settings transformed from hexagonal settings). Table II lists all single-phase LSFN compositions studied; they fall in the region $0 \leq x \leq 0.3$, $0 \leq y \leq 0.2$. Similar to the LSCN system, a primary unwanted impurity, La$_7$Ni$_2$O$_{19}$, was formed outside the above compositional range. In solely Sr-doped LaFeO$_3$, the orthorhombic lattice parameters $a$, $b$, and $c$ were found to decrease with increasing Sr content (JCPDS 35-1478). Accordingly, the orthorhombic lattice parameters $a$, $b$, and $c$ decrease with both Sr and Ni doping, a trend also reported previously. In the rhombohedral LSFN phases, unlike in the LSCN system, Sr doping at the same Ni doping increases slightly the $\alpha$ parameter while decreasing $\alpha$; the larger Sr$^{2+}$ favors the cubic structure. Ni doping at a given Sr doping does not alter the $\alpha$ parameter, but it decreases $\alpha$ as the smaller Ni$_{2+}$ ion, like the larger Sr$^{2+}$ ion, increases the geometric tolerance factor.

**Thermal analysis**—Figure 2 shows DTA and TGA curves of composition La$_{1-x}$Sr$_x$Fe$_{1-y}$Ni$_y$O$_3$, measured in a mixture of 21%O$_2$ + 79%N$_2$. The DTA curves of Fig. 2a showed only a broad endothermic peak starting from about 700°C on heating; it is related to the onset temperature near 650°C of oxygen loss shown in the TGA curve of Fig. 2b. The material is thermally stable up to 1150°C; the exothermic peaks at 300 and 340°C, respectively, are observed for the first run, but not in an immediately following second run. Obayashi and Kudo$^{11}$ pointed out a similar peak at 335°C in the DTA curve of pure LaNiO$_2$ and attributed it to oxidation of the Mo$_{3+}$ array, but the TGA data do not support this speculation in our case. The TGA curve indicates a reversible oxygen loss and gain during the heating and cooling cycles.

The DTA and TGA curves of composition La$_{1-x}$Sr$_x$Fe$_{1-y}$Ni$_y$O$_3$ are shown in Fig. 3a and b, where two successive runs are shown. It is very clear that an extra endothermic peak at around 180°C followed by two exothermic peaks at 300 and 340°C, respectively, are observed for the first run, but not in an immediately following second run. Obayashi and Kudo$^{11}$ pointed out a similar peak at 335°C in the DTA curve of pure LaNiO$_2$ and attributed it to oxidation of the Mo$_{3+}$ array, but the TGA data do not support this speculation in our case. The TGA curves, Fig. 3b, indicate a corresponding weight loss at 100°C for the first run, but no weight loss at this temperature for the immediately following second run. This observation definitely implies a desorption of adsorbed species.
that are formed via a slow reaction with the atmosphere at room temperature. Since the phenomenon appears to be related to the Ni atoms, we assume that the adsorption process is associated with a reduction of Ni$^{+}$ to Ni$^{0}$ by an exchange of H$_2$O for 1/2O$_2$, for instance, to form Ni(OH)$_2$. The exothermic peaks at 300 and 340°C do not show any weight change, which implies that an internal oxidation-reduction reaction is occurring. We postulate this to be the Fe$^+$ + Ni$^{2+}$ $\rightarrow$ Fe$^{2+}$ + Ni$^{3+}$ reaction. A broad endothermic peak starting around 700°C appears to reflect the oxygen loss that sets in close to this temperature in the TGA curve.

The TECs of all compositions investigated in this study are summarized in Table III. Compared with undoped LaCoO$_3$, and Sr- and Fe-doped LaCoO$_3$, the Sr- and Ni-doped LaCoO$_3$ system has a lower TEC. The Sr- and Ni-doped LaFeO$_3$ system has a TEC similar to that of the electrolytes La$_{1-x}$Sr$_x$Ga$_2$O$_4$ (LSGM) and Zr$_{1-x}$Y$_x$O$_2$-YSZ (YSZ), which is a necessary requirement for the cathode of a practical SOFC. We demonstrate that LSFN also has better electrochemical properties than the cathode material La$_{1-x}$Sr$_x$MnO$_3$ (LSM), which makes it a very promising candidate to replace LSM as a cathode material in SOFCs.

**Electrical properties.**—Figure 4 presents the temperature dependence of the electrical conductivity $\sigma(T)$ for seven polycrystalline samples of the system La$_{1-x}$Sr$_x$Co$_{1-y}$Ni$_y$O$_3$. These $\sigma(T)$ curves are typical of a bad metal or semimetal, as reported for the La$_{1-x}$Sr$_x$CoO$_3$ system by others. Nominal LaCoO$_3$ is a polaronic conductor at low temperatures, but it becomes a metal at high temperatures. However, since the periodic potential at both the Ni and Co atoms of a Co$_{1-y}$Ni$_y$O$_3$ array is strongly perturbed by the presence of the other ions, we could expect to find polaronic conduction or a variable-range hopping with charge carriers moving primarily on a like-cation array in a pathway requiring the least energy.

Polaronic conductivity is usually described by

$$\sigma = A \exp \left( -\frac{E_a}{kT} \right)$$

where $k$ is the Boltzmann factor and $T$ is the absolute temperature. The pre-exponential factor $A$ is proportional to $c(1-c)$, where $c$ is the fraction of mobile charge carriers on a set of like transition-metal atoms that are mixed-valent. $E_a$ is the activation energy for hopping of the small polarons. The corresponding Arrhenius plots of log($\sigma$) vs.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Temperature range (°C)</th>
<th>$\alpha \times 10^6$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCoO$_3$</td>
<td>0–1100</td>
<td>22.0</td>
<td>11</td>
</tr>
<tr>
<td>LaCo$<em>{0.95}$Ni$</em>{0.05}$O$_3$</td>
<td>20–850</td>
<td>15.9</td>
<td>This study</td>
</tr>
<tr>
<td>LaCo$<em>{0.9}$Ni$</em>{0.1}$O$_3$</td>
<td>20–850</td>
<td>14.3</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.85}$Sr$</em>{0.15}$Co$<em>{0.85}$Ni$</em>{0.15}$O$_3$</td>
<td>20–850</td>
<td>17.6</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$Co$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>20–850</td>
<td>16.1</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.75}$Sr$</em>{0.25}$Co$<em>{0.75}$Ni$</em>{0.25}$O$_3$</td>
<td>20–850</td>
<td>16.1</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.7}$Sr$</em>{0.3}$Co$<em>{0.7}$Ni$</em>{0.3}$O$_3$</td>
<td>20–850</td>
<td>15.6</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.65}$Sr$</em>{0.35}$Co$<em>{0.65}$Ni$</em>{0.35}$O$_3$</td>
<td>20–850</td>
<td>16.5</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.6}$Sr$</em>{0.4}$Co$<em>{0.6}$Ni$</em>{0.4}$O$_3$</td>
<td>20–850</td>
<td>15.6</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.55}$Sr$</em>{0.45}$Co$<em>{0.55}$Ni$</em>{0.45}$O$_3$</td>
<td>20–850</td>
<td>12.3</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.5}$Ni$</em>{0.5}$O$_3$</td>
<td>20–850</td>
<td>12.8</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.45}$Sr$</em>{0.55}$Co$<em>{0.45}$Ni$</em>{0.55}$O$_3$</td>
<td>20–850</td>
<td>12.4</td>
<td>This study</td>
</tr>
<tr>
<td>La$<em>{0.4}$Sr$</em>{0.6}$Co$<em>{0.4}$Ni$</em>{0.6}$O$_3$</td>
<td>20–850</td>
<td>12.7</td>
<td>This study</td>
</tr>
<tr>
<td>LaNiO$_3$</td>
<td>0–1100</td>
<td>10.0</td>
<td>11</td>
</tr>
</tbody>
</table>
obtained by perturbations of the periodic site potential and energy lies only a little below the Ni\(^{2+}/Ni^{3+}\) redox energy, intermediate-spin Co\(^{2+}\) ions. However, the Co\(^{2+/Co^{3+}\) redox energy is only a little below the Ni\(^{2+/Ni^{3+}\) redox energy, and spreading of the energy ranges of each redox couple by perturbations of the periodic site potential and entropy considerations may produce some overlap of the couples. Therefore, it is necessary to consider the equilibrium reaction

\[
Co^{3+} + Ni^{3+} \rightleftharpoons Co^{4+} + Ni^{2+}
\]

corresponding to the charge transfer

\[
t^e_0 + t^e_1 \rightleftharpoons t^e_0 + t^e_1
\]

The more this reaction is shifted to the right, the larger the fraction \(c\) of the mobile charge carriers on the cobalt and the nickel arrays. For \(y > 0.5\), the nickel pathways are more numerous than the cobalt pathways; for \(y < 0.5\) the cobalt pathways are more numerous than nickel pathways. The data of Table IV show a difference of 0.04 eV between the \(E_a\), for \(y = 0.4\) and \(y = 0.6\), which suggests that positive polarons on the cobalt array have a larger motional enthalpy \(\Delta H_m\), and hence a lower mobility, than the electrons in the nickel array.

Substitution of Sr\(^2+\) for La\(^3+\) on the A sites creates an equal number of Co\(^{3+/Co^{4+}\) ions, which tends to shift reaction 4 to the left. Moreover, the Ni-atom pathways do not percolate through the lattice for \(y = 0.1\); they begin to percolate only near \(y = 0.2\); therefore, hole conduction on the cobalt array dominates for \(0.1 \leq x \leq 0.3\) and \(p < 0.2\). However, the Sr\(^2+\) ions have a negative lattice charge and trap Co\(^{4+}\) ions by an energy \(\Delta H_1\), while repelling Ni\(^{2+}\) ions. Percolation pathways for holes trapped at Sr\(^2+\) ions set in near \(x = 0.20\). Therefore, \(E_a = \Delta H_1 + (1/2)\Delta H_1\) for the \(x = 0.1\) samples, whereas \(E_a = \Delta H_1\) for the Co\(^{2+/Co^{3+}\) polaron mobility in the \(x = 0.3\) sample. It follows from Table IV that \(\Delta H_1 \approx 0.03\) eV and \(\Delta H_1 = 0.08\) eV for positive polarons on the cobalt array. The small increase in \(E_a\), with increasing \(y\) for fixed \(x = 0.1\) or 0.2 is associated with a large increase in the conductivity. An increase in nickel concentration would increase the number of untrapped holes created by reaction 4 and introduce percolation pathways for the Ni\(^{2+}\) ions. The small change in the activation energy reflects a domination of the hole conduction.

Above 600°C, the loss of oxygen not only reduces the transition-metal cations, it also introduces mobile oxygen vacancies. An oxygen vacancy has a positive lattice charge, it therefore traps Ni\(^{3+}\) ions and repels Co\(^{4+}\) ions. Consequently, \(\Delta H_1\) for the holes on the cobalt array remains essentially unchanged by the introduction of oxygen vacancies, but a progressive reduction in the density of Co\(^{3+}\) ions with increasing oxygen loss flattens the \(\log(\sigma(T))\) vs. \(1/T\) curve for \(T > 600°C\) in samples where hole conduction dominates. Where negative polarons on the nickel array dominate the conduction, as we predicted should be the case for the \(x = 0\) with \(y = 0.6\) sample, the extra Ni\(^{2+}\) ions added by the oxygen vacancies are trapped by the vacancy and only move with the vacancy, which has a much larger \(\Delta H_m\). Therefore, neither the concentration nor

![Fig. 4. Temperature dependence of conductivity for the La\(_{1-x}\)Sr\(_x\)Co\(_{y}\)NiO\(_{3-x}\) system.](image)

![Fig. 5. Plots of log \(\sigma\) vs. 1/T for the La\(_{1-x}\)Sr\(_x\)Co\(_{y}\)NiO\(_{3-x}\) system.](image)
the mobility of the fast negative charge carriers is altered appreciably by the introduction of oxygen vacancies, which is consistent with the observation that this compound shows no change of slope of the log($\sigma$T) vs. 1/T curve above 600°C.

Since the electrical conductivity of the system LSCN is polaronic, Eq. 3 should apply to the La$_{1-x}$Sr$_{x}$Fe$_{1-y}$Ni$_y$O$_{3-z}$ samples prepared in this study. The Arrhenius plots for these samples are compared in Fig. 6 with the plot for La$_{0.65}$Sr$_{0.35}$MnO$_3$ (LSM). The slight curvatures occurring for samples with lower Sr and Ni doping level in Fig. 6 are possibly the result of oxygen loss beginning above 550°C; therefore, some of the $E_a$ values given in Table V were taken from the slopes of the curves over the temperature range 320 ≤ T ≤ 550°C.

Interpretation of the data is analogous to that for the La$_{1-x}$Sr$_{x}$Co$_{1-y}$Ni$_y$O$_3$ samples except that reaction 4 is replaced by

$$\text{Fe}^{3+} + \text{Ni}^{3+} \rightarrow \text{Fe}^{4+} + \text{Ni}^{2+}$$

[5]

corresponding to the charge transfer

$$t^3\text{e}^2 + t^2\text{e}^1 \leftrightarrow t^2\text{e}^1 + t^3\text{e}^2$$

[5a]

Reactions 4 and 5 are both applicable because the Ni$^{3+}$/Ni$^{2+}$ redox energy lies between the Co$^{3+}$/Co$^{2+}$ and Fe$^{3+}$/Fe$^{2+}$ redox energies. The literature data for $x = 0.3$ and $y = 0$ gives $E_a = 0.29$ eV[6], and we can anticipate a larger $\Delta H_a$ for polaronic conduction in the Fe$^{3+}$/Fe$^{2+}$ array compared to that in the Co$^{3+}$/Co$^{2+}$ array of La$_{1-x}$Sr$_x$Co$_{1-y}$Ni$_y$O$_3$. The data of Table V suggest a $\Delta H_a = 0.1$ eV and a $\Delta H_a = 0.4$ eV for the Fe$^{3+}$/Fe$^{2+}$ couple; a $\Delta H_a = 0.04$ eV for the Ni$^{3+}$/Ni$^{2+}$ couple compared to 0.03 eV in LSCN. A greater electron localization can be expected to make Jahn–Teller electron coupling to a local site deformation stronger at high-spin Fe$^{3+}$ than at low-spin Ni$^{3+}$. The large increase in $\sigma(T)$ on increasing $y$ from 0.1 to 0.2 and $x$ from 0.1 to 0.3 signals the introduction at $y = 0.2$ and $x = 0.2$ of percolation pathways for Ni$^{2+}$ and Fe$^{3+}$ conduction, respectively. Percolation pathways decrease the trapping energy $\Delta H$, and hence the activation energy $E_a$. This decrease is particularly marked with increasing $x$ for a fixed value of $y$ since the trapping energy $\Delta H = 0.4$ eV of Fe$^{3+}$ by Sr$^{2+}$ ions is large.

Figure 6 shows that the log ($\sigma$T) vs. 1/T curves for La$_{0.65}$Sr$_{0.35}$MnO$_3$ and La$_{0.65}$Sr$_{0.35}$Fe$_{0.95}$Ni$_{0.05}$O$_3$ are nearly identical while La$_{1-x}$Sr$_x$Fe$_{1-y}$Ni$_y$O$_3$ has a much higher $\sigma(T)$. In addition, loss of oxygen above 550°C in the LSFN compounds makes them mixed electronic and oxide-ion conductors in the oxidizing atmosphere of the cathode, which makes them excellent candidate cathode materials for SOFCs.

### Table V. Activation energy of La$_{1-x}$Sr$_x$Fe$_{1-y}$Ni$_y$O$_3$ system.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$y$</th>
<th>Temperature range (°C)</th>
<th>$E_a$ (eV)</th>
<th>$\rho/\rho_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6</td>
<td>320–800</td>
<td>0.04</td>
<td>0.96</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>320–550</td>
<td>0.28</td>
<td>0.80</td>
</tr>
<tr>
<td>0.20</td>
<td>0.10</td>
<td>320–550</td>
<td>0.24</td>
<td>0.93</td>
</tr>
<tr>
<td>0.20</td>
<td>0.20</td>
<td>320–550</td>
<td>0.14</td>
<td>0.95</td>
</tr>
<tr>
<td>0.20</td>
<td>0.30</td>
<td>320–550</td>
<td>0.13</td>
<td>0.94</td>
</tr>
<tr>
<td>0.20</td>
<td>0.30</td>
<td>320–800</td>
<td>0.10</td>
<td>0.92</td>
</tr>
<tr>
<td>0.20</td>
<td>0.30</td>
<td>320–800</td>
<td>0.08</td>
<td>0.91</td>
</tr>
</tbody>
</table>

*Note: $\rho_0$ is the theoretical density, $\rho$ is the sample density.*
This formalism allows a qualitative interpretation of Fig. 7 and 8.

According to our model of the conduction process, the $x = 0$ samples should be dominated by positive polarons for $y < 0.5$ and by negative polarons for $y > 0.5$. Accordingly, the $y = 0.6$ and 0.8 samples of Fig. 7 and 8 all show a nearly temperature-independent $\alpha < 0$ below 500°C with a decrease in $\alpha$ with increasing temperature $T > 500°C$ that correlates with a progressive loss of oxygen and also an anticipated increase in charge carriers via thermal excitation of reactions 4 or 5. Moreover, all the $y < 0.4$ samples have an $\alpha > 0$ at temperatures $T < 400°C$. Only the $x = 0$, $y = 0.4$ sample of Fig. 7 definitely shows a change of sign of $\alpha$ at higher temperatures. In this sample, equal numbers of electrons and holes are created by reaction 4, and percolation pathways are available to both $\text{Co}^{4+}$ and $\text{Ni}^{2+}$ ions. However, a greater number of pathways for $\text{Co}^{4+}$ motion would favor $p$-type conduction at lower temperatures. Loss of oxygen at higher temperatures would increase the concentration of $\text{Ni}^{2+}$ ions and decrease the concentration of $\text{Co}^{4+}$, which favors the change to an $\alpha < 0$.

In Fig. 7 and 8, the $y = 0.1$, $p = 0.2$ samples have the smallest concentration of mobile holes and therefore the largest $\alpha_0$ of a given system. Since the Ni atoms do not form percolation pathways, the negative contribution to $\alpha$ from $\alpha_0$ is minimal; therefore, $\alpha > 0$ is large and increases with decreasing temperature due to a progressive trapping of the mobile holes at the Sr$^{2+}$ ions. Any contribution from the disproportionation reaction $2\text{Co}^{4+}\text{t}^+\text{e}^- = \text{Co}^{2+}\text{t}^+\text{e}^- + \text{Co}^{3+}\text{t}^+\text{e}^-$ appears to be small in view of the large $\alpha > 0$ at the highest temperatures of this study. The larger magnitude of $\alpha(T)$ in Fig. 8 compared to Fig. 7 reflects the larger $\Delta H_n$ in the LSFN sample. At temperatures $T > 600°C$, oxygen loss decreases the concentration of mobile holes, and $\alpha(T)$ flattens out.

Increasing $y$ to $y = 0.2$ introduces percolation pathways for the negative polarons that are created by reactions 4 and 5; it also creates more positive polarons, which lower $\alpha_0$, and $\alpha > 0$ reflects the dominance of the hole conduction at high temperatures. At low temperatures, most of the holes introduced by the Sr$^{2+}$ ions are trapped, and $\alpha$ is determined by the untrapped holes and electrons created by reaction 4 or 5. Where the conduction remains dominated by the holes, an increase in $\alpha$ with decreasing temperature reflects trapping of the holes at Sr$^{2+}$ ions, and this situation is found in the LSCN system of Fig. 7. In the LSFN system of Fig. 8, the negative charge carriers have a much lower motional enthalpy $\Delta H_{m}^{n}$, which makes $\alpha_0$ competitive with $\alpha$, even above room temperature as the holes introduced by the Sr$^{2+}$ ions are trapped.

At the lowest temperatures, holes introduced by $x = 0.1$ Sr$^{2+}$ ions are trapped and a nearly equal number of mobile holes and electrons is generated by reaction 5. The larger number of conduction pathways for the holes might be expected to make $\mu_{\alpha_0}$ dominate $\mu_{\alpha_n}$, but the negative polarons have a significantly lower $\Delta H_{m}^{n}$, which makes $\mu_{\alpha_0}$ increase relative to $\mu_{\alpha_n}$ as the temperature decreases. In order to determine whether $\mu_{\alpha_0}$ dominates $\mu_{\alpha_n}$ at lower temperatures, the $\alpha(T)$ data of Fig. 9 were taken. The $\alpha(T)$ curve becomes negative only for $x = 0.1$ but also for 0.2 and 0.3, where fewer holes are trapped by Sr$^{2+}$ ions because they have access to percolation pathways. Nevertheless, the relatively large motional enthalpy for the holes on the iron array allows $\mu_{\alpha_n}$ to be dominant at the lowest temperatures in the $x = 0.2$ and 0.3 samples also.

Impedance spectroscopy—Figure 10 compares two-probe impedance spectroscopy data taken in air at 800°C with LSGM as the solid electrolyte sandwiched between two like cathode materials consisting of (a) $\text{La}_{0.95}\text{Sr}_{0.05}\text{Co}_{0.8}\text{Ni}_{0.2}\text{O}_{3-δ}$, (b) $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-δ}$, (c) $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.3}\text{O}_{3-δ}$, and (d) $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3}$ (LSM). The electrode resistances, taken as $R_{0\theta} = R_{0\theta} - R_{\theta}$, are given in Table VI. $\Delta R$ for the LSCN electrode is smaller than that for the LSCo electrode. $\Delta R$ for the LSFN electrode is higher, but it is half that of the LSM electrode. Combining the impedance data with the TEC data of Table III shows that the LSCN and LSFN materials are promising replacements of LSCo and LSM cathodes in a SOFC. Confirmation of the superiority of these electrodes is awaiting results from commercial tests on prototype fuel cells.

Conclusions

The electrical conductivities of both the LSCN and LSFN systems appear to be polaronic with an overlap of the $\text{Co}^{3+}/\text{Co}^{4+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$ couples in the former and of the $\text{Fe}^{4+}/\text{Fe}^{3+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$ couples in the latter. This overlap provides two types of polaronic conduction, $p$-type and $n$-type, with the $p$-type carriers moving on the Co- or Fe-atom array and the $n$-type carriers on the Ni-atom array. The motional enthalpies are estimated to be $\Delta H_{m}^{n} = 0.03$, ...
tives to the conventional cathode materials now employed. The LSCN and LSFN systems thus offer attractive alternatives with good catalytic activity for oxygen reduction.

600°C, which makes them mixed electronic/oxide-ion conductors. With TEC of LSCo, and they show a comparable electrode resistance at an operating temperature T > 700°C. In contrast to the conventional La$_{1-x}$Sr$_x$MnO$_3$ cathode, these materials lose oxygen reversibly at T > 800°C, which makes them mixed electronic/oxide-ion conductors with good catalytic activity for oxygen reduction.

LSFN electrode

LSM electrode

0.02, and 0.08 eV for Ni$^{2+}$, Co$^{2+}$, and Fe$^{3+}$ polaronic species, respectively. At lower Sr contents, the mobile holes become trapped by the Sr$^{2+}$ ions by an energy $\Delta H_1 = 0.08$ eV for Co$^{2+}$ and $\Delta H_2 = 0.4$ eV for Fe$^{3+}$. As a result of the larger trapping energy $\Delta H_2$ for holes in the Fe-atom array, the thermoelectric power measurements explicitly show the dominance of n-type carriers at lower temperatures with a transition from a positive to a negative effective Seebeck coefficient on cooling. The compositions La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Ni$_{0.2}$O$_3$ and La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Ni$_{0.2}$O$_3$ have a TEC better matched to that of electrolyte than the TEC of LSCo, and they show a comparable electrode resistance at an operating temperature $T_{op} \approx 700^\circ$C. In contrast to the conventional La$_{1-x}$Sr$_x$MnO$_3$ cathode, these materials lose oxygen reversibly at $T > 800^\circ$C, which makes them mixed electronic/oxide-ion conductors with good catalytic activity for oxygen reduction.

The LSCN and LSFN systems thus offer attractive alternatives to the conventional cathode materials now employed in SOFCs.

Table VI. Comparison of electrode resistance of several cathode materials at 800°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>$R_{\mu}$ (Ω)</th>
<th>$R_{\text{res}}$ (Ω)</th>
<th>$\Delta R$</th>
<th>$R_{\text{res}} - R_{\mu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCN</td>
<td>29.8</td>
<td>36.1</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>LSFN</td>
<td>34.4</td>
<td>53.2</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>LSCo</td>
<td>32.7</td>
<td>45.5</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>LSM</td>
<td>31.6</td>
<td>68.7</td>
<td>37.1</td>
<td></td>
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