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Sr- and Ni-Doped LaCoO₃ and LaFeO₃ Perovskites

New Cathode Materials for Solid-Oxide Fuel Cells

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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 O₂ 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 O²⁻ ions to the electrolyte for transfer to the anode where they combine with the fuel to form H₂O and CO₂ 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 Tₐ ≥ 700°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 electrochemically conducting in an O₂ atmosphere can perform the first two functions. At Tₐ, the loss of bound water from the surface of an oxide creates surface-oxygen vacancies, which we denote by □. If the oxide is an electronic conductor, the vacant bond of the dioxygen molecule may be broken by the reactions

\[ O₂ + □ + 2e^- = (O₂)²⁻ \]
\[ (O₂)²⁻ + □ + 2e^- = 2 O²⁻ \]

However, unless the surface oxygen contacts an interconnected oxide-ion subarray that also contains oxygen vacancies, conduction of O²⁻ 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 La₉Sr₅MnO₁₅, that has been used extensively as a cathode in ZrO₂-based SOFCs. It remains a good electronic conductor, but the lack of oxide-ion vacancies, and hence of oxide-ion conduction, at Tₐ forces the use of oxide-ion conductors at temperatures T > 1100°C where they lose oxygen to form H₂O and CO₂ with the release of electrons to the external circuit. 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 La₉Sr₅CoO₁₅, 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.  Several nickelates are also good oxide-ion conductors in an oxidizing atmosphere at 700 ≤ Tₐ ≤ 1000°C. For this purpose, we have used the Ni₃²⁺/Ni⁴⁺ redox couple in association with the Fe⁴⁺/Fe³⁺ and the low-spin/intermediate-spin Co⁵⁺/Co³⁺ couples in the perovskite structure. It was anticipated that the presence of the Ni₃²⁺/Ni⁴⁺ redox couple would suppress low-spin-to-high-spin and/or itinerant-to-polaronic transitions so as to reduce the thermal expansion without loss of electrical conductivity.

Unfortunately, the thermal expansion of the La₉Sr₅CoO₁₅ 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 Co⁵⁺ ions even where an intermediate-spin state has been stabilized over most of the CoO₂₋₃ matrix. However, these nickelates are thermally unstable and quickly lose oxygen to form H₂O and CO₂ with the release of electrons to the external circuit. For this reason, we have used the Ni₃²⁺/Ni⁴⁺ redox couple in association with the Fe⁴⁺/Fe³⁺ and the low-spin/intermediate-spin Co⁵⁺/Co³⁺ couples in the perovskite structure. The early observations of metallic conductivity in the Na₁WO₄, La₉MnO₁₅, and La₉SrMnO₁₅, mixed-valent perovskite systems became clarified with the prediction by Goodenough and demonstration by Raccah of the metallic conductivity and Pauli paramagnetism of stoichiometric LaNiO₃, containing low-spin Ni²⁺. The metallic conductivity is due to strong Ni²⁺-O covalent bonding, which causes the σ-bonding e orbitals of octahedral-site, low-spin Ni²⁺ to be transformed into itinerant σ*-band states as a result of (180°-) Ni-O-Ni interactions in the NiO₂⁻ array. Subsequently, the systems La₉M₉NiO₁₅, M = Ca, Sr, and Ba, 0 ≤ x ≤ 0.05, were studied extensively by several groups. However, these nickelates are thermally unstable at temperatures T ≥ 1100°C where they lose oxygen to form Ruddlesden-Popper intergrowth structures (La₉Sr₉₋ₓNiₓO₃₋ₓ). Below 1100°C, the Ni⁵⁺ ions retain their low-spin configuration, and LaNiO₃ has a relatively small thermal-expansion coefficient of 10.0 × 10⁻⁶ K⁻¹. By contrast, the low-spin Co⁵⁺, t²⁰ configuration makes LaCoO₃ a diamagnetic insulator at the lowest temperatures, but it becomes more metallic at the highest temperature where an intermediate-spin state t²²σ⁺ is stabilized at the Co⁴⁺ ions. In the system La₉Sr₅CoO₁₅, the intermediate-spin state Co⁴⁺ becomes stabilized at lower temperatures, but as a ferromagnetic itinerant polaronic state, the presence of the low-spin-to-high-spin transition is more difficult to achieve in the nickelate system. The larger Sr²⁺ ion may induce a change from itinerant to polaronic behavior above the Curie temperature in the fer-
romagnetic phase. These electronic transitions give \( \text{La}_{1-x} \text{Sr}_{x} \text{CoO}_3 \) a large thermal expansion coefficient (TEC ~ \( 22.0 \times 10^{-6} \) K\(^{-1}\)), but the stability of the Co\(^{3+}/\text{Co}^{4+}\) couple makes it difficult to oxidize fully the Co\(^{3+}\) array and therefore introduces oxygen vacancies into this array while retaining itinerant \( \sigma \)-band states in the ferromagnetic phase.\(^{22}\) Substitution of Ni\(^{3+}\) for Co\(^{3+}\) in \( \text{La}_{1-x} \text{Sr}_{x} \text{CoO}_3 \) is designed to retain mixed-valent polaronic conduction at temperatures \( T > 300 \) K while eliminating the Co\(^{3+}-\text{rich phase and with the low-spin to higher-spin transitions that contribute to the large TEC in} \text{La}_{1-x} \text{Sr}_{x} \text{CoO}_3 \). At the same time, operation on the Co\(^{3+}/\text{Co}^{4+}\) and/or Ni\(^{3+}/\text{Ni}^{4+}\) redox couples should retain oxygen vacancies in the Co\(^{3+}\) array. Undoped \( \text{LaFeO}_3 \) contains high-spin Fe\(^{3+}\)-t\(^2\)g localized-electron configurations; it is an antiferromagnetic insulator with a Néel temperature \( T_N = 750 \) K.\(^{17,18}\) In the \( \text{La}_{1-x} \text{Sr}_{x} \text{FeO}_3 \) system, a thermally activated hopping of small polarons between Fe ions appears to describe the transport properties. Abbate et al.\(^{21}\) have shown, with soft X-ray absorption spectroscopy, that the initial substitution of Sr\(^{2+}\) for La\(^{3+}\) in \( \text{La}_{1-x} \text{Sr}_{x} \text{FeO}_3 \) oxidizes primarily the oxygen rather than the iron atoms of the FeO\(_3\) array; the holes occupy molecular antibonding states of an FeO\(_3\) complex in which the dominant component of the ground state is 3d\(^5\)L, where L denotes a ligand hole. However, as the Sr\(^{2+}\)-ion concentration increases, the spectral weight shifts to an increasing Fe-5d component in the hole ground state. The band bending under SrO\(_2\)-redox con- 

undation: The crystal structure was determined by powder X-ray diffraction with a Philips PW1729 diffractometer and Cu K\(\alpha\) radiation; a Ni filter was used for all measurements. The scanning angles ranged from 10 to 80° with a step of 2°/min. Silicon powder was used for the internal standard in order to subtract the equipment errors from the data. The diffraction patterns were then indexed, and the lattice parameters obtained by Rietveld refinement.

**Thermal analysis.**—The thermal behaviors of the prepared samples were monitored with a Perkin-Elmer 7 Series thermal analysis system. Thermogravimetric analysis (TGA) was conducted in an artificial atmosphere of air from room temperature to 850 or 900°C with heating and cooling rates of 1.0°C/min. Thermal mechanical analysis (TMA), including the TEC, and differential thermal analysis (DTA) were carried out separately in open air from room temperature to 850°C and room temperature to 1150°C, respectively, with a heating rate of 10°C/min.

**Electrical conductivity.**—The conductivity of sintered samples was measured with the standard dc four-point method described by van der Pauw.\(^{25}\) The sintered pellets were cut into slices with a large length/cross section ratio. Two Pt electrodes were used for conducting current along the length, and two Pt electrodes were used for measuring voltage across the section at a certain distance. The measurements were carried out in open air from 320 to 800°C in both heating and cooling cycles. The applied current and the resulting voltage were supplied and 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.\(^{24}\)

**Impedance spectroscopy with prepared electrodes** LSCN and LSFN.—Impedance spectroscopy of the \( \text{La}_0.7 \text{Sr}_0.3 \text{Ga}_0.5 \text{Mg}_0.5 \text{O}_3 \) (LSGM) electrolyte with 10 mol% Fe Oxford 99.5% and SSFN, was performed in a 1 Hz to 100 kHz range in an HP4192A LF impedance analyzer from 800 to 320°C in open air. The frequencies of the measurements scan 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 \( \text{La}_0.7 \text{Sr}_{0.3} \text{CoO}_3 \) (LSCO) and \( \text{La}_0.7 \text{Sr}_{0.3} \text{MnO}_3 \) (LSM) were also measured and compared with the investigated electrodes.

**Results and Discussion**

**Crystal structure.**—Typical X-ray diffraction patterns are shown in Fig. 1. The compositions \( \text{La}_0.7 \text{Sr}_{0.3} \text{CoO}_3 \text{Ni}_0.5 \text{O}_3 \) and \( \text{La}_0.7 \text{Sr}_{0.3} \text{FeO}_3 \text{Ni}_0.5 \text{O}_3 \) were chosen as examples.
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 $a$ parameter is essentially invariant within experimental error. However, comparison of the distortion angles $\alpha$ at the same Ni dopings reveals a decrease with Sr doping, which is consistent with the finding that $a$ becomes 90° (cubic) when the Sr doping becomes $x = 0.5$. In contrast, at the same Sr concentration, $a$ increases with Ni content, since Ni favors the rhombohedral structure.

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

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a$, Å</th>
<th>$c$, Å</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCoO$_3$</td>
<td>5.5647(1)</td>
<td>5.5580(1)</td>
<td>17, 18</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$Fe$_2$O$_3$</td>
<td>5.5342(2)</td>
<td>5.509(1)</td>
<td>This work</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$Ni$_2$O$_3$</td>
<td>5.548(3)</td>
<td>5.506(2)</td>
<td>This work</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$Fe$_2$O$_3$</td>
<td>5.5342(2)</td>
<td>5.509(1)</td>
<td>This work</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$Ni$_2$O$_3$</td>
<td>5.548(3)</td>
<td>5.506(2)</td>
<td>This work</td>
</tr>
</tbody>
</table>

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

For Sr doping at a given Ni doping does not alter the a parameter, but it decreases as a smaller Ni atom, like the larger Sr$^{2+}$ ion, increases the geometric tolerance factor.

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

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a$, Å</th>
<th>$c$, Å</th>
<th>Angles (°)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFeO$_3$</td>
<td>5.5647(1)</td>
<td>5.5580(1)</td>
<td>$\alpha = \beta = \gamma = 90°$</td>
<td>17, 18</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$Fe$_2$O$_3$</td>
<td>5.5342(2)</td>
<td>5.509(1)</td>
<td>$\alpha = \beta = \gamma = 90°$</td>
<td>This work</td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$Ni$_2$O$_3$</td>
<td>5.5342(2)</td>
<td>5.509(1)</td>
<td>$\alpha = \beta = \gamma = 90°$</td>
<td>This work</td>
</tr>
</tbody>
</table>

### Thermal analysis

Figure 2 shows DTA and TGA curves of composition La$_{1-x}$Sr$_x$Co$_{y}$Ni$_{1-y}$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, 20 mol % Ni doping does not deteriorate the thermal stability of the Sr-doped LaCoO$_3$ system. The TGA curve indicates a reversible oxygen loss and gain during the heating and cooling cycles.

The DTA and TGA curves of composition La$_{0.5}$Sr$_{0.5}$Fe$_2$O$_3$, 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$^{15}$ pointed out a similar peak at 335°C in the DTA curve of pure LaNiO$_3$, and attributed it to oxidation of the Mo$_{5}$Mo 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$^{4+}$ to Ni$^{2+}$ 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$^3+$ + Ni$^{4+}$ $\rightarrow$ 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$_{2.5}$ (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 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

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

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. $T$ are shown in Figure 4. The activation energy is highest for the end members, LaNiO$_3$ and LaCoO$_3$, and lowest for the intermediate compositions La$_{0.5}$Sr$_{0.5}$Co$_{0.5}$Ni$_{0.5}$O$_3$ and La$_{0.5}$Sr$_{0.5}$Fe$_{0.5}$Ni$_{0.5}$O$_3$.

**Table III.** Thermal expansion coefficients $\alpha$, of the studied compositions.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Temperature range (°C)</th>
<th>$\alpha \times 10^4$/K</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>LaCo$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>20–850</td>
<td>17.6</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.1}$Co$</em>{0.9}$Ni$_{0.1}$O$_3$</td>
<td>20–850</td>
<td>16.1</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.15}$Co$</em>{0.85}$Ni$_{0.1}$O$_3$</td>
<td>20–850</td>
<td>16.1</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.2}$Co$</em>{0.8}$Ni$_{0.2}$O$_3$</td>
<td>20–850</td>
<td>15.6</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.25}$Co$</em>{0.75}$Ni$_{0.25}$O$_3$</td>
<td>20–850</td>
<td>16.5</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.3}$Co$</em>{0.7}$Ni$_{0.3}$O$_3$</td>
<td>20–850</td>
<td>15.3</td>
<td>This study</td>
</tr>
<tr>
<td>LaFe$<em>{0.1}$Ni$</em>{0.9}$O$_3$</td>
<td>20–850</td>
<td>11.6</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.1}$Fe$</em>{0.9}$Ni$_{0.1}$O$_3$</td>
<td>20–850</td>
<td>11.7</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.15}$Fe$</em>{0.85}$Ni$_{0.1}$O$_3$</td>
<td>20–850</td>
<td>12.6</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.2}$Fe$</em>{0.8}$Ni$_{0.2}$O$_3$</td>
<td>20–850</td>
<td>12.3</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.25}$Fe$</em>{0.75}$Ni$_{0.25}$O$_3$</td>
<td>20–850</td>
<td>12.6</td>
<td>This study</td>
</tr>
<tr>
<td>LaSr$<em>{0.3}$Fe$</em>{0.7}$Ni$_{0.3}$O$_3$</td>
<td>20–850</td>
<td>12.4</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>
The temperature dependence of conductivity for the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_3$ system is shown in Fig. 4. Curve-fitting below 600°C yield activation energies in the range 0.02 < $E_a$ < 0.07 eV (see Table IV). With such low activation energies in polycrystalline samples, it is unclear to what extent they reflect grain-boundary as against intragrain conduction; therefore, the densities of the measured samples are also shown in Table IV.

Interpretation of these data as representative of intragrain conduction begins with the observation that the oxygen content does not vary below 600°C. Therefore, we assume that the oxygen content is essentially stoichiometric over the temperature range in which $E_a$ was obtained from Eq. 3. We also note that the substitution of Sr for La on the A sites creates an equal number of Co$^{3+}$ ions, which tends to shift reaction 4 to the left. Moreover, the Ni-atom pathways do not percolate through the lattice for $y < 0.1$; hence, hole conduction on the cobalt array dominates. Where negative polarons on the nickel array are trapped by the vacancy and only move with the vacancy, which has a nickel concentration of $0.3$ or $0.4$, they begin to percolate only near $p = 0.2$; therefore, hole conduction on the cobalt array dominates for $0.1 < x < 0.3$ and $p < 0.2$. However, the Sr$^{2+}$ ions have a negative lattice charge and trap Co$^{3+}$ ions by an energy $\Delta H_m$, while repelling Ni$^{2+}$ ions. Percolation pathways for holes trapped at Sr$^{2+}$ ions set near $x = 0.2$. Therefore, $E_a = \Delta H_m + (1/2)\Delta H_f$ for the $x = 0.1$ samples. The small increase in $E_a$ for fixed $y$ or $x = 0.1$ 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$^{2+}$ ions and repels Co$^{3+}$ ions. Consequently, $\Delta H_m$ 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 conductivity, 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 the reaction 4.

Table IV. Activation energy of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_3$ system.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$y$</th>
<th>Temperature range (°C)</th>
<th>$E_a$ (eV)</th>
<th>$\rho/\rho_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.4</td>
<td>320–800</td>
<td>0.07</td>
<td>0.91</td>
</tr>
<tr>
<td>0.00</td>
<td>0.6</td>
<td>320–800</td>
<td>0.03</td>
<td>0.97</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>320–700</td>
<td>0.06</td>
<td>0.95</td>
</tr>
<tr>
<td>0.10</td>
<td>0.20</td>
<td>320–700</td>
<td>0.05</td>
<td>0.91</td>
</tr>
<tr>
<td>0.20</td>
<td>0.20</td>
<td>320–700</td>
<td>0.04</td>
<td>0.89</td>
</tr>
<tr>
<td>0.30</td>
<td>0.10</td>
<td>320–700</td>
<td>0.02</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Note: $\rho_m$ is the theoretical density, $\rho$ is the sample density.

cobalt atoms are present as intermediate-spin Co$^{3+}$ and Ni$^{2+}$ in the samples of Fig. 4 and 5.

We begin with the $x = 0$ samples, which might be expected to be single valent with only low-spin Ni$^{2+}$ and intermediate-spin Co$^{3+}$ ions. However, the Co$^{3+}$/Co$^{4+}$ redox energy lies 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

$$\text{Co}^{3+} + \text{Ni}^{2+} \leftrightarrow \text{Co}^{4+} + \text{Ni}^{3+}$$

(corresponding to the charge transfer)

$$t^e + t^e \leftrightarrow t^{2e} + t^e$$

The more this reaction is shifted to the right, the larger the fraction 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$^{3+}$ ions, which tends to shift reaction 4 to the left. Moreover, the Ni-atom pathways do not percolate through the lattice for $y = 0.1$; hence, hole conduction on the cobalt array dominates for $0.1 < x < 0.3$ and $p < 0.2$. However, the Sr$^{2+}$ ions have a negative lattice charge and trap Co$^{3+}$ ions by an energy $\Delta H_m$, while repelling Ni$^{2+}$ ions. Percolation pathways for holes trapped at Sr$^{2+}$ ions set near $x = 0.2$. Therefore, $E_a = \Delta H_m + (1/2)\Delta H_f$ for the $x = 0.1$ samples. The small increase in $E_a$ for fixed $y$ or $x = 0.1$ 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$^{2+}$ ions and repels Co$^{3+}$ ions. Consequently, $\Delta H_m$ 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 conductivity, 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 $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_3$ system.

Fig. 5. Plots of log $\sigma T$ vs. $1/T$ for the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_3$ system.
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(αT) vs. 1/T curve above 600°C.

Since the electrical conductivity of the system La$_{1-x}$Sr$_x$Fe$_{1-y}$Ni$_y$O$_3$ is polaronic, the Eq. 3 should apply to the La$_{1-x}$Sr$_x$Fe$_{1-y}$Ni$_y$O$_3$ 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 conventional cathode material for SOFCs. The slight curvatures occurring for samples with lower Sr and Ni doping level in Fig. 6 are possibly the result of oxygen loss beginning about 550°C, therefore, some of the Ea values given in Fig. 7 are possibly the result of oxygen loss beginning above 550°C; therefore, some of the Ea 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:

$$\text{Fe}^{3+} + \text{Ni}^{3+} \rightarrow \text{Fe}^{2+} + \text{Ni}^{4+}$$  \[5\]

corresponding to the charge transfer:

$$\text{t}^+\text{e}^- + \text{t}^+\text{e}^- \rightarrow \text{t}^+\text{e}^- + \text{t}^+\text{e}^-$$  \[5a\]

Reactions 4 and 5 are both applicable because the Ni$^{3+}$/Ni$^{4+}$ redox energy lies between the Co$^{3+}$/Co$^{4+}$ and Fe$^{3+}$/Fe$^{2+}$ redox energies. The literature data for x = 0.3 and y = 0 gives $E_c$ = 0.29 eV\(^{39}\) and we can anticipate a larger $\Delta H_f$ for polaronic conduction in the Fe$^{3+}$/Fe$^{2+}$ array compared to that in the Co$^{3+}$/Co$^{4+}$ array of La$_{1-x}$Sr$_x$Co$_{1-y}$Ni$_y$O$_3$. The data of Table V suggest a $\Delta H_f$ = 0.1 eV and a $\Delta H_f$ = 0.4 eV for the Fe$^{3+}$/Fe$^{2+}$ couple; a $\Delta H_f$ = 0.04 eV for the Ni$^{3+}$/Ni$^{4+}$ 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 α(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$^{3+}$ and Fe$^{3+}$ conduction, respectively. Percolation pathways decrease the trapping energy $\Delta H_t$ 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 $\Delta H_t$ = 0.4 eV of Fe$^{3+}$ by Sr$^{2+}$ ions is large.

Figure 6 shows that the log α(T) vs. 1/T curves for La$_{0.65}$Sr$_{0.35}$MnO$_3$ and La$_{0.65}$Sr$_{0.35}$Fe$_{0.97}$Ni$_{0.03}$O$_3$ are nearly identical while La$_{0.65}$Sr$_{0.35}$Fe$_{0.9}$Ni$_{0.1}$O$_3$ has a much higher α(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.

**Thermolectric power.**—Figures. 7 and 8 show the temperature dependence of the Seebeck coefficient α(T) from room temperature to 700°C for samples of the LSCN and LSFN systems. For small-polaron conduction and two types of charge carriers simultaneously present:\(^{35}\)

$$\alpha = \frac{\mu_a \alpha_a c_a + \mu_b \alpha_b c_b}{\mu_a c_a + \mu_b c_b}$$  \[6\]

where $\mu_a$ and $\mu_b$ are the mobilities of the electron and hole carriers, respectively, and:

$$\alpha_e = \frac{k_e}{e} \ln \left[ \frac{\beta (1 - c_e)}{c_e} \right] = \frac{k_e}{e} \ln \left[ \frac{\beta (1 - c_p)}{c_p} \right]$$  \[7\]

The spin-degeneracy factor is $\beta = 2$ in our case, and:

$$c_e = p/[M], \quad c_p = n/[Ni]$$  \[8\]

with $M = \text{Co or Fe}$. Trapping of charge carriers by $\Delta H_{in}$ and $\Delta H_{ho}$, respectively, reduces the concentration of free charge carriers to:

$$n = [\text{Ni}^{3+}] \exp \left( \frac{-\Delta H_{in}}{2kT} \right)$$

$$p = [\text{M}^{4+}] \exp \left( \frac{-\Delta H_{ho}}{2kT} \right)$$  \[9\]
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 $p = 0.4$ 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. This sample, equal numbers of electrons and holes are created by reaction 4, and percolation pathways are available to both Co$^{IV}$ and Ni$^{II}$ ions. However, a greater number of pathways for Co$^{IV}$ motion would favor p-type conduction at lower temperatures. Loss of oxygen at higher temperatures would increase the concentration of Ni$^{II}$ ions and decrease the concentration of Co$^{IV}$, which favors the change to an $\alpha < 0$.

In Fig. 7 and 8, the $x = 0.1, y = 0.1$ samples have the smallest concentration of mobile holes and therefore the largest $\alpha_p$ of any given system. Since the Ni atoms do not form percolation pathways, the negative contribution to $\alpha$ from $\alpha_p$ 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 $2\text{Co}^{IV}_{\text{O}^2} + \text{Co}^{III}_{\text{O}^2} = \text{Co}^{III}_{\text{O}^2} + \text{Co}^{IV}_{\text{O}^2}$ 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 $\Delta H_m$ 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 $\alpha_n$ 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 $\Delta H_m$, which makes $\alpha_n$ competitive with $\alpha_p$ 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 $\mu_{p,\alpha_n}$ dominate $\mu_{p,\alpha_m}$, but the negative polarons have a significantly lower $\Delta H_m$, which makes $\mu_{p,\alpha_n}$ increase relative to $\mu_{p,\alpha_m}$ as the temperature decreases. In order to determine whether $\mu_{p,\alpha_m}$ dominates $\mu_{p,\alpha_n}$ at lower temperatures, the $\alpha(T)$ data of Fig. 9 were taken. The $\alpha(T)$ curve becomes negative not 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 $\mu_{p,\alpha_n}$ to become 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) La$_{0.85}$Sr$_{0.15}$MnO$_3$ (LSM), (b) La$_{0.85}$Sr$_{0.15}$Fe$_{0.2}$Ni$_{0.8}$O$_{3-δ}$, (c) La$_{0.85}$Sr$_{0.15}$Co$_{0.8}$O$_{3-δ}$, and (d) La$_{0.85}$Sr$_{0.15}$MnO$_3$ (LSM). The electrode resistances, taken as $R_0$, $R_b$, $R$ are given in Table VI. $AR$ for the LSCN electrode is smaller than that for the LSCo electrode, $AR$ 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 Co$^{IV}$/Co$^{III}$ and Ni$^{II}$/Ni$^{III}$ couples in the former and of the Fe$^{IV}$/Fe$^{III}$ and Ni$^{II}$/Ni$^{III}$ 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 $\Delta H_m = 0.03$, ...
S0FCs.

The LSCN and LSFN systems thus offer attractive alternatives with good catalytic activity for oxygen reduction. At 600°C, which makes them mixed electronic/oxide-ion conductors with a TEC better matched to that of the TEC of LSCo, and they show a comparable electrode resistance at an operating temperature of 700°C. In contrast to the conventional La0.7Sr0.3Fe0.8Ni0.2O3–δ, which have a TEC better matched to that of LSCo, the compositions La0.8Sr0.2Co0.8Ni0.2O3–δ have a TEC matched to that of the TEC of LSCo, and they show a comparable electrode resistance at an operating temperature of 800°C. In contrast to the conventional La0.7Sr0.3Mn0.7Fe0.3O3–δ, these materials lose oxygen reversibly at T > 800°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>Cathode Material</th>
<th>ρ (Ω)</th>
<th>Rct (Ω)</th>
<th>ΔR = Rct - ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCN</td>
<td>29.8</td>
<td>31.6</td>
<td>3.2</td>
</tr>
<tr>
<td>LSFN</td>
<td>34.4</td>
<td>35.2</td>
<td>0.8</td>
</tr>
<tr>
<td>LSCo</td>
<td>22.7</td>
<td>42.5</td>
<td>19.8</td>
</tr>
<tr>
<td>LSM</td>
<td>31.6</td>
<td>65.7</td>
<td>34.1</td>
</tr>
</tbody>
</table>

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