Supporting Information

Highly Efficient Bifunctional Electrode Fashioned with \textit{in situ} Exsolved NiFe Alloy for Reversible Solid Oxide Cells

\begin{align*}
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\end{align*}

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Twelve pages (page S1~page S17), one table (Table S1), eleven figures (Figure S1~S11), and references (page S15~S17) are contained in the Supporting Information.
Table S1. Performance comparison table of CO₂ electrolysis over ceramic-based cathodes with exsolved metal or alloy nanoparticles.

<table>
<thead>
<tr>
<th>Parent oxide catalyst</th>
<th>Exsolved element</th>
<th>Gas condition</th>
<th>Current density at 1.5 V (A·cm⁻²)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr₀.₈Sr₁.₂(Fe,Ni)₀.₄Nb₀.₂O₄₋₀</td>
<td>NiFe</td>
<td>30% CO/CO₂</td>
<td>1.59 (850°C)</td>
<td>This work</td>
</tr>
<tr>
<td>Sr₁.₅Fe₁.₅Mo₀.₄Ni₀.₄O₆₋₀</td>
<td>NiFe</td>
<td>100% CO₂</td>
<td>c.a. 2.16 (800°C)</td>
<td>S1</td>
</tr>
<tr>
<td>La₁.₂Sr₀.₈Mn₀.₄Fe₀.₄O₄₋₀</td>
<td>Fe</td>
<td>30% CO/CO₂</td>
<td>2.04 (850°C)</td>
<td>S2</td>
</tr>
<tr>
<td>PrBaMn₁₄Co₂₂O₅</td>
<td>Co</td>
<td>30% CO/CO₂</td>
<td>1.6 (850°C)</td>
<td>S3</td>
</tr>
<tr>
<td>La₆.₆Sr₆.₄Fe₆.₄Ni₃.₄O₃₋₀</td>
<td>NiFe</td>
<td>30% CO/CO₂</td>
<td>c.a. 1.49 (850°C)</td>
<td>S4</td>
</tr>
<tr>
<td>(La₀.₆₅Sr₀.₃Ce₀.₀₅)₀.₉(Cr₀.₅Fe₀.₅)₀.₈₅Ni₀.₁₅O₃₋₀</td>
<td>NiFe</td>
<td>30% CO/CO₂</td>
<td>c.a. 1.43 (850°C)</td>
<td>S5</td>
</tr>
<tr>
<td>La₁.₂Sr₀.₈Co₄₂Mn₀.₄O₄₋₀</td>
<td>CoNi</td>
<td>30% CO/CO₂</td>
<td>c.a. 1.08 (850°C)</td>
<td>S6</td>
</tr>
<tr>
<td>La₁.₂Sr₀.₈Co₄₂Mn₀.₄O₄₋₀</td>
<td>Co</td>
<td>30% CO/CO₂</td>
<td>c.a. 1.03 (850°C)</td>
<td>S7</td>
</tr>
<tr>
<td>Sr₂Fe₁.₃₅Mo₀.₄₅Ni₀.₅O₄₋₀</td>
<td>FeNi₃</td>
<td>5% N₂/CO₂</td>
<td>c.a. 0.89 (850°C)</td>
<td>S8</td>
</tr>
<tr>
<td>Sr₂Fe₁.₃₅Mo₀.₄₅O₆₋₀</td>
<td>Fe</td>
<td>100% CO₂</td>
<td>c.a. 0.86 (850°C)</td>
<td>S9</td>
</tr>
</tbody>
</table>
Figure S1. The SEM images of (a) cross-section of button cell (PSFNNb-GDC|LSGM|LSCF-GDC) and (b) porous structure of PSFNNb-GDC electrode.
Figure S2. XRD patterns of reduced PSFNNb after treated in ambient air condition at the temperature range from 500 °C to 800 °C.
Figure S3. XPS survey of (a) as-prepared and (b) reduced PSFNNb.
Figure S4. XRD patterns of PSFNNb after treated in 20% H$_2$/Ar atmosphere at the temperature range from 200℃ to 800 ℃.
Figure S5. The CO$_2$ TPD profiles of as prepared PSFNNb and reduced PSFNNb.
Figure S6. (a) Electrical conductivities of PSFNNb under air atmosphere and (b) NiFe-R.P.PSFNNb under 20% H\textsubscript{2}/Ar and 30% CO/CO\textsubscript{2} over the temperature range from 850 °C to 450 °C.

Figure S4 showed the electrical conductivities of as-prepared PSFNNb and NiFe-R.P.PSFNNb measured under various gas conditions in the temperature range between 850 °C and 450 °C. Under the ambient air condition, the as-prepared PSFNNb exhibited metal-like behavior with a decreased conductivity with increasing temperature (72.2 S·cm\textsuperscript{-1} at 850 °C). In most perovskite oxides, it is well known that the liberation rate of lattice oxygen increases rapidly above 450 °C, producing more oxygen vacancies in lattice\textsuperscript{10–12}. The defect formation reaction can be represented by the equation (7). In PSFNNb, electrical conduction is mainly governed by small polaron hopping via Fe\textsuperscript{3+}-O\textsuperscript{2−}-Fe\textsuperscript{4+}, where Fe 3d and O 2p orbitals are overlapped\textsuperscript{13–15}. Therefore, created oxygen vacancies could interfere with the B-O-B periodicity, which is main conduction pathway, thus inducing the decrease in overall electrical conductivities of oxide as the temperature increases\textsuperscript{16,17}.

\[ 2B \cdot B + O^X_{0} \leftrightarrow 2B^X_{B} + V \cdot O + \frac{1}{2}O_2 \] (S1)

The electrical conductivities of reduced PSFNNb (i.e., NiFe-R.P.PSFNNb) were also measured under 20% H\textsubscript{2}/N\textsubscript{2} and 30%
CO/CO₂ atmospheres, resulting in 0.44 S·cm⁻¹ and 0.065 S·cm⁻¹ at 850 °C, respectively, which are slightly lower than the ones of niobium-doped perovskite oxides such as La₀.₉Ca₀.₁Fe₀.₉Nb₀.₁O₃₋δ,¹⁸ La₀.₈Sr₀.₂Fe₀.₉Nb₀.₁O₃₋δ,¹⁷ and Ba₀.₉₅La₀.₀₅Fe₀.₉Nb₀.₁O₃₋δ,¹³ etc. This is presumably because R.P. oxides have intrinsically fewer conduction pathway with B-O-B bonds due to the intercalated AO rock-salt planes between ABO₃ structures.
Figure S7. IV curves of NiFe-R.P.PSFNNb electrode under 100% CO and 3% H\textsubscript{2}O/CO gas conditions at 850 °C.
Figure S8. The EIS profiles of NiFe-R.P.PSFNNb-GDC symmetric cell under (a) humidified syngas (H$_2$/CO=3) and (b) 30% CO/CO$_2$ at the temperature of 850, 800, and 750 °C, respectively.
Figure S9. Production rate of CO and faraday efficiency for CO$_2$ electrolysis at 850 °C in 30% CO/CO$_2$ at 850 °C.
Figure S10. The SEM images of fuel electrode after being (a) reduced in dry H₂ for 30 min, (b) tested in humidified syngas (H₂/CO=3) under constant current density of 180 mA·cm⁻² for 10 h, and (c) tested in 30% CO/CO₂ under constant current density of -1.8 A·cm⁻² for 10 h at 850 °C with instant N₂ quenching; Corresponding particle sized distributions of (d) dry H₂, (e) humidified syngas, and (f) 30% CO/CO₂.
**Figure S11.** Reversible cyclic operation consisting of SOFC mode in humidified syngas under constantly applied voltage of -0.3 V vs OCV for 1 h and SOEC mode in 30% CO/CO$_2$ under constantly applied voltage of 0.3 V vs OCV for 0.5 h.
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