A Novel Approach to Synthesize Double-perovskite Sr$_{2-x}$La$_x$CoNbO$_{6.5}$ for High-temperature Solid-oxide Electrolysis Cells

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Abstract
Searching for an alternative energy source becomes an important issue. H$_2$ has been identified as an alternative fuel for its cleanliness, high energy density, and abundance. The high-temperature solid-oxide electrolysis cells (SOECs) show great efficiency and economy to produce H$_2$ by electrolyzing H$_2$O in high temperature. A novel double-perovskite Sr$_{2-x}$La$_x$CoNbO$_{6.5}$ (0 ≤ x ≤ 1) has been prepared from the modified Pechini method and solid reaction method while the former successfully produces smaller particle sizes than the latter. Substituting Sr$^{2+}$ by La$^{3+}$ increases the presence of trivalent Co-ion and oxygen vacancies, improving the electrical conductivity and ionic diffusivity. The influence of the preparation process and substitution portion on the structure and morphology was investigated by X-ray Diffraction and Scanning Electron Microscopy. The results demonstrate that the structure stability and phase purity highly depend on the preparation process, which shows a good substitution tolerance in solid reaction method.

Experimental procedure
1) The molar ratio of metal ion (Sr$^{2+}$; La$^{3+}$) : Co$^{2+}$; Nb$^{5+}$ = 2 : 1 : 1.
2) At first, (CH$_3$COO)$_2$Co 4H$_2$O dissolved in 20 ml NH$_3$ solution.
3) After a sufficient stirring, 20 ml H$_2$O$_2$ was dropped into the solution, thus oxidizing Co$^{2+}$ and producing H$_2$ bubbles.
4) Citric acid was then added into the solution. The molar ratio of citric acid and total metal ions was controlled to 2 : 1.
5) La(NO$_3$)$_3$ 6H$_2$O, (CH$_3$COO)$_2$Sr 1/2H$_2$O$_2$, and Nb$_2$(C$_2$O$_4$)$_3$ 1/2H$_2$O was sequentially added into the solution and kept stirring for 1 hour.
6) When the solution was heated at 90°C to remove the solvent, ethylene Glycol was slowly dropped into it to polymerize with citric acid.
7) Finally, the production was calcined at 300°C, 800°C, and 1150°C, sequentially.

Structure identification: Sr$_{2-x}$La$_x$CoNbO$_{6.5}$

![XRD patterns of SCNO at different calcination temperatures](image)

- The pure Sr$_2$CoNbO$_6$ (SCNO) was synthesized from the modified Pechini method in which H$_2$O$_2$ and NH$_3$ solution acted as oxidizer and chelating agent, respectively.
- Pure SCNO with double-perovskite structure was produced after calcined above 1150°C. The similar XRD patterns in Figs 3 (c) and (d) suggested that the different preparation steps did not influence the SCNO final structure.
- The unexpected Sr$_2$CoNbO$_6$ would appear without using H$_2$O$_2$ and NH$_3$ solution because H$_2$O$_2$ maintained Co ions as the valence state of 2$^+$. 

![SEM images of SCNO](image)

- The modified Pechini method can effectively reduce the particle sizes of SCNO as compared to the solid reaction method, which gives a potential application in high temperature SOECs.
- The La substitution can further reduce particle sizes and change the morphology of SCNO. However, to prevent the presence of impurity, the substitution ratio need to be controlled below La$_{0.5}$-SCNO.

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