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Unraveling the relationship between Sr stoichiometry in $\text{Sr}_x\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6 - \sigma$ and its catalytic performance for high-temperature CO$_2$ electrolysis

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A B S T R A C T

The solid oxide electrolytic cell (SOEC) is one of the most promising energy conversion and storage devices, which could convert CO$_2$ to CO with high Faradaic efficiency and production rate. However, the lack of active and stable cathode materials impedes their practical applications. Here we focus on the promising perovskite oxide cathode material $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6 - \sigma$, with the aim of understanding how A-atom stoichiometry and catalytic performance are linked. We find that increasing the strontium content in the perovskite improves the chemisorption of CO$_2$ on its surface, forming a SrCO$_3$ phase. This hinders the charge transfer and oxygen exchange processes. Simultaneously, strontium segregation to the cathode surface facilitates coking of the surface during CO$_2$ electrolysis, which poisons the electrode. Consequently, a small number of Sr deficiencies are optimal for both electrochemical performance and long-term stability. Our results provide new insights for designing high-performance CO$_2$ electrolysis cathode materials.
is through impregnation/in situ exsolution, where a nanocatalyst is loaded on the framework of the perovskite cathode to increase the surface catalytic reaction sites. However, most studies have focused on the B-site transition metals. Regarding the A-site elements, some disputes remain, such as those around A-site Sr segregations. For example, Xie et al. claimed that the segregation of SrO nanoislands on LSTO perovskite surfaces enables high-temperature chemical CO₂ adsorption and activation, with electrolyzer performances 4–5 times higher than those observed for titanates without surface modification.

Conversely, Hu et al. found that excessive SrO segregation on the cathode surface would occupy the catalytic sites, hindering charge transfer and the diffusion of oxygen species on the cathode surface. Because the A-site stoichiometry is closely related to the electrochemical performance and stability of CO₂ electrolysis, understanding its effects is crucial.

Here we study the A-site Sr stoichiometry in the perovskite oxide SrₓFe₁.₅Mo₀.₅O₆/C₀, and its effects on crystalline structures, physicochemical properties, and electrochemical performance. We find that increasing the Sr stoichiometric ratio improves the chemisorption of CO₂, and that Sr segregation promotes coking during CO₂ electrolysis, deteriorating the electrolyzer’s performance and stability. Consequently, a small number of Sr deficiencies are optimal for both electrochemical performance and long-term stability improvements.

The A-site Sr stoichiometry has a great effect on the crystal structure parameters of the resultant SrₓFe₁.₅Mo₀.₅O₆/C₀. As shown in Fig. 1, all the four catalysts with Sr contents ranging from 1.8 to 2.1 possess cubic perovskite structures with Fm–3m space groups (Fig. 1d and Fig. S1) but their corresponding diffraction-peak positions gradually shifted towards high angles with Sr ratio increasing (Fig. 1b). This is because larger Sr amount can lead to smaller unit-cell volume (Fig. 1c).

The variations of the unit-cell volumes are closely related to the oxygen vacancy concentration and Fe valence state. As shown in Fig. 1e and f, with increasing Sr content in SrₓFe₁.₅Mo₀.₅O₆/C₀, the spins of the lone electrons are gradually increased, suggesting that their oxygen vacancy concentrations are increased. The increased oxygen vacancy concentration possibly induces the further oxidation of Fe ions, leading to the

![Scheme 1. Schematic of the cell configurations of SOECs for CO₂ electrolysis.](image)

![Fig. 1.](image)
increased Fe valence state as shown in Fig. 1g and Fig. S2. Because the radius of the high-valence Fe ion is smaller than that of the low-valence one, its unit-cell volume decreases.

The increase of Fe valence state and oxygen vacancy concentration is closely related to the formation of the SrMoO4 phase. As shown in Fig. 1h, with increasing Sr content in Sr$_x$Fe$_{1.5}$Mo$_{0.5}$O$_{6-δ}$, the quantity of the SrMoO4 phase is gradually increased. Because the formation of the SrMoO4 phase would cause the loss of Mo in the parent Sr$_x$Fe$_{1.5}$Mo$_{0.5}$O$_{6-δ}$, as shown in Equation (1), some oxygen vacancies must form to maintain the charge balance and structural stability. Simultaneously, the Fe ions are also easily oxidized.

\[
\text{Sr}_{x-y}\text{Fe}_{1.5-y}\text{Mo}_{0.5-y}\text{O}_{6+y} = \text{Sr}_{x-y}\text{Fe}_{1.5-y}\text{Mo}_{0.5-y}\text{O}_{6-δ} + y\text{SrMoO}_4 + y\text{V}_\text{O} \tag{1}
\]

As shown in Fig. 2a, the Sr stoichiometry has a great effect on the TPD–CO$_2$ properties of the resultant Sr$_x$Fe$_{1.5}$Mo$_{0.5}$O$_{6-δ}$ samples. In the case of the Sr$_{1.8}$Fe$_{1.5}$Mo$_{0.5}$O$_{6-δ}$ sample, there are two main desorption peaks in the temperature range of 50–900 °C, which correspond to the physical adsorption (approximately 100 °C) and chemical adsorption (approximately 500 °C) of CO$_2$, respectively. Surprisingly, with increasing Sr content in Sr$_x$Fe$_{1.5}$Mo$_{0.5}$O$_{6-δ}$, not only the adsorption of CO$_2$ is increased, but also the desorption temperatures are greatly shifted toward a high-temperature range.

There are some possible reasons for this. First, the overall BET surface area is influenced by the Sr content, and the value is about 1.6, 1.3, 3.2 and 3.8 m$^2$ g$^{-1}$ for the sample of Sr$_x$Fe$_{1.5}$Mo$_{0.5}$O$_{6-δ}$ ($x = 1.8, 1.9, 2.0, 2.1$), respectively. Second, the number of oxygen vacancies increases with increasing Sr content, creating more sites for CO$_2$ chemisorption. This is confirmed by the X-ray photoelectron spectroscopy (XPS) O 1s spectra in Fig. 2b, where the quantity of adsorbed oxygen species increases, while the lattice oxygen decreases. Third, Sr segregation is greatly enhanced with increasing Sr content, as shown in Fig. 2c. This, in turn, increases the surface SrCO$_3$ content (cf. Fig. 2d and Fig. S3). SrCO$_3$ bonds strongly to CO$_2$ molecules, increasing the desorption temperature.$^{29,30}$

In addition, the A-site Sr stoichiometry also has a great influence on the electrical conductivity and oxygen ion exchange properties. As shown in Fig. 3a, in the presence of the Sr$_{2}$Fe$_{1.5}$Mo$_{0.5}$O$_{6-δ}$ sample (standard Sr stoichiometric ratio), its electrical conductivity values are approximately 22.5, 20.6, 18.8, and 17.3 S cm$^{-1}$ at the operating temperatures of 850,

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**Fig. 2.** (a) TPD–CO$_2$ of the as-prepared Sr$_x$Fe$_{1.5}$Mo$_{0.5}$O$_{6-δ}$ powders. (b) X-ray photoelectron spectroscopy (XPS) of O 1s spectra of the different samples. (c) Sr/(Fe + Mo) ratio as a function of Sr content. (d) XPS Sr 3d spectra of the different samples.
800, 750, and 700 °C, respectively. With a small number of Sr deficiencies (Sr1.9Fe1.5Mo0.5O6/C0-σ), not only its electrical conductivity but also oxygen ion exchange property is improved, as shown in Fig. 3c and d. Conversely, the electrical conductivity and oxygen ion exchange property deteriorate in the case of the Sr segregation sample (Sr2.1Fe1.5Mo0.5O6/C0-σ, and Fig. S4), which leads to the increased Sr content on the surface.

This phenomenon is closely related to the oxygen vacancy concentration determined by Sr stoichiometric ratio. With a small number of Sr deficiencies, the oxygen vacancy concentration is relatively low (as shown in Fig. 1e), and it is beneficial to the electrical electrons and oxygen ions transport. However, with the Sr content increasing, the oxygen vacancy concentration is gradually increased owing to the formation of more SrMoO4 phase, which would induce local structure collapse of the parent perovskite oxide, deteriorating their conduction to ions and electrons.

The materials were tested using symmetrical cells to assess their electrochemical performance (see Fig. 4). As shown, the polarization resistance of the sample with a small number of Sr deficiencies (Sr1.9Fe1.5Mo0.5O6/C0-σ) is much lower than that of the standard Sr stoichiometric sample (SrFe1.5Mo0.5O6/C0-σ) and their $R_p$ values are approximately 0.5 Ω cm$^{-2}$ and 1.2 Ω cm$^{-2}$ at the operating temperature of 800 °C, respectively, suggesting that the Sr deficiency improves CO2 reduction. The improved electrochemical performance may reflect the enhanced electrical conductivity and oxygen ion exchange property, as shown in Fig. 3.

To gain insight into the catalytic process, we analyzed the electrochemical impedance spectroscopy (EIS) data using distribution of relaxation time (DRT, see Fig. 4b). The reaction process corresponding to the low-frequency range (0.1–10 Hz) is enhanced by a small number of Sr deficiencies. To further clarify the detailed reasons, the flow rate and oxygen partial pressures of the testing gas were adjusted as shown in Fig. 4c and d. This process is identified as an oxygen-partial-pressure-dependent process, and its corresponding polarization resistance is obviously improved by decreasing the oxygen partial pressure (as shown in Fig. S5), which is consistent with the variations of the electrical conductivity and oxygen ion exchange property as shown in Fig. 3, indicating that this process is closely related to the charge transfer and gas conversion reactions of CO2 molecules.

Finally, the materials were tested as SOEC cathodes to assess their performance in CO2 electrolysis. We used LSGM-supported single cells for the electrochemical testing, with a configuration of SrFe1.5Mo0.5O6/C0-σ/LDC/LSGM/LSCF-SDC (see supporting information for details). As expected, the single cell with SrFe1.5Mo0.5O6/C0-σ as the cathode exhibits the highest current density toward CO2 electrolysis, of which the values are approximately 2.1, 1.7, 1.3, and 0.75 A cm$^{-2}$ under the applied potentials of 1.5, 1.4, 1.3, and 1.2 V, respectively (Fig. 5a and Fig. S6). These values are consistent with the variations of the EIS analysis, as shown in Fig. 4. Furthermore, the single cell with the Sr-deficient sample as the cathode also shows higher stability than that of the single cell with Sr segregation samples, as shown in Fig. 5b and c, especially under a higher applied potential. This might be because the Sr segregation is conductive to the SrCO3 phase formation on the catalyst surface. Because the SrCO3 is an electronic and ionic insulator phase, it not only occupies the catalytic sites on the catalyst surface, hindering the charge transfer and oxygen species exchange processes, but also easily causes carbon deposition during the CO2 electrolysis reactions, as shown in Fig. 5d, which deteriorates the electrolysis stability seriously.

In summary, the A-site Sr stoichiometry in SrFe1.5Mo0.5O6/C0-σ ($x = 1.8, 1.9, 2.0$, and 2.1) perovskite was successfully adjusted, and the
relationship between the Sr stoichiometry and catalytic performance was clarified in detail. Increasing Sr content in perovskite of Sr\(_x\)Fe\(_{1.5}\)Mo\(_{0.5}\)O\(_6\)/C\(_0\) boosts the chemical adsorption of CO\(_2\) on its surface, and nonetheless contributes to the SrCO\(_3\) phase formation with ease, which rains on the parade of charge transfer and oxygen species exchange processes. Conversely, Sr segregation easily facilitates carbon formation during the electrolysis of CO\(_2\), which deteriorates the electrolysis performance and stability seriously. Consequently, a small number of Sr deficiencies have been proved to be most helpful for both electrochemical performance and long-term stability improvement. This work serves as a pilot light for the future design of high-performance CO\(_2\) electrolysis catalytic materials.

**Experimental section**

Sr\(_x\)Fe\(_{1.5}\)Mo\(_{0.5}\)O\(_6\)/C\(_0\) (\(x = 1.8, 1.9, 2.0, 2.1\)) powders were synthesized by the conventional combustion method. The detailed procedures are as follows. First, the starting materials of Sr(NO\(_3\)) (99%), Fe(NO\(_3\))\(_9\)H\(_2\)O (99.99%), and (NH\(_4\))\(_6\)Mo\(_7\)O\(_24\)\(_4\)H\(_2\)O were dissolved in deionized water with a concentration of approximately 0.1 M, while ethylenediaminetetraacetic acid (EDTA) was dissolved in an ammonia solution. Then, the prepared metal ion solutions were added dropwise to the as-prepared EDTA solution with strong stirring. After stirring for approximately 10 min, citric acid was added. The pH value was maintained at approximately 7.0 by ammonia addition. After stirring for approximately 10 min, citric acid was added. The pH value was maintained at approximately 7.0 by ammonia addition. Subsequently, the prepared solution was transferred to the evaporation dish for drying and combustion, before the precursors were collected. Finally, the Sr\(_x\)Fe\(_{1.5}\)Mo\(_{0.5}\)O\(_6\)/C\(_0\) powders were obtained after calcining at 1100 °C for 10 h.

The La\(_0.8\)Sr\(_0.2\)Ga\(_{0.8}\)Mg\(_0.2\)O\(_3\)/C\(_0\) (LSGM) electrolyte-supported single cell was used to for performance testing (see diagram in Fig. S7). First, the LSGM green body was prepared by dry pressing, and then the green body was sintered at 1500 °C for 6 h. After sintering, the LSGM electrolyte was polished, and the thickness of the resultant electrolyte sheet was approximately 250 μm. Subsequently, a buffer layer of La\(_0.4\)Ce\(_0.6\)O\(_2\)/C\(_0\) (LDC) was coated and sintered on the LSGM electrolyte to avoid the chemical reaction between the electrolyte and the electrode materials. Then the Sr\(_x\)Fe\(_{0.5}\)Mo\(_{0.5}\)O\(_6\)/C\(_0\) cathode paste (fuel electrode) was screen printed on the buffer layer. After calcining at 1100 °C for 2 h, the anode paste (50%LSCF–50%SDC, air electrode) was printed on the other side of the electrolyte, and the corresponding electrode material is obtained after sintering at 1000 °C for 2 h. Finally, an Au conductive collecting layer was coated on the surfaces of the cathode and the anode, respectively. Subsequently, the electrochemical performances of the cathode and anode were evaluated using an electrochemical workstation (Solartron Analytical, England) at the operating temperatures of 700–850 °C, and the corresponding electrochemical impedance spectroscopy (EIS) was recorded in the range of 10^5–0.01 Hz under different applied potentials with an applied magnitude of 10 mV.

The as-synthesized powders were analyzed by X-ray diffraction (XRD; Bruker D8 Advance, Germany) with Cu-K\(_{α}\) radiation (\(λ = 0.1542\) nm). The morphologies of the powders were observed by high-resolution transmission electron microscopy (HR-TEM; JEM-F200, Japan). The elemental distribution of the prepared composite cathode was identified by TEM-EDS elemental mappings. The oxidized states of the Sr, Fe, Mo, and O in the as-prepared powders were determined using X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi (Al K\(_{α}\) radiation)). The oxygen vacancy defects were detected by EPR (EMXmicro-6/1/P/L,
Karlsruhe, Germany), and the testing condition was low temperature degassing environment. For the electrical conductivity testing, the prepared powders were first compressed into bars and sintered at 1350°C for 5 h. Then, the four-probe direct current method was used to measure the electrical conductivity in the temperature range of 700–850°C with a Keithley 2420 source meter. The electrical conductivity relaxation (ECR) testing was conducted by switching the gas stream from low $p_{O_2}$ (CO/CO$_2$ 2:1) to relatively high $p_{O_2}$ (CO/CO$_2$ 1:1) at a total gas flow rate of 200 mL min$^{-1}$. The DRT of the EIS spectra was analyzed by RelaxIS 3.0 software. The adsorption properties of the CO$_2$ molecules were measured by CO$_2$-temperature programmed desorption (CO$_2$-TPD) with a Micromeritics AutoChem II chemisorption analyzer (2920). The carbon formation was evaluated by laser confocal Raman microscopy.

Declaration of competing interest
There are no conflicts of interest to declare.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.matre.2023.100179.

References
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