Cr doping regulates FeNi alloy nanoparticles exsolution on $Sr_2Fe_{1.1}Ni_{0.2}Cr_{0.2}Mo_{0.5}O_{6-\delta}$ cathode to facilitate CO_2 electrolysis

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Computational details

The unit cell of $Sr_2Fe_{1.5}Mo_{0.5}O_6$ (SFM) consists of eight Sr atoms, six Fe atom, two Mo atoms, and twenty-four O atoms. The optimized lattice constant of SFM is "a=b=c=7.939 Å". To investigate the CO_2 electrolysis activities and the segregation energy of metals of the $Sr_2Fe_{1.1}Ni_{0.2}Cr_{0.2}Mo_{0.5}O_{6-\delta}$ (SFNCM) and SFNCM reduced for 2 h (SFNCM-R), a series of surface models were constructed based on the X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) results, including SFM(110), SFCMN (110)-V_O (SFNCM), and FeNi/SFNCM(110)-V_O (SFNCM-R). SFM(110) were constructed by a p(1×1) cell with two repeat unit layers. During the calculations of CO_2 activation, the Cr and Ni atoms were introduced into the surface to simulate SFNCM catalyst. One oxygen atom on the surface was removed to mimic the oxygen vacancy. A Fe_3Ni_3 cluster was positioned on the surface of SFNCM to represent the model of exsolved FeNi cluster supported on the perovskite (SFNCM-R). During the calculations, the bottom unit layer was frozen, while the surface unit layer with the Fe_3Ni_3 cluster and the adsorbate were relaxed. The optimized surface models are shown in **Figure S15-17**.

The segregation energy (E_{seg}) of M dopant (Fe or Ni) with oxygen vacancy is defined as the difference between the system with M located on the surface and in the bulk by the following formula:

$$E_{seg} = E_{(M\text{-}Vo)\_bulk} - E_{(M\text{-}Vo)\_surf}$$

where $E_{(M\text{-}Vo)\_bulk}$ and $E_{(M\text{-}Vo)\_surf}$ are the energy of the system M located in the bulk and on the surface, respectively.

The adsorption energies (E_{ads}) of CO_2 on oxygen vacancy or interface were estimated by the following formula:

$$E_{ads} = E_{CO_2 + support} - E_{support} - E_{CO_2}$$

where $E_{CO_2 + support}$ is the total energy of the support decorated with H_2O molecule, $E_{support}$ is the total energy of the suppor, and E_{CO_2} is the total energy of CO_2 molecule.

The reaction energies (ΔE) of CO_2 on oxygen vacancy or interface were estimated by the following formula:

$$\Delta E = E_{FS} - E_{IS}$$

where E_{FS} is the total energy of the support adsorbed with final species, E_{IS} is the total energy of the support adsorbed with initial species.

The difference charge densities ($\Delta\rho$) of CO_2 adsorbed on metal or metal oxides could be expressed as:

$$\Delta\rho = \rho_{AB} - \rho_A - \rho_B$$

where ρ_{AB} is the total charge density of the support adsorbed with CO_2 molecule, ρ_A and ρ_B are the unperturbed charge densities of the support and CO_2 molecule, respectively.

The CO_2 electrolysis Faradaic efficiency (FE) was calculated based on the Faraday law from the formula below,

$$FE = \frac{q_{CO}'}{q_{CO}} \times 100\%$$

where q_{CO}' denotes the experimentally determined CO production rate (mL min^{-1}) obtained via gas chromatography, while q_{CO} refers to the theoretical value derived from the principle of electrochemical equivalence. The latter is calculated based on the applied current density i (A cm^{-2}) passing through the electrolysis cell, as follows:

$$q_{CO} = \frac{i(A \cdot cm^{-2}) \cdot 60\left(s \cdot min^{-1}\right) \cdot 22.4 \times 10^3 (ml \cdot mol^{-1})}{2(equiv \cdot mol^{-1}) \cdot 96485(C \cdot equiv^{-1})}$$

where i is the electrolytic current density, F is Faraday constant (96485 C mol^{-1}), 2 is electron transfer number in electrochemical CO_2 reduction reaction.

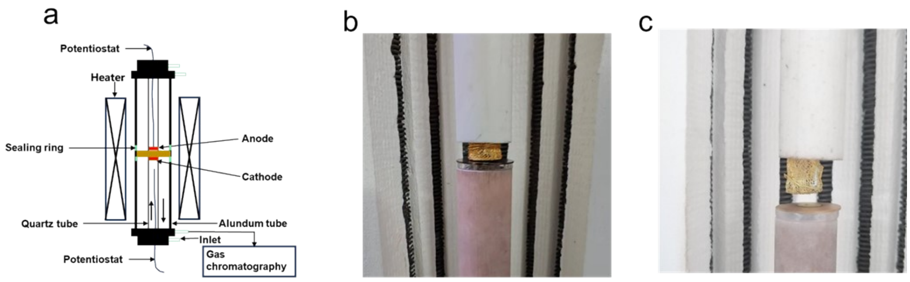

Figure S1. (a) Schematic diagram of the SOEC testing device. (b-c) The photograph of the testing device before heating and after CO_2 electrolysis test.

Figure S1a shows a schematic diagram of the test setup: the sealing glass ring begins to melt at 750 °C and remains in a semi molten state at 800 °C, which ensures the airtightness between the cell and the alumina tube.

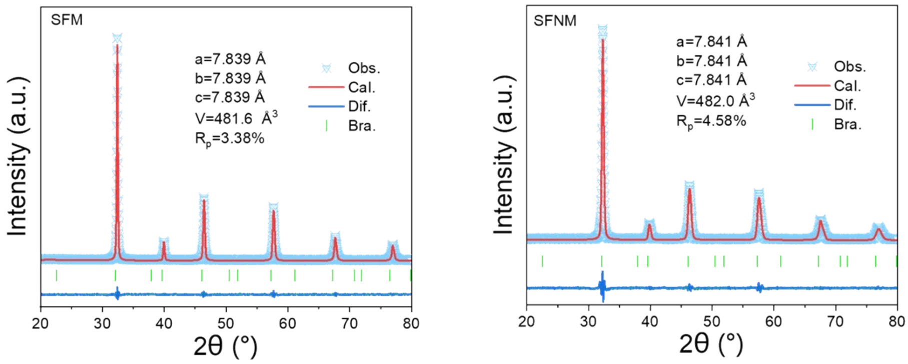

Figure S2. Rietveld-refinement XRD patterns of the pristine SFM and $Sr_2Fe_{1.5}Ni_{0.2}Mo_{0.5}O_{6-\delta}$ (SFNM).

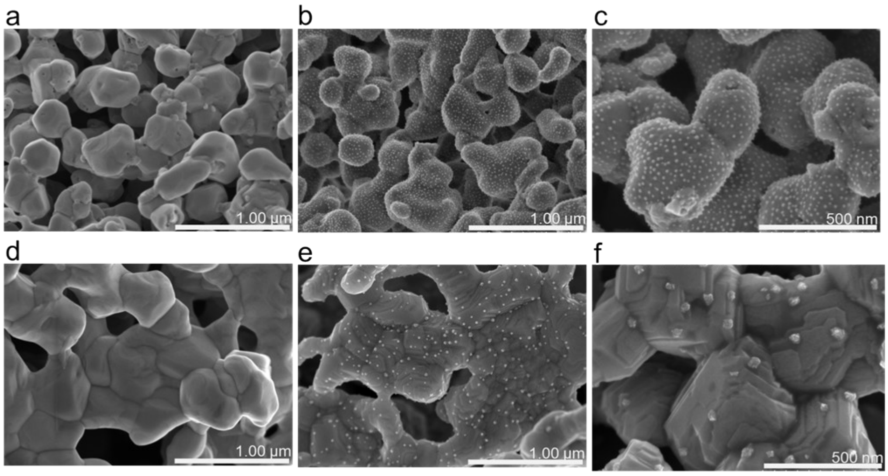

Figure S3. (a) SEM images of the pristine SFNCM. (b-c) SEM images of SFNCM powders after reduction at 800 °C for 2 h (SFNCM-R). (d) SEM images of the pristine SFNM. (e-f) SEM images of SFNM powders after reduction at 800 °C for 2 h (SFNM-R).

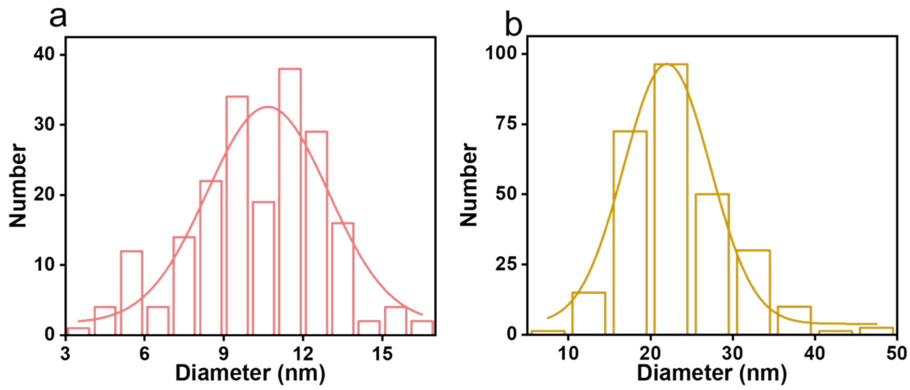

Figure S4. Statistics on FeNi alloy nanoparticles size distribution of (a) SFNCM-R (201 NPs were counted, Figure 2d) and (b) SFNM-R (223 NPs were counted, Figure S3e).

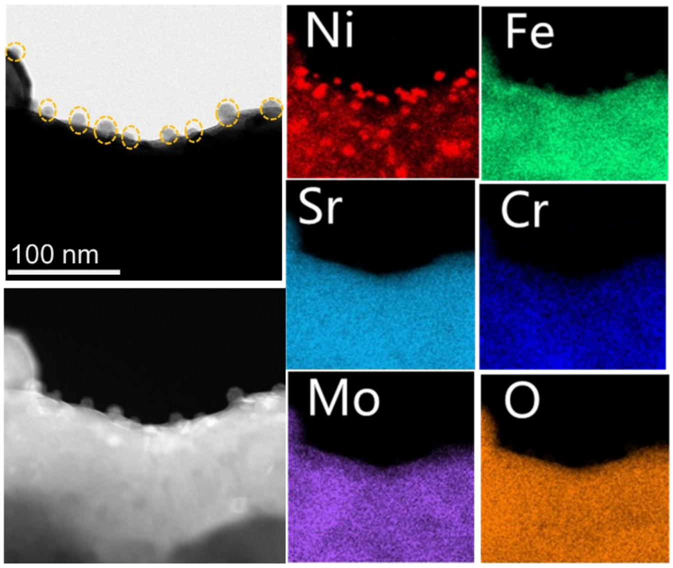

Figure S5. Bright-field scanning transmission electron microscopy image and scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy elemental maps of SFNCM-R.

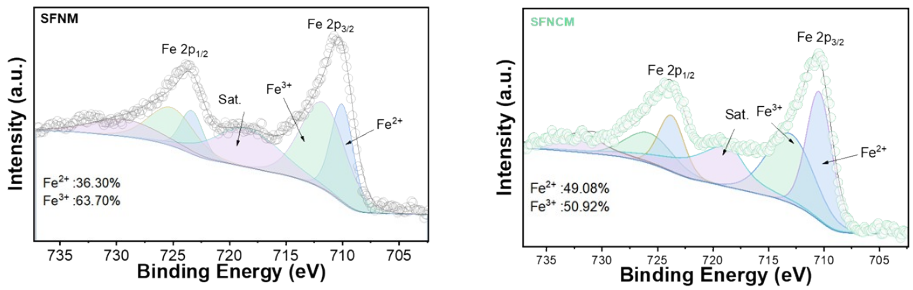

Figure S6. The fitted X-ray photoelectron spectroscopy (XPS) spectra of Fe 2p of SFNM and SFNCM.

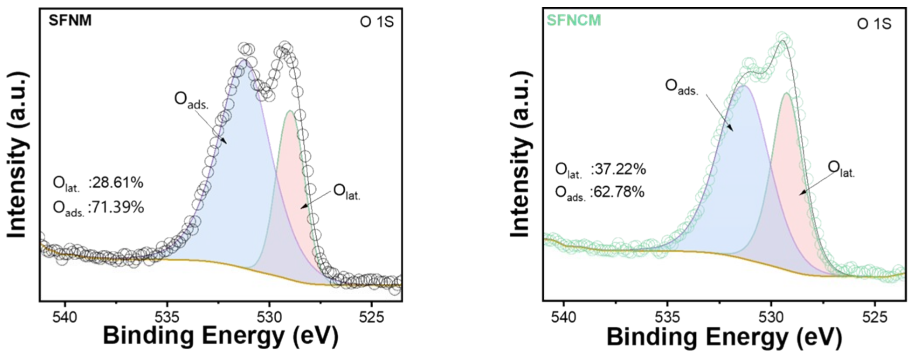

Figure S7. The fitted XPS spectra of O 1s of SFNM and SFNCM.

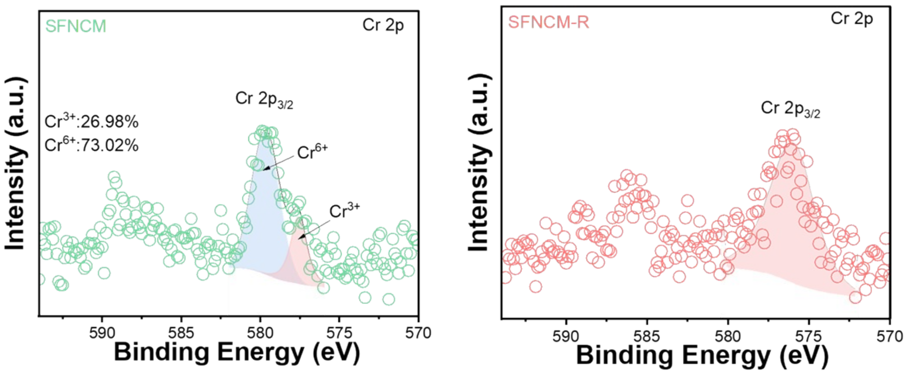

Figure S8. The fitted Cr 2p XPS spectra of SFNCM and SFNCM-R.

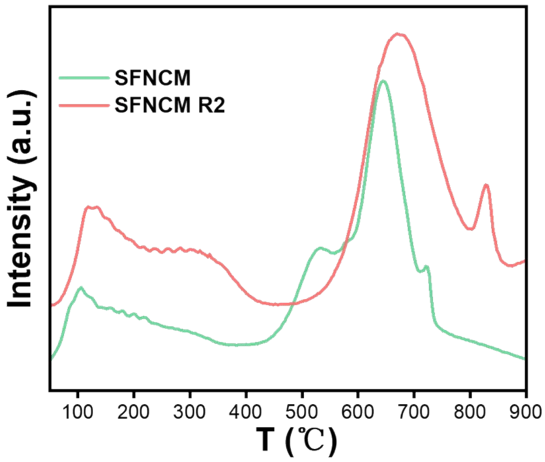

Figure S9. CO_2-TPD profiles of SFNCM and SFNCM-R.

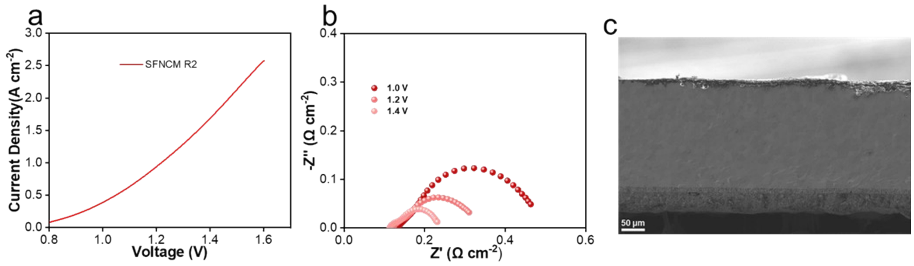

Figure S10. CO_2 electrolysis test using LSGM electrolyte membrane with a thickness of 250 μm at 800 °C for SFNCM-R of (a) Linear sweep voltammetry curves. (b) Electrochemical impedance spectroscopy (EIS) spectrum. (c) Cross-sectional SEM image of the cell.

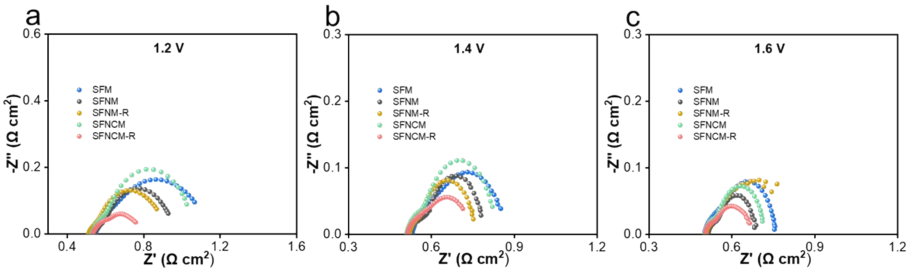

Figure S11. EIS of SFM, SFNM, SFNM-R, SFNCM, and SFNCM-R at (a) 1.2 V, (b) 1.4 V, and (c) 1.6 V during CO_2 electrolysis.

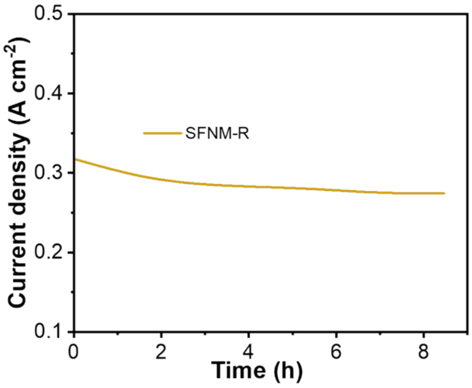

Figure S12. Stability test of SFNM-R based SOEC at 800 °C and 1.2 V.

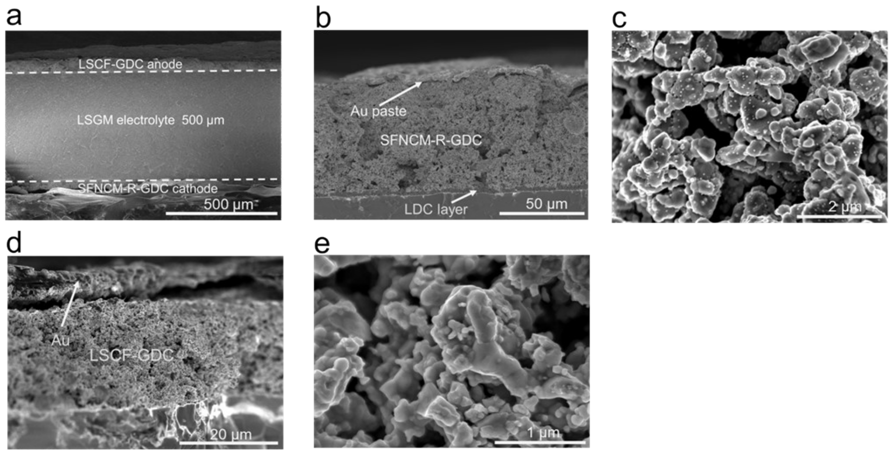

Figure S13. SEM images of SFNCM-R based SOEC after stability test for 100 h. (a) Cross-sectional image of the electrolyte supported SOEC. (b-c) SFNCM-R cathode. (d-e) LSCF-GDC anode.

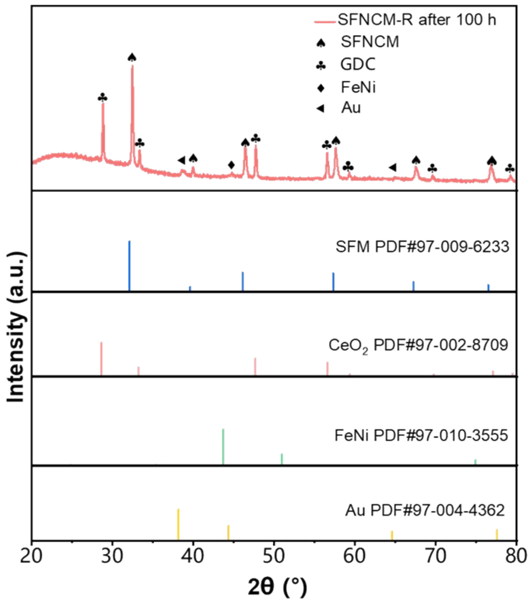

Figure S14. XRD patterns of SFNCM-R based cathode after stability test for 100 h.

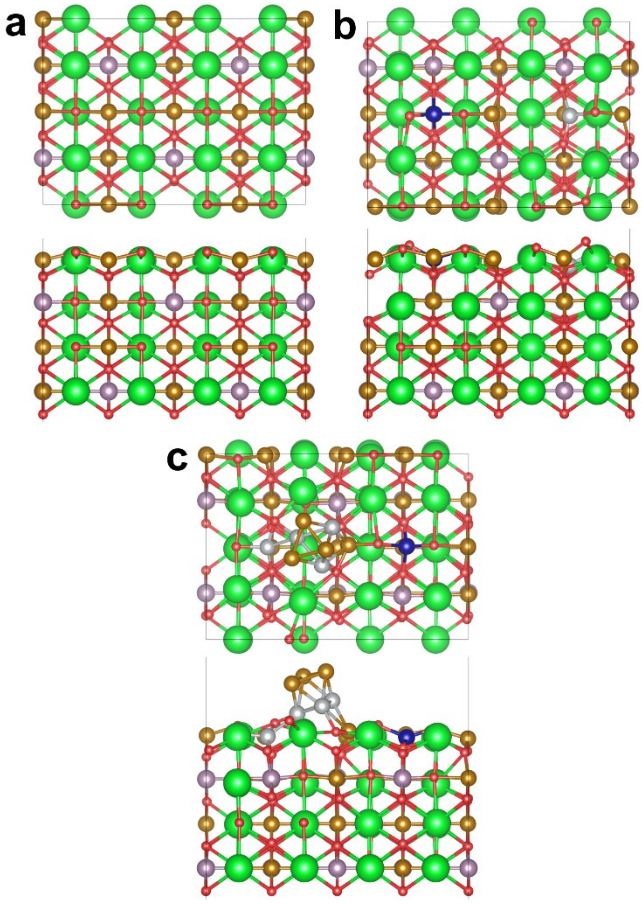

Figure S15. Diagram illustration. Top (top) and side (down) view of the optimized (a) SFM(110), (b) SFNCM and (c) SFNCM-R surface models. Sr, Fe, Mo, Ni, Cr, and O atoms are represented by green, yellow, purple, grey, blue and red balls, respectively.

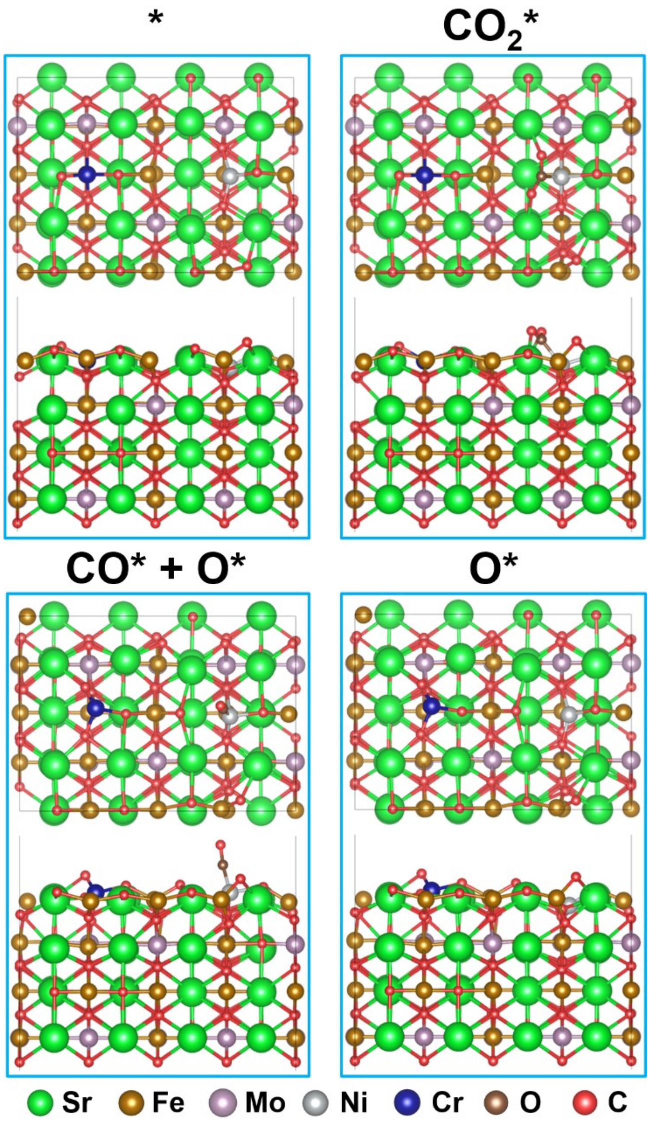

Figure S16. Top (up) and side (down) views of the geometric structures of CO_2 electrolysis on the oxygen vacancy of SFNCM. Sr, Fe, Mo, Ni, Cr, C and O atoms are represented by green, yellow, purple, grey, blue, brown and red balls, respectively.

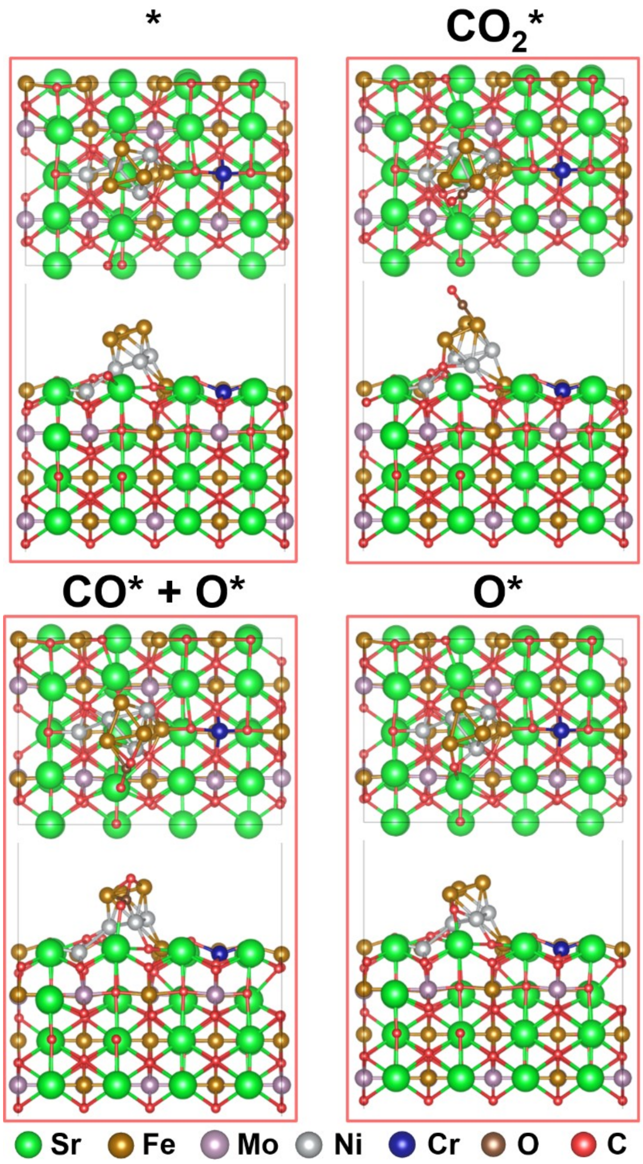

Figure S17. Top (up) and side (down) views of the geometric structures of CO_2 electrolysis on the interface of SFNCM-R. Sr, Fe, Mo, Ni, Cr, C and O atoms are represented by green, yellow, purple, grey, blue, brown and red balls, respectively.