Supporting Information

Unveiling Critical Role of Metal Oxide Infiltration in Controlling the Surface Oxygen Exchange Activity and Polarization of $SrTi_{1-x}Fe_xO_{3-\delta}$ Perovskite Oxide Electrodes

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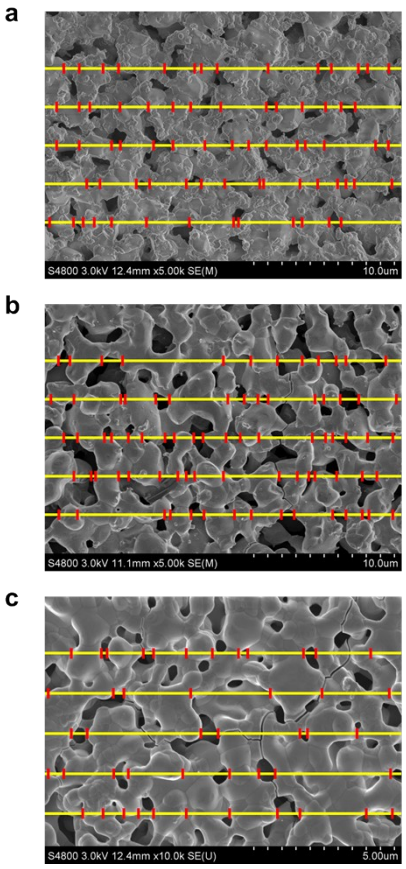


Figure S1. Scanning electron microscopy images of specimens used in determining surface-area-to-volume ratios. (a) $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$, (b) $SrTi_{0.5}Fe_{0.5}O_{3-\delta}$, and (c) $SrTi_{0.2}Fe_{0.8}O_{3-\delta}$.

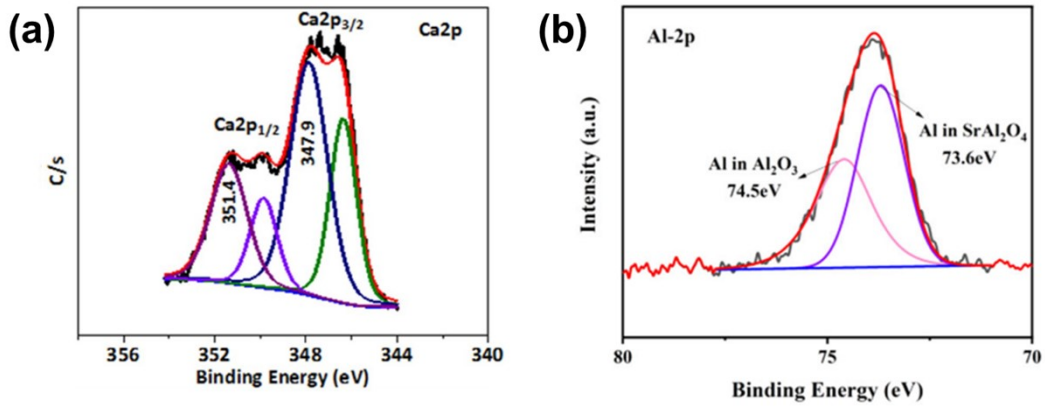


Figure S2. X-ray photoelectron spectroscopy (XPS) analysis on (a) Ca 2p of $CaTiO_3$, showing a Ca $2p_{3/2}$ peak at 347.9 eV, compared with $CaCO_3$, which exhibits a Ca 2p3/2 peak at 346 eV;[1] and (b) Al 2p of Al_2O_3, displaying a peak at 74.5 eV, compared with $SrAl_2O_4$, which shows a peak at 73.6 eV.[2]

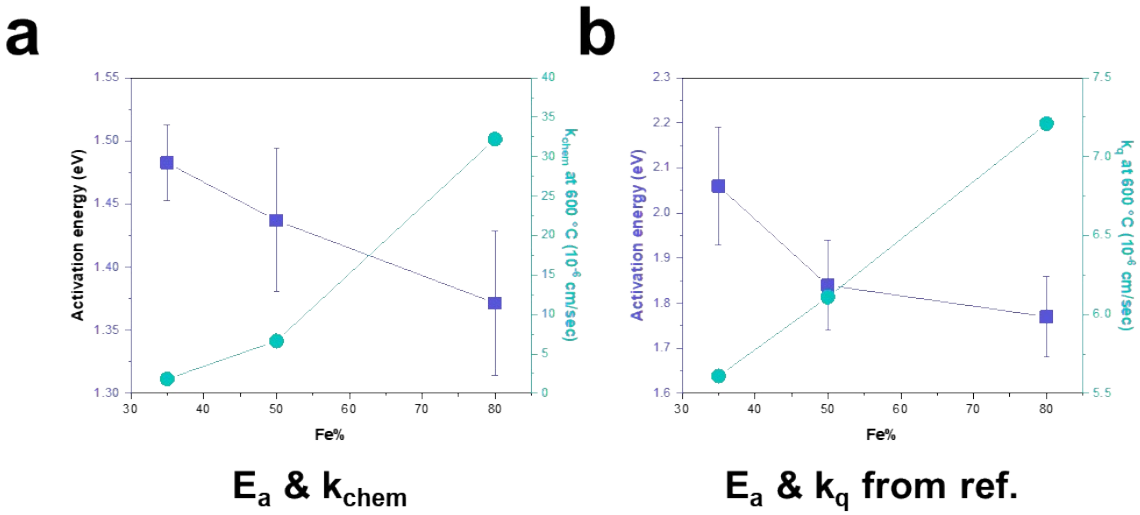


Figure S3. Activation energy (in violet, left) and k_{chem} at 600 °C (in turquoise, right) as function of iron content in $SrTi_{1-x/100}Fe_{x/100}O_{3-\delta}$ (STFx). (b) Activation energy (in violet, left) and k_q at 600 °C (in turquoise, right) of STFx, derived from electrochemical impedance spectroscopy measurements on thin-film. Source: Jung et al.[3]

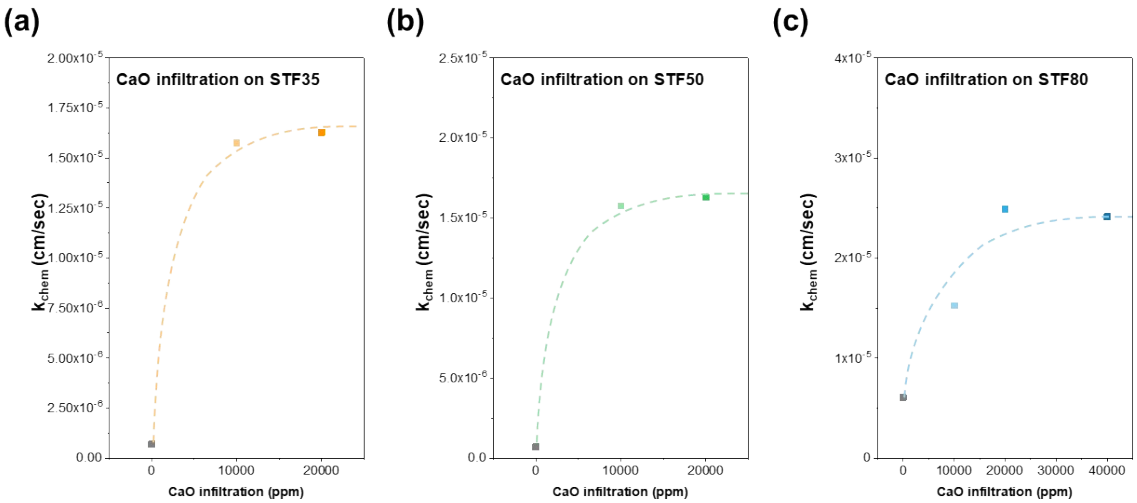


Figure S4. Surface oxygen exchange coefficient, k_{chem}, of (a) $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$, (b) $SrTi_{0.5}Fe_{0.5}O_{3-\delta}$, and (c) $SrTi_{0.2}Fe_{0.8}O_{3-\delta}$ at 525 °C as a function of CaO infiltration amount.

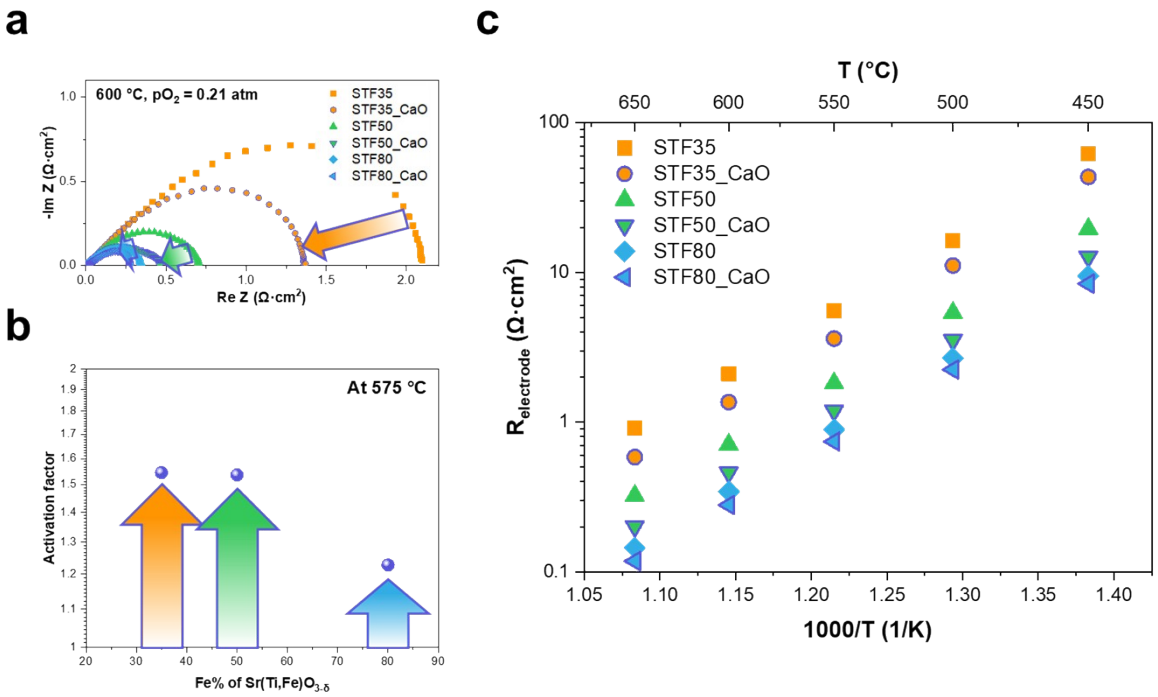


Figure S5. Enhanced surface activity of $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$, $SrTi_{0.5}Fe_{0.5}O_{3-\delta}$, and $SrTi_{0.2}Fe_{0.8}O_{3-\delta}$ by CaO infiltration. (a) Electrochemical impedance spectroscopy Nyquist plot measured at 600°C for symmetrical cells (Electrode|$(Sm,Ce)O_{2-\delta}$|Electrode). (b) Activation factor calculated for each $SrTi_{1-x/100}Fe_{x/100}O_{3-\delta}$ (STFx) cell measured at 575 °C. (c) Arrhenius plots of STFx electrode resistance ($R_{electrode}$) before and after CaO infiltration.

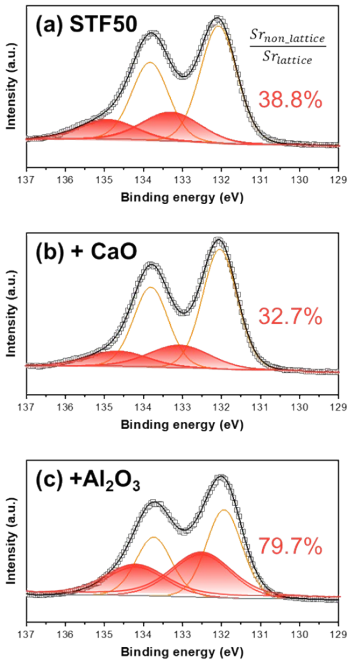


Figure S6. X-ray photoelectron spectroscopy (XPS) analysis on Sr 2p for (a) $SrTi_{0.5}Fe_{0.5}O_{3-\delta}$ (STF50), (b) CaO-infiltrated STF50, and (c) Al_2O_3-infiltrated STF50 after annealing at 700 °C for 10 hours.

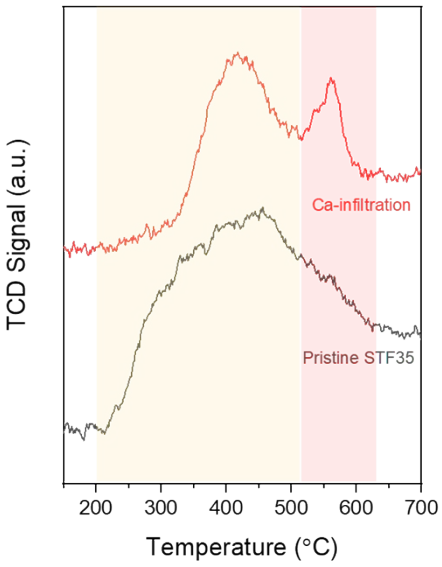
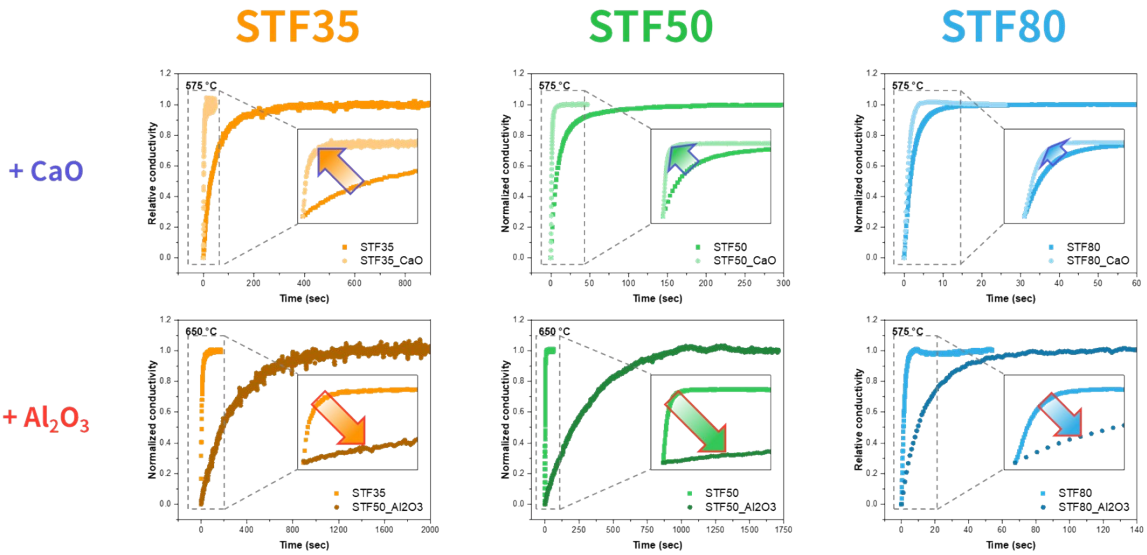


Figure S7. CO_2 temperature programmed desorption (CO_2-TPD) analysis result on the pristine and CaO-infiltrated STF35.

To further confirm that the CaO was uniformly deposited across the entire surface, CO_2 temperature programmed desorption analysis was conducted on both the pristine and CaO-infiltrated STF35. Here, two distinct regions of CO_2 desorption were observed: desorption of weakly adsorbed CO_2 at lower temperatures (200-500 °C) and strongly adsorbed CO_2 at high temperatures (500-600 °C). The CaO-infiltrated specimen, which strongly chemisorbed CO_2, exhibited an additional peak at 560 °C compared to the pristine sample, indicating the presence of additional strong base sites, which is in good agreement with our observations. It also shows that CaO infiltration not only caused the appearance of a high-temperature peak for strongly adsorbed CO_2 in the 500-600 °C range but also shifted the peak for weakly adsorbed CO_2 in the 200-500 °C range toward higher temperatures. This indicates that the CaO infiltration enhanced the overall CO_2 adsorption strength of the STF surface, suggesting the infiltration was applied across the entire surface.



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73 **Figure S8. Conductivity relaxation profiles measured on $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$,**
74 **$SrTi_{0.5}Fe_{0.5}O_{3-\delta}$, and $SrTi_{0.2}Fe_{0.8}O_{3-\delta}$ samples before and after infiltration of CaO and**
75 **Al_2O_3.**

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References:

[1] M. A. Ehsan, R. Naeem, V. McKee, A. Rehman, A. S. Hakeem, M. Mazhar, *Journal of Materials Science: Materials in Electronics* **2019**, *30*, 1411.

[2] B. Lu, M. Shi, Z. Pang, Y. Zhu, Y. Li, *Journal of Materials Science: Materials in Electronics* **2021**, *32*, 17382.

[3] W. Jung, H. L. Tuller, *Adv Energy Mater* **2011**, *1*, 1184.