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Research Article

Sr-anchoring-directed gradient shell architecture in $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ cathodes for reversible protonic ceramic electrochemical cells

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Abstract:

Strontium segregation remains a critical challenge for Sr-containing double perovskite cathodes, wherein outward-migrating Sr species accumulate at the surface and severely deteriorate interfacial electrochemical kinetics in reversible protonic ceramic electrochemical cells (R-PCECs). Herein, we develop a Sr-anchoring–driven interfacial catalytic architecture on $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFM) via vanadium-assisted near-surface phase engineering. The incorporation of V introduces Lewis-acidic centers that effectively immobilize migrating Sr species and simultaneously induce the in situ reconstruction of a nanoscale $\text{SrMoO}_4/\text{SrVO}_3$ heterointerface. More importantly, this reconstructed interface functions as a catalytically active region with enhanced electronic delocalization and optimized oxygen-defect chemistry, which collectively promote oxygen adsorption, dissociation, and charge-transfer kinetics. The gradient shell architecture not only suppresses detrimental Sr segregation but also establishes fast and continuous pathways for coupled ion–electron transport across the interface. Electrochemical impedance and distribution of relaxation time (DRT) analyses reveal substantially reduced polarization resistance and decreased activation energy, indicating accelerated oxygen electrocatalysis. Consequently, the SFM-V cathode exhibits markedly enhanced reversible electrochemical performance compared to pristine SFM, delivering a peak power density of 1.23 W cm^{-2} at 650°C together with high electrolysis activity and robust cycling stability, ranking among state-of-the-art SFM-based air electrodes for R-PCECs. This work demonstrates that Sr-anchoring interfacial engineering is an effective strategy to stabilize perovskite cathodes while maintaining fast interfacial kinetics.

Keywords: Sr anchoring; Gradient shell architecture; Strontium segregation; Reversible protonic ceramic electrochemical cell

1. Introduction

The advancement of energy storage and conversion technologies has significantly reduced reliance on fossil fuels and mitigated environmental impacts [1-4]. Among various pathways, coupling reversible solid-oxide systems with renewable electricity to produce and reconvert hydrogen offers an efficient route for long-duration storage and sector coupling [4-7]. However, conventional reversible solid-oxide cells (R-SOCs) employing oxygen-ion electrolytes typically require $700\text{--}900^\circ\text{C}$ to achieve acceptable kinetics, which leads to materials degradation, electrode delamination, thermal mismatch, gas leakage, and system-level efficiency losses [6, 8-10]. Lowering the practical operating temperature without compromising durability necessitates air electrodes capable of sustaining rapid oxygen electrocatalysis, particularly oxygen evolution reaction (OER) activity under high steam conditions, while maintaining stable and active interfacial catalytic sites during repeated redox cycling.

Double perovskite $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFM) combines pronounced structural robustness with mixed ionic–electronic conduction in the intermediate-temperature regime and has therefore been widely regarded as a promising air-electrode candidate[11-13]. Its interconnected electronic and oxide-ion conduction networks

enable the triple-phase boundary (TPB) to extend from the conventional interface region into the bulk of the electrode, thereby significantly increasing the effective TPB length and facilitating oxygen ion transport and exchange in the vicinity of the electrode-electrolyte interface[14-16]. From a catalytic perspective, such extended active regions are beneficial for promoting oxygen adsorption, dissociation, and subsequent charge-transfer steps. To further tailor defect chemistry and broaden the operational window, B-site substitution with transition metals is commonly employed to modulate the local Fe/Mo environment and promote oxygen vacancy formation [17-19]. However, under prolonged high-temperature operation, particularly in humid humid and/or CO₂-containing atmospheres, Sr²⁺ tends to migrate toward the surface driven by elastic energy minimization and the coulomb interactions with oxygen vacancies (V_O^{••}). The segregated Sr subsequently reacts with ambient species such as H₂O and CO₂, forming insulating secondary phases such as SrCO₃, Sr(OH)₂, and SrO[20-22]. These secondary phases often evolve into continuous or semi-continuous surface layers that impede interfacial charge transfer and ion transport, ultimately leading to deteriorated the oxygen reduction (ORR) and oxygen evolution (OER) kinetics, increased polarization resistance, and progressive losses in power density and Faradaic efficiency [23, 24]. As a result, the long-term durability of SFM under practical high-humidity reversible operating conditions is severely constrained.

Previous efforts to mitigate Sr segregation have primarily centered on suppressing Sr outward migration or alleviating the detrimental effects of surface insulating phases. One approach relies on stoichiometry and valence-state control (e.g., adjusting A/B-site ratios, introducing multicomponent B-site doping) to regulate oxygen-vacancy concentrations and charge compensation, thereby reducing the driving force for Sr segregation from the bulk[25-28]. Alternatively, heterostructure engineering and composite interface design, including infiltration-derived multiphase electrodes, conformal surface coatings, and acidic oxide layers, have been employed to spatially confine or passivate exsolved Sr species[29, 30]. More recently, research attention has shifted from passive isolation toward active capture and interfacial catalytic reconstruction. For instance, acidic surface oxides can react with segregated Sr via acid–base interactions to form thermodynamically stable Sr-containing phases in situ [31], while multielement reconfiguration strategies have been employed to construct catalytically active biphasic heterointerfaces that modulate electronic structure and oxygen-defect chemistry [32, 33]. These studies have established reverse capture as an effective strategy for mitigating alkaline-earth segregation in perovskite electrodes. Nevertheless, Sr stabilization alone does not necessarily guarantee favorable electrode kinetics, because the newly formed Sr-containing phases may also alter electronic conduction, ion transport, surface exchange, and the accessibility of active reaction sites. This issue becomes particularly important under humid and reversible R-PCEC operation, where the air electrode must simultaneously sustain Sr chemical stability, efficient charge transport, rapid oxygen surface exchange, and proton-coupled interfacial reactions. Therefore, a key challenge is to develop a surface-regulation strategy that does not merely immobilize segregated Sr, but also integrates Sr stabilization with favorable interfacial transport and reaction

kinetics. For the intrinsically Sr-rich SFM double perovskite, this requires regulation of Sr redistribution without sacrificing the mixed-conducting SFM framework, while converting the redistributed Sr into secondary phases that can contribute differently to structural stabilization and interfacial electrochemical processes.

In this work, Sr segregation and the associated TPB passivation in SFM cathodes under intermediate-temperature and humid conditions are addressed through V-assisted regulation of the near-surface chemistry. The introduction of V promotes the formation of SrMoO_4 (SMO) and SrVO_3 (SVO) secondary phases, generating a multiphase near-surface configuration while largely retaining the SFM framework. This configuration is proposed to couple Sr stabilization with interfacial kinetic regulation: SMO preferentially accommodates redistributed Sr and suppresses excessive surface enrichment, whereas SVO related domains facilitate interfacial electronic transport and surface-exchange kinetics. Through the synergistic regulation of Sr distribution, defect chemistry, and interfacial charge transfer, the resulting SFM-V electrode exhibits enhanced reversible electrochemical performance and improved resistance to Sr-related degradation under humid, intermediate-temperature operation. This work provides a strategy for simultaneously regulating cation stability and interfacial reaction kinetics in Sr-containing air electrodes for R-PCECs.

2. Experimental

2.1 Materials synthesis and cell fabrication

The pristine SFM powder was synthesized via an EDTA–citric acid chelating sol-gel route. Stoichiometric amounts of SrCO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Aladdin Reagent Co., Ltd., Shanghai) were used as starting materials. The total molar ratio of metal cations: EDTA: citric acid was fixed at 1:1:2. After complete dissolution and complexation, the solution was heated at 80 °C under continuous stirring for 6 h until a viscous gel was formed, which subsequently self-ignited to yield a foamy precursor. The resulting ash was ground and calcined in air at 1000 °C for 3 h to obtain SFM powder.

The SFM-V powders were subsequently prepared from the preformed SFM powder through a secondary impregnation treatment. A prescribed amount of V-containing precursor was uniformly introduced onto the SFM powder by impregnation, followed by drying and a secondary heat treatment at 900 °C. This treatment promoted the surface reaction between the V-containing species and SFM, resulting in the formation of SrVO_3 (SVO) and SrMoO_4 (SMO) secondary phases. The samples prepared with nominal V molar ratios of 0.025, 0.050, and 0.075 were denoted as SFM-V25, SFM-V, and SFM-V75, respectively. SFM-V refers to the sample with a nominal V molar ratio of 0.050, which was selected as the optimized composition for the main discussion.

The $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) electrolyte and NiO-BZCYYb composite anode powders were prepared by the same sol-gel process. For the anode functional layer (AFL), NiO and BZCYYb powders were mixed at a weight ratio of 6:4, ball-milled in ethanol for 24 h, and then dried at 80 °C. Anode-supported half-cells were fabricated using a three-layer co-pressing procedure. First, 0.36g of NiO-BZCYYb anode support powder was pressed into a green pellet (20 mm in

diameter, ~1.5 mm in thickness) at 300 MPa using a stainless-steel die. Subsequently, 0.014g of AFL powder and 0.005g of BZCYYb electrolyte powder were sequentially spread on top and co-pressed at 200 MPa. The laminated half-cells were co-sintered in air at 1350 °C for 5h to form dense BZCYYb electrolyte membranes supported on porous NiO–BZCYYb anodes. For cathode fabrication, the SFM and SFM-V powders were each mixed with terpineol and 10wt. % ethyl cellulose in an agate mortar for 2h to obtain homogeneous screen-printing pastes. The slurries were printed onto the electrolyte surface using a circular mask to define an active area of 0.196 cm², followed by drying at 80 °C. After drying at 80 °C, the symmetric cells were microwave-sintered at 900 °C for 20 min in air to ensure sufficient electrode adhesion and interfacial contact. For symmetric-cell fabrication, dense BZCYYb electrolyte pellets were prepared by pressing BZCYYb powder into disks followed by sintering at 1350 °C for 5 h. SFM or SFM-V electrode paste was symmetrically screen-printed onto both sides of the BZCYYb electrolyte pellet. After drying at 80 °C, the symmetric cells were microwave-sintered at 900 °C for 20 min in air to ensure sufficient electrode adhesion and interfacial contact. The resulting symmetric-cell configuration was SFM|BZCYYb|SFM or SFM-V|BZCYYb|SFM-V.

2.2 Basic Characterizations

The crystalline phases of the samples were identified by X-ray diffraction (XRD, Bruker D8 Advance) using Cu K α radiation. Surface chemical environments of the cathode powders were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The morphology and crystallinity were examined by transmission electron microscopy (TEM, JEOL JEM-2100F), while the microstructures of the fabricated cells were observed by scanning electron microscopy (SEM, ZEISS Sigma 300). Thermogravimetric analysis (TGA, PerkinElmer STA 6000) was conducted to track mass variation as a function of temperature. H₂O temperature-programmed desorption (H₂O-TPD) measurements were carried out using a Micromeritics AutoChem II 2920 instrument to investigate the water adsorption/desorption behavior of the samples. The thermal expansion coefficients (TECs) were determined in air using a dilatometer (Netzsch TMA 402F3) on dense bar specimens. Electron paramagnetic resonance (EPR, Bruker E500, 9 GHz, 100 kHz modulation) was employed to probe and compare the concentration of oxygen vacancies in the different samples. The proton concentration in hydrated samples was determined by Karl Fischer titration through quantification of thermally released water originating from protonic species, using a Karl Fischer moisture analyzer (MKC-710, Kyoto Electronics). After hydration at 600 °C for 24 h in humidified Ar–20% O₂–3% H₂O, dense bulk samples were heated to 1000 °C, and the released water was carried by dry N₂ into the KF titration cell. The water content was quantified electrochemically based on the iodide/iodine redox reaction and further converted to proton uptake.

2.3 Electrochemical testing

After sample fabrication, a series of electrochemical measurements were carried

out to assess cell performance and application potential. Single cells were contacted with silver paste and connected to a custom-designed testing fixture. Electrical conductivity relaxation (ECR) was measured on dense bar specimens in air using a four-probe configuration (Keithley 2400, Tektronix) with four silver leads attached to the sample, in order to determine electrical conductivity and the equilibration time upon changes in oxygen partial pressure. The SFM and SFM-V powders were pressed into rectangular bars and sintered at 1250 °C for 5 h in air. The final dimensions of the dense bar samples were approximately 0.84 cm × 0.43 cm × 0.18 cm. During the ECR measurements, the samples were heated from 350 to 700 °C, and the nitrogen/oxygen ratio in the gas mixture was adjusted from 1:1 to pure air to induce a step change in oxygen partial pressure. The transient conductivity relaxation curves were recorded and analyzed using Matlab to extract the bulk diffusion coefficients and surface exchange rates.

During fuel-cell operation, humidified hydrogen (3% H₂O) was supplied to the fuel electrode at 40 mL·min⁻¹, while ambient air was fed to the air electrode as the oxidant. For electrolysis (EC) mode, the same flow of humidified hydrogen (3% H₂O) was introduced to the fuel electrode and 40 mL·min⁻¹ of humidified air was delivered to the air electrode to mimic electrolysis conditions. All electrochemical measurements were performed on a Naval Admiral electrochemical workstation. The cell current and impedance were recorded using this system; current–voltage (I–V) and power density (I–P) curves were obtained under linear sweep voltammetry (LSV) to evaluate overall cell performance. Electrochemical impedance spectroscopy (EIS) was conducted under open-circuit voltage (OCV), with a frequency range of 0.1 Hz–1 MHz and an AC perturbation amplitude of 10 mV, to analyze dynamic electrochemical behavior and polarization characteristics.

The Faradaic efficiency (FE) was determined as the ratio between the experimentally measured hydrogen production rate and the theoretical value at a given current density. Hydrogen concentration was monitored under both OCV and constant-current electrolysis conditions by gas chromatography, enabling accurate quantification of the actual H₂ generation rate. During FE measurements, 10 mL·min⁻¹ of H₂ and 40 mL·min⁻¹ of N₂ were supplied to the fuel electrode, while 40 mL·min⁻¹ of humidified air was fed to the air electrode. All measurements were repeated at least three times to ensure reproducibility and to obtain statistically averaged data.

2.4 Computational methods

All first-principles calculations were performed within the framework of density functional theory (DFT) using the projector-augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP) [40]. The exchange–correlation energy was treated with the Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA), and electron–ion interactions were described using PAW pseudopotentials[34]. Two atomistic models were considered: pristine SFM and an SFM/SVO/SMO interfacial model representing the local near-surface environment associated with V-assisted SrVO₃ formation. The experimental designation SFM-V is therefore not used to represent a homogeneous

V-substituted bulk phase in the calculations. A plane-wave kinetic energy cutoff of 520 eV was employed. Brillouin-zone integrations used Monkhorst-Pack k-point grids of $3\times4\times2$ for bulk supercells and $2\times2\times1$ for slab models. During geometry optimization, atomic positions were relaxed until the residual forces on each atom were less than $0.02\text{ eV \AA}^{-1}$. The pristine SFM bulk model was constructed using 80-atom $\text{Sr}_{16}\text{Fe}_{12}\text{Mo}_4\text{O}_{48}$ supercell. Surface calculations were based on the SFM (001) orientation, and a vacuum layer of $15\text{ \AA}$ was introduced along the surface-normal direction to minimize interactions between periodic images. Reaction pathways were explored using the climbing-image nudged elastic band (CI-NEB) method with six intermediate images, and all transition states were confirmed by vibrational analysis to exhibit a single imaginary frequency. Long-range dispersion effects were included via the DFT-D3 van der Waals correction scheme[35]. Spin-polarized DFT+U calculations were performed using the rotationally invariant Dudarev approach to account for the on-site Coulomb interactions of the localized transition-metal d states. The effective Hubbard parameters U_{eff} were set to 4.0 eV for Fe 3d and 3.25 eV for V 3d, while no Hubbard correction was applied to Mo 4d, following previous first-principles studies of SFM- and SrVO_3 based systems. Gibbs free energy changes associated with proton-coupled electron transfer (PCET) steps were evaluated on the basis of the computational hydrogen electrode (CHE) model, explicitly accounting for electronic energies, zero-point energy corrections, and entropic contributions. For defect chemistry, oxygen-vacancy formation energies were obtained from the total-energy differences between defective and pristine structures referenced to molecular O_2 , while hydration energies were determined by comparing hydrated and vacancy-containing structures with an isolated H_2O molecule in vacuum.

3. Result and discussion

3.1 Interface-Driven Sr Capture and Catalytic Phase Reconstruction

The introduction of V_2O_3 provides Lewis-acidic sites that chemically bind and reverse-capture outward-migrating Sr species from the SFM surface[36]. Driven by acid-base neutralization and interfacial redox, the extruded Sr reacts with surface anionic motifs to form SMO and SVO in situ, while simultaneously introducing A-site (Sr) vacancies within the near-surface SFM lattice[29]. SFM and V-modified $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}\text{-V}_x$ (SFM-V), $V=0, 0.025, 0.05, 0.075$) were synthesized by a conventional nitrate sol-gel route. Phase constitution was identified by X-ray diffraction (Fig. 1a). Compared with pristine SFM, subtle shifts of the principal SFM reflections are observed after V modification, indicating a structural response of the SFM phase [37]. Rietveld refinement (Fig. 1b) confirms SFM as the major double-perovskite phase (Pm-3m), accompanied by characteristic peaks of SMO ($I4_1/a$) and SVO (Pm-3m), with no detectable residual V_2O_3 . Quantitative refinement yields phase fractions of approximately 2.7% SMO and 2.5% SVO for SFM-V ($R_{\text{exp}}=9.89\%$, $R_p=14.4\%$ and $R_{\text{wp}}=10.5\%$). These results directly demonstrate that V_2O_3 captures Sr expelled from SFM: part combines with MoO_4^{2-} units to form SMO, while another fraction is reduced with V to generate SVO. Supplementary Fig. S1 and Table S1 presents the Rietveld refinement of SFM, SFM-V25 and SFM-V75. The

coexistence of SMO and SVO corroborates the proposed reverse-capture process. As shown in later sections, maintaining the air electrode calcination temperature at ≤ 900 °C preserves three-phase coexistence and ample TPB length while suppressing re-segregation. In this architecture, SMO acts as nanoscale anchors that immobilize Sr and prevent passivating overlayer formation, whereas SVO serves as discrete electron hotspots that lower interfacial charge-transfer resistance and accelerate surface exchange-together balancing activity and durability. Moreover, the double-perovskite framework and the relatively large effective B-site radius introduced by V help mitigate lattice strain and suppress secondary Sr segregation [38].

High-resolution TEM and EDS were performed to elucidate the microstructural characteristics of SFM and SFM-V. For phase-pure SFM (Supplementary Fig. S2), EDS elemental mapping shows uniform elemental distributions, while clear lattice fringes with an interplanar spacing of 0.278 nm can be indexed to the (110) planes of SFM. The SFM-V lattice was also resolved by HR-STEM (Fig. 1c), where the magnified region distinctly resolves multiple lattice domains with interplanar spacings of 0.304, 0.329, and 0.198 nm, corresponding to the (020) planes of SVO, the (112) planes of SMO, and the (200) planes of SFM, respectively. EDS mapping reveals local aggregation of Sr and Mo (Fig. 1d). Based on these structural and compositional observations, a proposed V-assisted near-surface reconstruction mechanism is schematically illustrated in Fig. 1e. During the secondary heat treatment, partial Sr redistribution from the near-surface SFM lattice is proposed to occur, and the redistributed Sr species can interact with local V- and Mo-containing species to form SVO and SMO, respectively. The coexistence of SVO and SMO therefore reflects a coupled near-surface reconstruction process rather than a strictly sequential reaction pathway. Because the present *ex situ* characterization does not resolve the temporal sequence of their formation, no specific reaction order between SVO and SMO is assigned. The formation of these Sr-containing secondary phases is accompanied by local compositional and defect-chemical rearrangement in the adjacent SFM region, which is consistent with the experimentally observed changes in surface oxygen chemistry and electronic structure[29]. Formation of these secondary phases near the surface generates Sr vacancies in the residual SFM lattice; each Sr vacancy is compensated by lattice-oxygen release to supply electrons and maintain charge neutrality[38, 39]. The resulting material thus features a near-surface region enriched in Sr-containing SMO/SVO nano-domains and abundant oxygen vacancies or Sr-vacancy-rich within the adjacent SFM lattice, a configuration beneficial for both electrochemical kinetics and long-term stability.

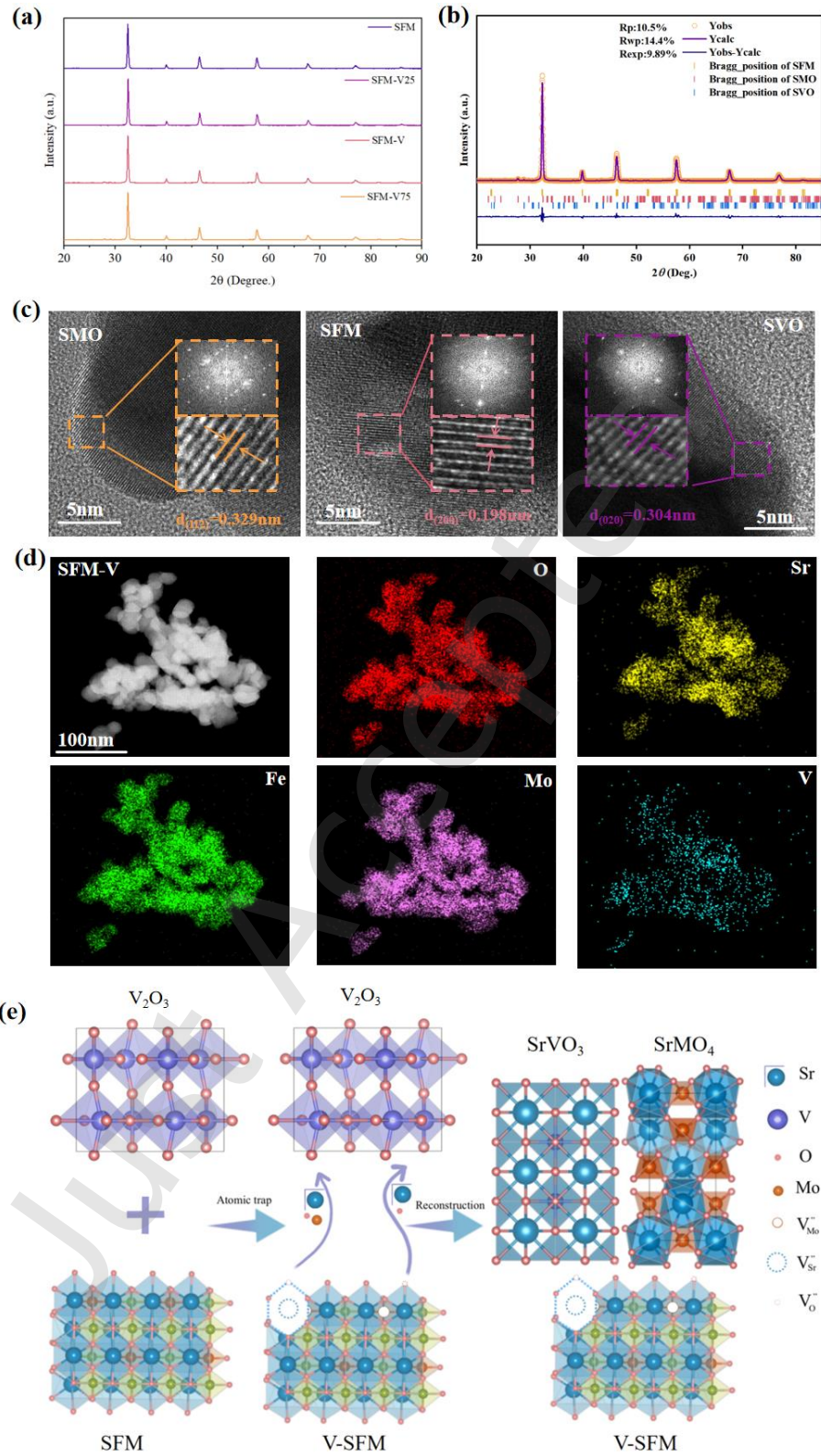


Fig. 1. Phase composition and crystal structure analysis. a) X-ray diffraction XRD patterns of SFM-V and SFM powders. The right panel shows an enlarged. b) Rietveld refinement of as-synthesized SFM-V powder. c) HR-TEM images of SFM-V and the corresponding lattice-fringe map. d) Elemental mapping of SFM-V obtained. e) Schematic diagram of the atom captures process and structure of SFM/V₂O₃.

3.2 Electronic Structure and Defect Chemistry Regulation

To further examine the interaction between V-containing species and the SFM surface, a model surface-reaction experiment was performed by coating V_2O_3 onto an SFM foil followed by calcination at 900 °C. Cross-sectional EDS mapping was then conducted to visualize the spatial distribution of Sr, Fe, Mo, and V after the surface reaction (Fig. 2a and Supplementary Fig. S3). The pristine SFM foil shows relatively uniform distributions of Sr, Fe, and Mo. In contrast, the calcined SFM/ V_2O_3 specimen exhibits obvious Sr enrichment near the surface reaction region, indicating that V-containing species can interact with the SFM surface and promote Sr migration toward the surface. The enriched Sr species are subsequently captured by V-containing species, leading to the formation of Sr–V-related reaction products. Meanwhile, the Mo signal also shows partial enrichment near the surface/interface region, suggesting that the surface reaction may be accompanied by Sr/Mo redistribution. The corresponding EDS line-scan analysis further supports this macroscopic Sr-capture behavior (Fig. 2b and Supplementary Fig. S4). The Sr and V signals are mainly enhanced in the near-surface reaction region, while the Fe signal is primarily retained in the SFM bulk region. These results provide qualitative evidence that V-containing species can induce near-surface Sr redistribution and promote interfacial association of Sr with the V-modified region. As this experiment was conducted on a model SFM/ V_2O_3 foil system, it is used to illustrate the possible interfacial reaction pathway rather than to directly establish the spatial architecture of the SFM-V powder.

The electronic structure was further assessed using X-ray photoelectron spectroscopy (XPS) to examine the chemical states of Sr, Fe, and O. As a triply conductive R-PCEC air electrode must couple electronic/oxide-ion/proton transport with rapid oxygen surface-exchange kinetics-properties closely tied to oxygen-vacancy content and transition-metal valence, the chemical states of Sr, Fe, and O in both SFM and SFM-V were compared after V-induced Sr trapping. The O1s spectrum of SFM and SFM-V (Fig. 2c and Supplementary Table S2) resolves into four components: lattice oxygen (O_{lat}), surface reactive oxygen ($\text{O}^-/\text{O}_2^{2-}$), adsorbed oxygen (O_{ads}), and adsorbed H_2O ($\text{H}_2\text{O}_{\text{ad}}$). Here, O_C represents the total contribution of non-lattice oxygen species, including $\text{O}^-/\text{O}_2^{2-}$, O_{ads} , and $\text{H}_2\text{O}_{\text{ads}}$. The $\text{O}_\text{C}/\text{O}_{\text{lat}}$ ratio is commonly used as an indirect indicator of surface oxygen defect chemistry and oxygen vacancy-related species[40-42]. After Sr capture, the $\text{O}_\text{C}/\text{O}_{\text{lat}}$ ratio in SFM-V increases to 4.93, versus 3.78 in pristine SFM, indicating a higher fraction of surface-accessible oxygen species and indirectly evidencing the creation of Sr-associated vacancies in the adjacent lattice[15, 43]. XPS also reveals metal-center redox adjustments. The Fe 2p spectrum (Fig. 2d) displays the expected spin-orbit doublet ($2p_{3/2}$, $2p_{1/2}$). Fitting results indicate that the Fe^{3+} content in SFM and SFM-V is 40.4% and 32.5%, respectively, while the Fe^{2+} content is 59.6% and 67.5%, respectively. Since oxygen-vacancy formation is energetically costly and induces local charge imbalance, partial $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ reduction acts to maintain charge neutrality (Supplementary Table S3)[44-47]. The Sr 3d region (Fig. 2e and Supplementary Table S4) resolves into surface and lattice components, $\text{Sr}_{\text{surface}} 3d_{3/2}$,

$\text{Sr}_{\text{surface}} 3d_{5/2}$, $\text{Sr}_{\text{lattice}} 3d_{3/2}$, and $\text{Sr}_{\text{lattice}} 3d_{5/2}$ -centered at 135.14, 133.29, 133.74, and 131.6 eV, respectively[48]. The results showed that the $\text{Sr}_{\text{lat}}/\text{Sr}_{\text{sur}}$ ratio decreased from 1.82 in SFM to 1.57 in SFM-V. Upon V incorporation, the surface-associated Sr signal intensifies, consistent with the formation of SVO and SMO and with a Sr-deficient residual SFM near the surface. Finally, the V 2p displays pronounced, well-defined features in SFM-V (Fig. 2f), confirming V incorporation and the associated redox-coupled interfacial chemistry.

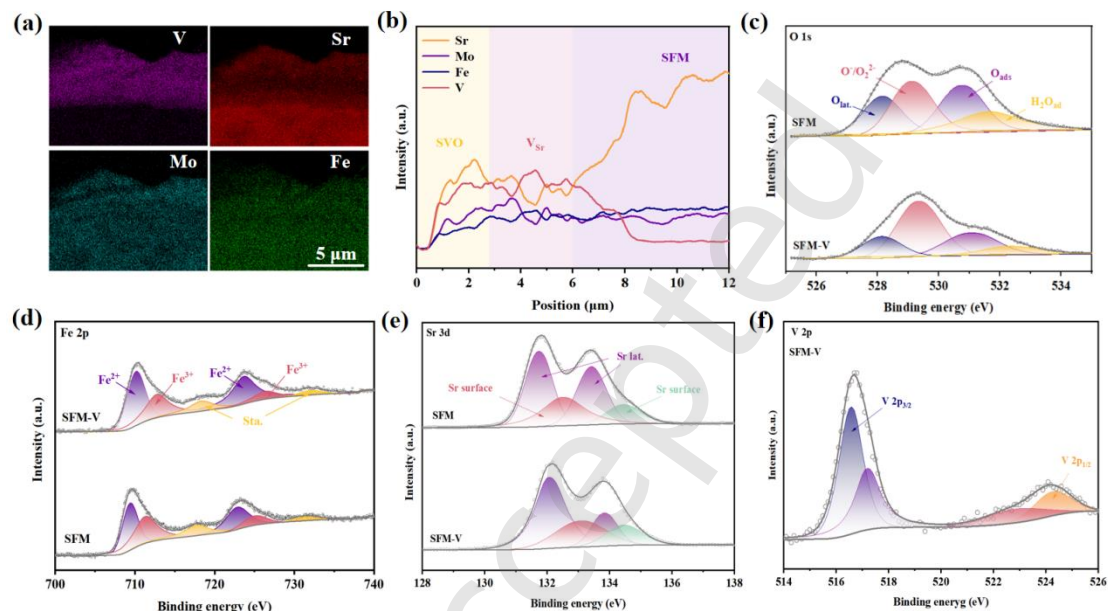


Fig. 2. Surface Valence-State Distribution and Sr-Vacancy Gradient. a,b) SEM images. a) the cross-section of a SFM sheet coated with a V_2O_3 layer after high-temperature treatments at 900°C and b) Line profiles of EDS intensities. c-f) XPS spectra of c) O 1s, d) Fe 2p, e) Sr 3d, and f) V 2p.

The mismatch in thermal expansion coefficients (TECs) between the cathode and the electrolyte inevitably generates thermally induced mechanical stress during heating and cooling. Excessive TEC disparity may lead to interfacial delamination, disrupted ionic transport, and ultimately the failure of catalytic functionality. As shown in Fig. 3a and 3b, the measured TEC of SMO over $30\text{-}800^\circ\text{C}$ is $11.0 \times 10^{-6} \text{K}^{-1}$, which is close to the reported TEC of the BZCYYb electrolyte, approximately $12.0 \times 10^{-6} \text{K}^{-1}$ [49]. Within the same temperature range, SFM-V exhibits a TEC of $14.2 \times 10^{-6} \text{K}^{-1}$, representing an approximate reduction of 15.5% relative to pristine SFM ($16.8 \times 10^{-6} \text{K}^{-1}$). More importantly, the TEC mismatch between SFM-V and BZCYYb is reduced to $2.2 \times 10^{-6} \text{K}^{-1}$, much lower than that between pristine SFM and BZCYYb ($4.8 \times 10^{-6} \text{K}^{-1}$), indicating improved thermo-mechanical compatibility with the electrolyte. This decrease arises not only from the intrinsically lower TEC of the SMO phase but also from the presence of Sr-deficient sites in SFM that further suppress thermal expansion[50, 51]. Following Sr capture, the oxygen adsorption and transport properties of SFM-V were investigated. Fig. 3c compares the thermal

gravimetric responses of SFM and SFM-V in dry air over 30-800 °C. The observed mass loss primarily results from the release of lattice oxygen and the formation of oxygen vacancies. This process is jointly governed by the oxidation state of B-site cations and the strength of the metal–oxygen bond. Upon incorporation of V_2O_3 , oxygen vacancies are more readily generated, leading to a higher mass-loss fraction. The mass-loss values of SFM and SFM-V at 800 °C are 5.2% and 6.6%, respectively. The measured mass loss may contain contributions from the desorption of surface-associated species as well as thermally induced lattice-oxygen release, and these contributions cannot be quantitatively separated from the present TG data. Therefore, the larger mass loss of SFM-V is interpreted as evidence of an altered oxygen-related thermochemical response after V modification, rather than as a direct quantitative measure of oxygen-vacancy concentration. Combined with the XPS and EPR results, the TG behavior further supports that V modification changes the local oxygen-defect and electronic environment of SFM. The H_2O -TPD profiles were measured to probe the water adsorption behavior of SFM and SFM-V (Fig. 3d). Compared with pristine SFM, SFM-V exhibits a much stronger H_2O desorption signal, especially a dominant high-temperature peak centered at approximately 670 °C. This indicates that SFM-V possesses more abundant and/or stronger water-interaction sites, which can facilitate water adsorption and activation under humidified conditions. The enhanced water affinity of SFM-V is consistent with its improved electrochemical performance in wet air and its lower polarization resistance, suggesting that V-induced surface reconstruction benefits hydration-assisted electrode reaction processes in R-PCECs.

To further understand the defect structure and local electronic environment, electron paramagnetic resonance (EPR) spectroscopy was performed for SFM and SFM-V (Fig. 3e). Both samples exhibit a clear resonance signal near $g = 2.003$, while SFM-V shows a higher signal intensity, indicating a larger number of paramagnetic centers with unpaired electrons. It should be noted that, in Fe-containing oxides, the signal near $g \approx 2.0$ may originate not only from oxygen-vacancy-related defect centers, but also from Fe^{3+} paramagnetic species. Therefore, the enhanced EPR signal of SFM-V more reasonably indicates that V modification regulates the local defect/electronic structure of the material, rather than serving as direct evidence for an increase in oxygen-vacancy concentration alone [52, 53]. This observation agrees well with TG results. Combined with XPS analysis, these findings demonstrate that oxygen vacancies in SFM-V compensate for the charge imbalance arising from A-site Sr deficiency in addition to the slight changes in B-site average valence. To elucidate the influence of Sr capture on oxygen adsorption and transport, conductivity-relaxation measurements were performed. Fig. 3f and Fig. 3g present the transient response curves under a step change in oxygen partial pressure from 0.2 to 0.5 atm. SFM-V exhibits a faster relaxation than SFM at all temperatures, reaching the new equilibrium more rapidly. At 700 °C, the relaxation time of SFM-V is approximately 14% shorter than that of SFM, indicating significantly accelerated surface-exchange and bulk-diffusion kinetics. This enhancement is attributed to the higher oxygen-vacancy concentration, which provides additional migration pathways

and lowers the activation barrier for transport[54]. The corresponding chemical diffusion coefficients (D_{chem}) and surface exchange coefficients (K_{chem}) extracted from fitting (Fig. 3h and Supplementary Table S5) show consistently higher values for SFM-V across 550-700 °C. This enhancement is considered to originate from coupled defect-chemical and electronic effects rather than from a single factor. The modified oxygen-defect environment in SFM-V is expected to facilitate oxygen incorporation and lattice oxygen transport, thereby contributing to the enhanced D_{chem} . Meanwhile, the conductive SVO-related domains can improve local electronic transport and interfacial charge transfer, providing an additional contribution to the enhanced surface exchange reflected by K_{chem} . The accompanying SMO phase may further contribute through Sr stabilization and modification of the near-surface defect environment. Because these effects coexist and are intrinsically coupled in SFM-V, the present ECR measurements provide effective transport parameters and do not allow the individual contributions of oxygen-defect regulation and SVO associated electronic conduction to be quantitatively separated. Fig. 3i shows the electrical conductivities of SFM and SFM-V measured by a four-probe DC method under dry and humidified atmospheres. Under dry conditions, both samples exhibit relatively low conductivities, while SFM-V consistently shows higher conductivity than pristine SFM over the investigated temperature range. After introducing water vapor, the conductivities of both SFM and SFM-V increase markedly, indicating that the humidified atmosphere facilitates charge transport and proton-related conduction processes in these Sr-containing double-perovskite electrodes. Notably, SFM-V maintains higher conductivity than SFM under both dry and wet conditions, confirming that V modification improves the transport properties of SFM. The enhanced conductivity of SFM-V can be attributed to the formation of conductive SrVO_3 related domains during the modification process. SrVO_3 has been widely reported as a highly conductive metallic perovskite with very low resistivity over a broad temperature range, and it can maintain high electronic conductivity under reducing atmospheres at elevated temperatures[55-57]. Therefore, the improved conductivity of SFM-V originates not only from Sr-related defect chemistry and humidified-atmosphere-assisted transport, but also from the contribution of conductive SVO related phases generated during V-induced surface reconstruction. To further quantify the incorporated protonic species, Karl Fischer titration was performed after hydration at 600 °C under 20% O_2 -3% H_2O for 24 h (Supplementary Fig. S5 and Table S6). SFM-V releases 7.63 $\mu\text{g g}^{-1}$ H_2O , corresponding to an H_2O uptake of 0.1172 mmol $\text{H}_2\text{O mol}^{-1}$ oxide and a proton uptake of 0.2344 mmol H mol^{-1} oxide. In comparison, SFM shows a substantially lower H_2O release of 5.58 $\mu\text{g g}^{-1}$, corresponding to 0.0836 mmol $\text{H}_2\text{O mol}^{-1}$ oxide and 0.1672 mmol H mol^{-1} oxide. The higher water uptake of SFM-V provides independent quantitative evidence that V modification enhances the hydration capability and favors proton incorporation into the oxide lattice. This result is consistent with the humidity-dependent conductivity and electrochemical impedance behavior, supporting the involvement of proton-related processes under humidified conditions.

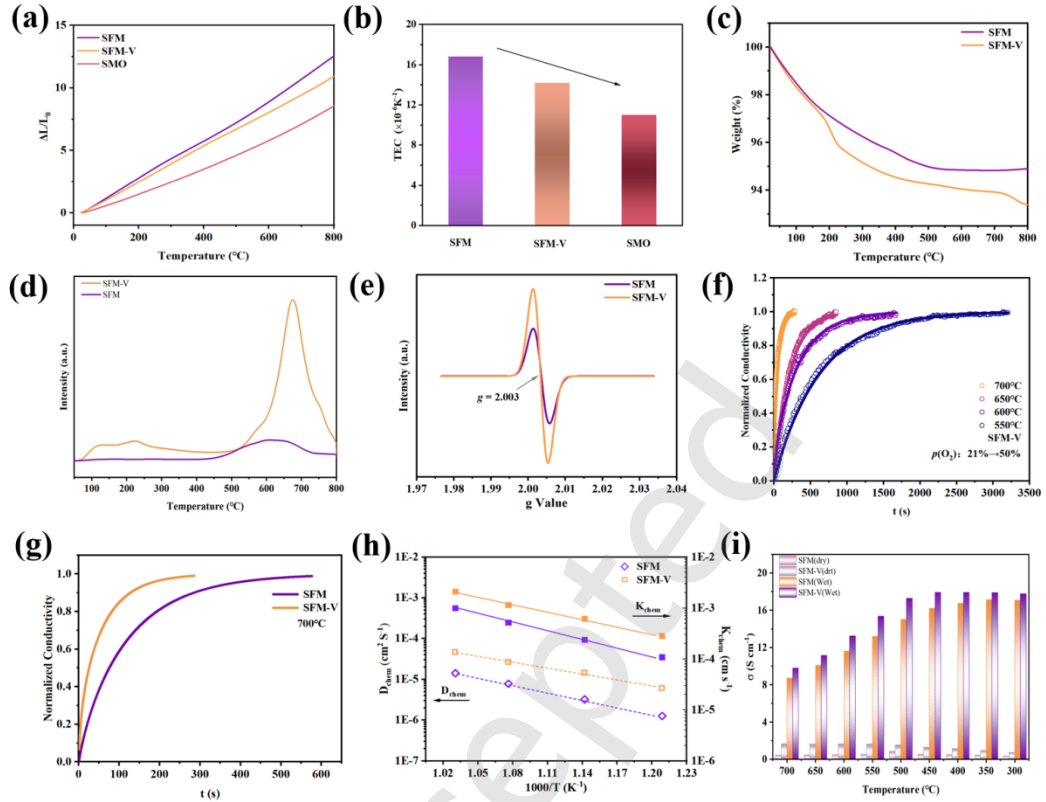


Fig. 3. Enhanced oxygen activation, ion conductivity. a) Thermal expansion curves from RT to 800 °C in air. b) Measured TECs of SFM, SFM-V and SMO. c) TG curves of samples from RT to 800 °C. d) H₂O-TPD profiles from room temperature to 800 °C. e) Electron paramagnetic resonance of the pristine SFM and SFM-V. f) ECR curves for SFM-V when switching the oxygen partial pressure in dry air tested at 550-700°C. g) Compare ECR curves for SFM and SFM-V when switching the oxygen partial pressure in dry air tested at 700°C. h) D_{chem} and K_{chem} from fits to the electrical conductivity relaxation curves of the air electrodes over 500-700 °C. i) Electrical conductivity of SFM and SFM-V measured in dry and humidified atmospheres from 350 to 700 °C.

3.3 Catalytic ORR Kinetics and Interfacial Transport

Electrochemical impedance spectroscopy (EIS) was measured on symmetric cells. At 600 °C, the polarization resistance R_p of SFM-V decreases monotonically as p_{O_2} decrease from 0.5 to 0.1 atm (0.11, 0.12, 0.13, 0.14 and 0.15 $\Omega \text{ cm}^2$) as show in Fig. 4a. Subsequently, the relaxation time distribution (DRT) method was used to fit the spectrum in order to decompose the complex EIS into independent electrochemical processes [58]: LF (<10 Hz) corresponds to the surface exchange (R_{ads}), IF (10-10³ Hz) corresponds to , ion migration (R_{rxn}) and HF (>10³) corresponds to the processes of charge transfer (R_{ion}). After Sr capture induced by V (forming SVO and SMO at the surface), the LF peak is markedly suppressed, indicating accelerated dissociative adsorption (Fig. 4b). Based on the relationship between the air electrode's R_p value and P_{O_2} , it can be defined as $R_p = k(P_{O_2})^{-n}$, where the value of n is related to the

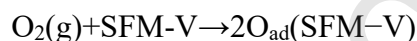
relevant electrochemical reaction steps, as shown in Fig. 4c[59]. The finding that Rads has $n=0.58$ in the low-frequency region indicates that the R_p of the air electrode is related to the oxygen adsorption/dissociation process ($O_2(g) \rightarrow 2O_{ad}$), which occurs at the air-electrode surface[60]. Additionally, the IF contribution gives $n=0.21$ (close to 0.25), consistent with surface oxygen exchange/diffusion $O_{ad} \rightarrow O_{ad-}$ (site-to-site migration of adsorbed oxygen). The HF contribution yields $n=0.07$ (close to 0) indicative of charge transfer ($O^-_{TPB} \rightarrow O^{2-}_{TPB}$) at the triple-phase boundary [61, 62]. Mechanistically, SMO nanodomains act as inert Sr-anchoring/sequestration sites that suppress passivating overlayer growth and preserve TPB exposure, contributing mainly to surface/morphological stabilization rather than catalytic oxygen activation. By contrast, SVO domains provide discrete electron that facilitate interfacial charge transfer/proton injection, thereby lowering R_{ion} . Supplementary Fig. S6 summarizes the polarization resistance R_p of SFM symmetric cells at 600 °C as a function of P_{O_2} . In comparison with SFM-V, after the Sr atom is captured, leads to a lower overall R_p and a markedly suppressed LF contribution, evidencing accelerated O_2 adsorption/dissociation. Fig. 4d presents a full-cell schematic of the SOFC operating mechanism. In an H-SOFC, H_2 at the anode dissociates into H^+ and e^- ; electrons flow through the external circuit, while protons migrate across the proton-conducting electrolyte to the cathode. On the cathode side, O_2 is first adsorbed and dissociated to form surface-reactive oxygen ($O^\cdot$), followed by proton-coupled reduction steps ($O^\cdot \rightarrow OH^- \rightarrow H_2O$). At the TPB, the arriving H^+ and electrons combine with the surface oxygen intermediates to produce water (formed at the cathode). The upper-right panel depicts the complete proton-coupled ORR pathway, where adsorption/dissociation, surface exchange/diffusion, and interfacial charge transfer correspond to the DRT-resolved elements Rads, R_{rxn} and R_{ion} , respectively. To assess the ORR activity of SFM and SFM-V under practical fuel-cell operating conditions, EIS was measured on BZCYYb anode-supported single cells over 550-700 °C. As shown in Fig. 4e, the polarization resistances R_p of SFM-V measured on BZCYYb anode-supported single cells are 0.05, 0.09, 0.21, and 0.54 $\Omega \cdot cm^2$ at 700, 650, 600, and 550 °C, respectively. Compared with pristine SFM (0.08 $\Omega \cdot cm^2$), SFM-V exhibits a clearly lower R_p at 700 °C (Supplementary Fig. S7). Supplementary Fig. S8 summarizes the R_p values of SFM, SFM-V25 and SFM-V75 over 550-700 °C. To further evaluate the temperature dependence of the polarization resistance, Arrhenius plots derived from the EIS results were constructed (Fig. 4f). The apparent activation energy (E_a) was determined according to the Arrhenius relationship:

$$\log_{10}(ASR) = \log_{10} A + e \frac{-E_a}{k_B T} \quad (1)$$

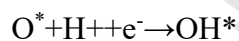
where A is the pre-exponential factor, E_a is the apparent activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. The calculated E_a values are 1.084 eV for SFM and 1.050 eV for SFM-V, respectively. The lower E_a of SFM-V indicates faster reaction kinetics. To gain deeper insight into how Sr atom capture affects the reaction processes occurring inside the SFM-V electrode under practical fuel-cell operating conditions, the EIS data were likewise further deconvoluted using the distribution of relaxation times (DRT) for an in-depth analysis of the electrochemical processes at the electrode surface. Fig. 4g depicts the deconvoluted

peaks of SFM-V, which can be divided into three distinct regions according to the frequency range, designated P1-P3. The results indicate that, at 600 °C, both SFM-V and SFM are clearly inclined to be influenced by electrochemical reactions occurring in the P1 stage. Considering the proton conducting nature of BZCYYb, the cathodic process should be described as a proton-coupled oxygen reduction reaction rather than a purely oxide-ion-mediated pathway. Oxygen is first adsorbed and dissociated on the SFM-V surface, followed by proton-coupled electron-transfer reactions involving surface oxygenated intermediates and subsequent water formation. A simplified reaction sequence can be expressed as follows:

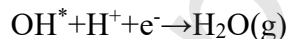
Oxygen adsorption and dissociation:



Proton coupled surface reduction:



Water formation:



In addition, to further demonstrate that the SFM-V air electrode has strong hydration capability and conductivity, we evaluated the EIS of single cells equipped with SFM-V air electrodes under different water vapor partial pressures (Fig. 4h). At $P_{\text{H}_2\text{O}}=20\%$, the ASR values of SFM-V are 0.11, 0.28, and $0.69 \Omega \cdot \text{cm}^2$ over 650-550 °C. Supplementary Fig. S9 describes the ASR of SFM-V under air with $P_{\text{H}_2\text{O}}=3\%$ and $P_{\text{H}_2\text{O}}=10\%$ in the 650-550 °C range. The results show that, as the water vapor partial pressure increases, the ASR of SFM-V decreases significantly; for example, at 600 °C the ASR decreases from 0.35 to $0.28 \Omega \cdot \text{cm}^2$, a reduction of 20%. This indicates that the SFM-V air electrode possesses a rapid hydration reaction rate and excellent proton conduction capability. In addition, at 600 °C and $P_{\text{H}_2\text{O}}=20\%$, the ASR of SFM-V is lower than that of pristine SFM ($0.46 \Omega \cdot \text{cm}^2$) by 39% (Supplementary Fig. S10), and is also lower than those of SFM-V25 and SFM-V75, further confirming the optimized electrochemical performance of SFM-V among the SFM-Vx series. Likewise, to evaluate the water-dependent kinetics, we fitted the EIS of SFM and SFM-V under the same conditions using the DRT method (Fig. 4i). The impedance response is also mainly concentrated in the low-frequency (LF) region, indicating that the LF response may be related to electrochemical processes occurring at the surface of the air electrode, such as oxygen adsorption, dissociation, and surface diffusion, which are usually the rate-limiting steps under oxidizing conditions[63-65]. Fig. 4j and Supplementary Table S7 show the ASR of SFM-V with state-of-the-art cathodes reported in the literature. Overall, these results demonstrate that Sr anchoring enabled by V-induced SVO/SMO formation effectively reduces polarization losses and enhances ORR activity under both dry and humid conditions by synergistically accelerating oxygen activation and interfacial charge-transfer/proton-injection steps. In addition, as shown in Fig. 4k, the EIS stability of SFM and SFM-V was evaluated at 600 °C for 100 h. Both materials

exhibit an initial increase in R_p , which gradually stabilizes after 30 h. Over the 100 h test, the R_p of pristine SFM increased from 0.430 to 0.488 $\Omega \cdot \text{cm}^2$, whereas that of SFM-V increased from 0.232 to 0.260 $\Omega \cdot \text{cm}^2$. The corresponding normalized increases, calculated as $(R_p - R_0)/R_0 \times 100\%$, are approximately 13.5% for SFM and 12.1% for SFM-V, respectively. Although the relative changes are comparable, SFM-V maintains a substantially lower absolute R_p throughout the test and exhibits a smaller absolute increase in polarization resistance. These results indicate that V modification helps maintain the lower polarization resistance of SFM-V over the investigated period rather than completely eliminating electrochemical degradation.

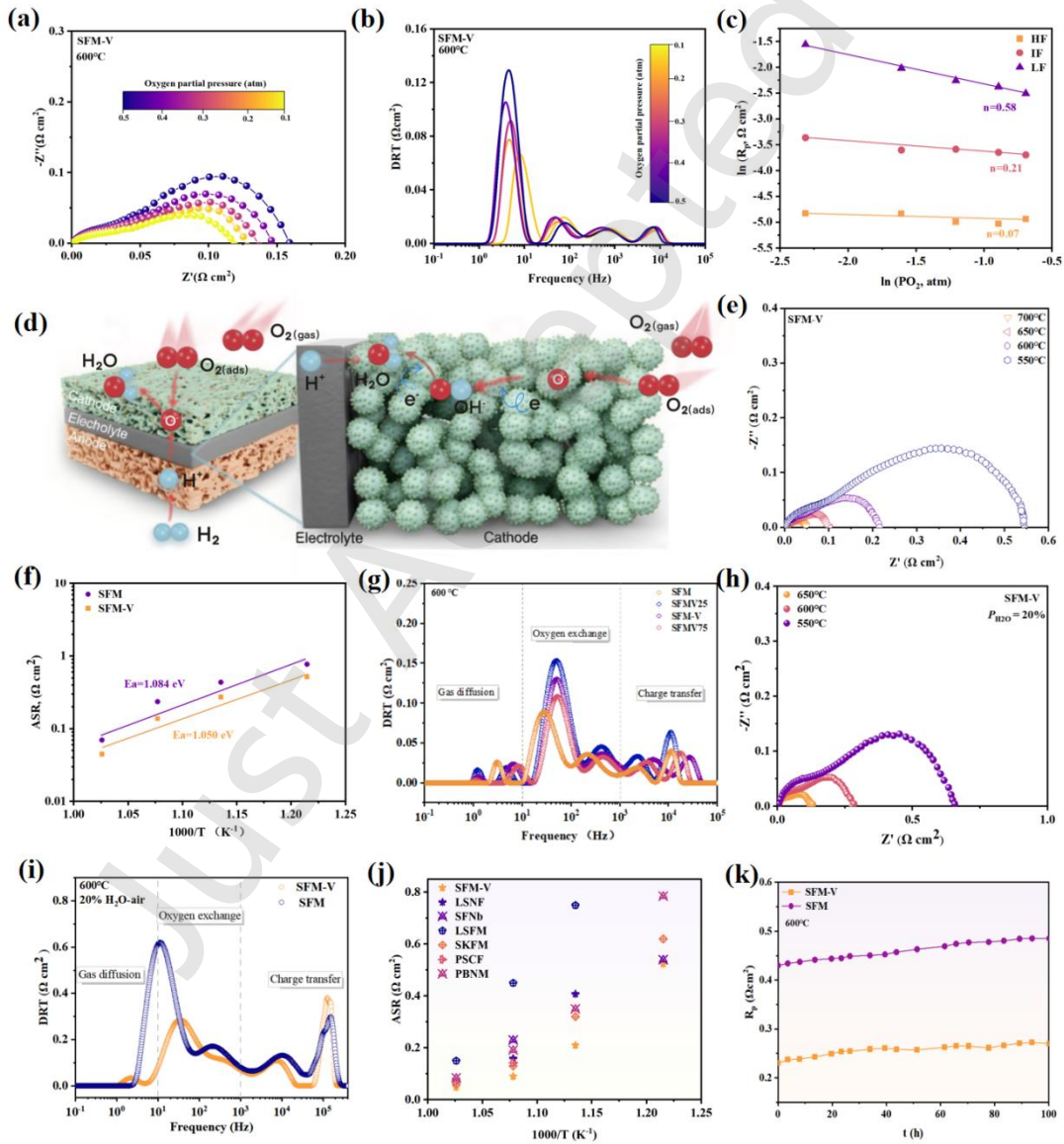


Fig. 4. Oxygen reduction kinetics. a) Nyquist plots of SFM-V symmetric cells at 600 °C under different oxygen partial pressures. b) The DRT analysis of EIS was measured at SFM-V air electrodes at 600 °C. c) Arrhenius plots of R_p of SFM-V. d) Schematic illustration of ORR pathways and charge/proton transport in an H-SOFC. e)

EIS of SFM-V single cells at 550-700 °C and f) Arrhenius plots of ASR for SFM and SFM-V. g) The DRT comparison of SFM and SFM-V at 600 °C. h) EIS plots of cell with SFM-V air electrode tested at 650-550 under 20% H₂O-air. i) The DRT comparison of SFM and SFM-V at 600 °C and 20% H₂O-air. j) Comparison of ASR from SFM-V and other high preference air electrodes. k) Comparison of ASR stability of SFM-V and SFM air electrodes.

3.4 Electrochemical Performance and Durability

To evaluate the ORR activity of SFM-V after Sr-capture when used as an air electrode, single-cell performances were measured for cells consisting of a Ni-BZCYYb fuel electrode, a dense BZCYYb electrolyte, and an SFM-V air electrode (Fig. 5a). The I-V and corresponding power density curves in FC mode are shown in Fig. 5b and Fig. 5c. The deviation of the OCV from the theoretical Nernst value may partly arise from minor electrolyte nonuniformity and possible electronic leakage through BZCYYb, which can influence both the measured FC power output and the EC current response and should therefore be considered when interpreting the overall cell performance. The SFM-V based single cell delivers peak power densities of 1.62, 1.23, 0.82 and 0.41 W cm⁻² at 700, 650, 600 and 550 °C, respectively, which are significantly higher than those of the undoped SFM cell under the same conditions (0.97, 0.67, 0.42 and 0.23 W cm⁻²). In comparison, the SFM-V25 and SFM-V75 cells show lower peak power densities than SFM-V, indicating that an appropriate Sr-capture/V-modification ratio is essential for maximizing ORR activity (Supplementary Fig. S11). The inferior performance at lower or higher V contents may be associated with insufficient interfacial reconstruction or excessive secondary-phase formation, respectively, both of which can limit surface oxygen exchange and charge-transfer kinetics. Fig. 5d and Supplementary Table S8 further compare the performance of the SFM-V cell with other reported air electrodes in similar fuel-cell architectures, demonstrating the pronounced advantage of SFM-V in the intermediate-temperature regime. To further verify the excellent oxygen-evolution reaction (OER) activity and durability of SFM-V, we carried out electrolysis performance, Faradaic efficiency, and cycling tests. Fig. 5e presents the I-V characteristics of the SFM-V air electrode in EC mode at 1.3 V. Current densities of -3.4, -1.6, -0.75 and -0.34 A cm⁻² are obtained at 650, 600, 550 and 500 °C, respectively, whereas the SFM cell reaches only about 0.8 A cm⁻² at 600 °C and 1.3 V (Supplementary Fig. S12). Moreover, at 600 °C under 20% H₂O-air, SFM-V also outperforms SFM-V25 and SFM-V75, confirming the optimized EC-mode performance of SFM-V among the SFM-V_x series. Supplementary Fig. S13 shows that I-V curves of the SFM-V cell at 550-650 °C under 3% and 10% H₂O-air atmospheres, demonstrating the influence of steam content on cell polarization behavior and electrochemical performance. Moreover, when benchmarked against other R-PCEC cells operated under comparable conditions, the SFM-V single cell exhibits superior EC mode performance, outperforming most state-of-the-art materials (Fig. 5f and Supplementary Table S9).

In electrochemical energy-conversion devices, the effective utilization of electrons is directly linked to device performance and reaction selectivity. The Faradaic efficiency (FE) is a key metric that quantifies what fraction of the input charge is used to drive the target reaction and generate the desired product. For reversible protonic ceramic electrochemical cells (R-PCECs), FE not only reflects the selectivity of electrons for the main reaction during electrocatalysis, but also indirectly reveals the extent to which side reactions are suppressed and the controllability of product formation and transport[14, 66]. In this work, the FE of single cells equipped with SFM-V air electrodes was measured at 600 °C using gas chromatography (GC) under various electrolysis current densities and steam partial pressures, as shown in Fig. 5g and Fig. 5h. As the applied electrolysis current density increases from 0.5 to 1.5 A cm⁻², the FE gradually decreases from 86% to 75%. This behavior can be attributed to the decrease in p_{O2} at the fuel electrode, which enhances the electronic conductivity of the electrolyte and induces limited electron leakage, thereby lowering the FE. In contrast, increasing the steam partial pressure suppresses electronic defects and promotes hydration and proton generation, leading to an increase in FE[67].

The durability of the SFM-V single cell in FC mode was further assessed. As shown in Fig. 5i, under a constant current density of 0.4 A cm⁻² at 600 °C, the cell voltage decreased from 0.900 to 0.867 V over 100 h, corresponding to an overall voltage decay of approximately 3.7% and a voltage retention of approximately 96.3%. The gradual voltage attenuation occurred without abrupt performance loss, indicating stable operation over the investigated 100 h period. The observed voltage decay may be associated with gradual polarization and interfacial/surface evolution during operation. To further clarify the possible origin of the voltage attenuation, post-test SEM and Sr 3d XPS analyses were performed (Supplementary Fig. S14 and S15). The SEM results show that the SFM-V air electrode maintains a porous and well-connected microstructure after the stability test, without obvious cracking, delamination, or severe structural collapse. Meanwhile, the Sr 3d XPS results show that the surface-associated Sr fraction remains nearly unchanged after prolonged operation, increasing only slightly from 38.90% to 39.09%. This limited variation indicates that the Sr-related surface chemistry of SFM-V remains relatively stable during the investigated operation period, with no pronounced additional Sr surface enrichment. Therefore, the gradual voltage attenuation is mainly attributed to slow interfacial/surface evolution and gradual polarization increase, rather than abrupt structural failure. In addition, to evaluate the stability of the single cell under R-PCEC operating conditions, an SFM-V air-electrode cell was cycled between FC and EC modes for 100 h. During the test, a current density of 0.5 A cm⁻² was applied in FC mode and -0.5 A cm⁻² in EC mode, defining one full cycle, and a total of 20 cycles were performed. As shown in Fig. 5j, throughout these cycles the current immediately follows the applied cell voltage without noticeable decay or hysteresis, indicating that the cathode maintains highly efficient and stable ORR kinetics even under harsh operating conditions. gas leakage.

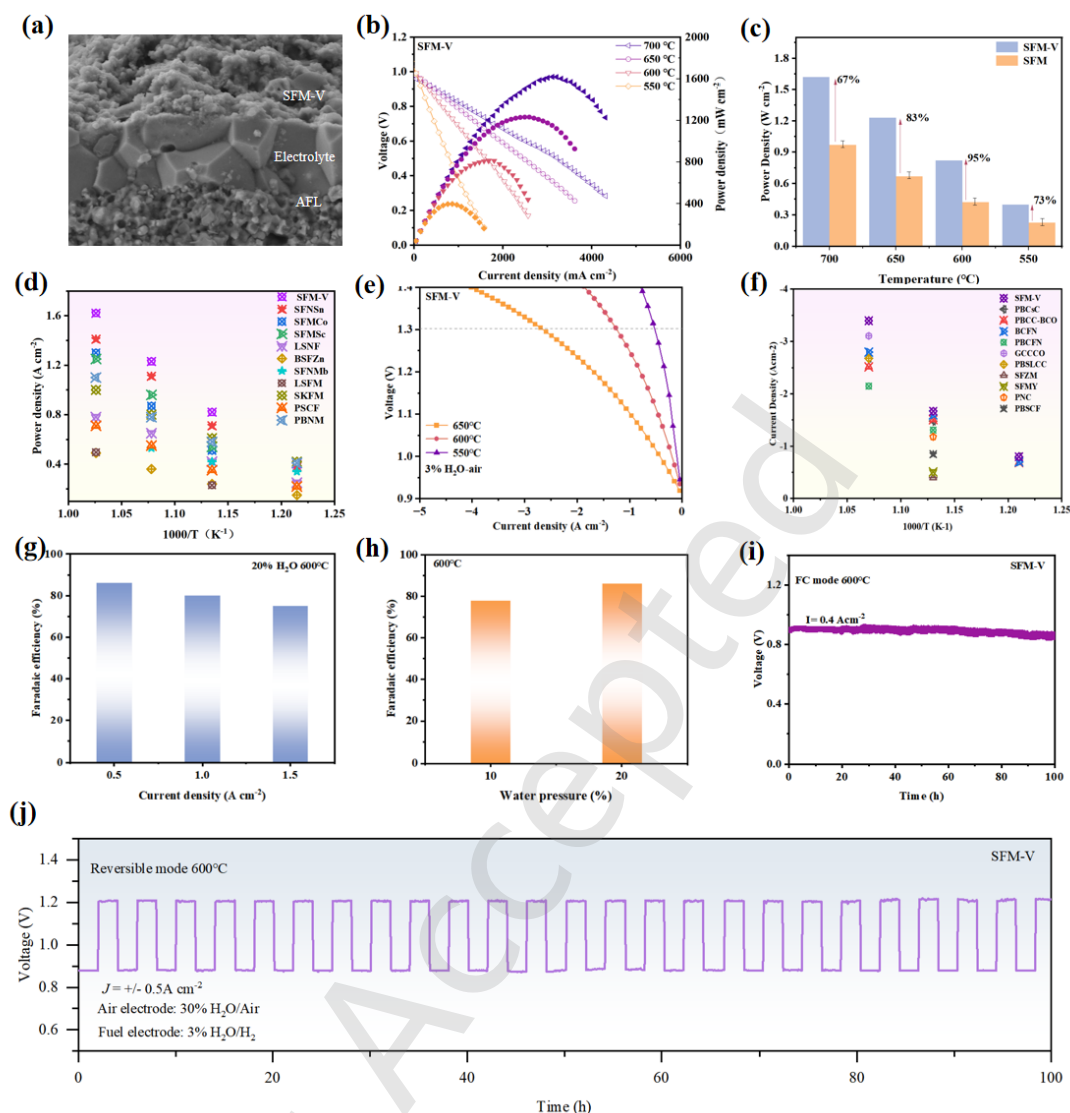


Fig. 5. Electrochemical performance and stability of single cells in fuel-cell (FC) mode. a) Cross-sectional SEM image of SFM-V single cell structure. b) I-V and I-P curves of single cell with SFM-V air electrode in FC mode at 550-700°C. c) Comparison of power density columns of SFM and SFM-V. d) Comparison of the PPDs of BZCYYb single cell with various cathodes materials at 550-700°C. e) I-V curves of cells with SFM-V electrode measured in EC mode at 650-550°C under 20% H₂O-air. f) Comparison of Current density obtained with SFM-V air electrode and advanced air electrodes in the literature at 650-550°C. g) FE of cells at different current densities. h) FE of cells at different P_{H₂O}. i) A short durability assessment of a SFM-V at a consistent current density of 0.4 A cm⁻² and a temperature of 600 °C. j) The R-PCEC with SFM-V air electrode performed cyclic tests in FC and EC modes.

3.5 DFT calculations and mechanism analysis

Density functional theory calculations were performed using pristine SFM and an SFM/SVO/SMO interfacial model to examine the influence of the locally formed SVO phase on the defect energetics and electronic structure of SFM. The SFM/SVO/SMO model was employed as an atomistic representation of the

V-modified near-surface environment rather than as a substitutionally V-doped bulk SFM structure. Oxygen-vacancy formation energies were evaluated at the selected Fe-O-Fe and Fe-O-Mo sites in both models (Supplementary Figs. S16–S17). For pristine SFM, the calculated vacancy formation energies at the Fe–O–Fe and Fe–O–Mo sites are 2.31 and 4.45 eV, respectively, whereas the corresponding values in the SFM/ SrVO₃ interfacial model are 1.13 and 1.49 eV. These results indicate that the local SFM/SVO/SMO interfacial environment lowers the energetic cost of oxygen-vacancy formation at the investigated sites. (Supplementary Fig. S18).

In addition, V incorporation into SFM leads to pronounced changes in the band structure and electronic configuration. The projected density of states (PDOS, Fig. 6a and b) reveals that V doping shifts the O 2p band center upward from -3.65 to -3.14 eV relative to the Fermi level (E_F), thereby narrowing the energy separation between the O 2p states and the transition-metal 3d orbitals. This upward shift enhances M 3d-O 2p hybridization and increases the covalency of the B-O bonds; as the O 2p band center moves closer to E_F , the mobility of lattice oxygen is improved. At the same time, the increased density of states near E_F provides additional pathways for coupled electron–ion transport. Consequently, the higher O 2p band center reduces the energetic penalty for generating oxygen vacancies and facilitates the transport of electrons and/or oxide ions within the perovskite lattice, which is consistent with the lower E_{vac} values and the experimentally observed enhancement in ORR/OER kinetics.

The electronic redistribution and bonding characteristics were further elucidated through differential charge-density (DCD) analysis (Fig. 6c). Compared with pristine SFM, the SFM/SVO/SMO interfacial model exhibits a visibly redistributed charge-density pattern around the interfacial metal–oxygen framework, indicating that the formation of the SrVO₃ containing interface modifies the local electronic environment and metal–oxygen interactions. The enlarged accumulation/depletion lobes and the more asymmetric isosurfaces point to stronger B–O electronic interactions in SFM-V. We ascribe this to the in-situ formed SVO metallic phase, whose interfacial electronic coupling with the SFM lattice drives charge redistribution from O-2p toward Fe/Mo-centered states, thereby increasing local bond polarization. Furthermore, to evaluate how the Sr capture induced heterointerface in SFM-V suppresses secondary Sr migration, we calculated the migration energy profile of neighboring Sr ions by examining the initial, transition, and final states along the diffusion pathway (Fig. 6d and Supplementary Fig. S19-20). The results show that the maximum migration barrier for Sr in pristine SFM is only 0.14 eV. In contrast, the corresponding barrier in SFM-V increases to 0.36 eV, demonstrating that the Sr-anchored gradient structure formed after Sr capture significantly hinders subsequent Sr migration.

Finally, the free-energy profiles for the elementary ORR/OER steps (Fig. 6e and Supplementary Fig. S21) provide a thermodynamic rationale for the experimentally enhanced bifunctional activity after Sr capture. Along the OER direction, both SFM and SFM-V follow the same adsorbate sequence. However, SFM-V exhibits a systematic downshift of the key intermediate energies relative to pristine SFM,

indicating that the SVO coupled surface/interfacial environment weakens the thermodynamic penalties of the uphill steps. In particular, the largest energy rise occurs at the oxygen-activation region around step 4, where the system reaches the $*O+H$ state (Fig. 6f). This peak is noticeably lower for the SFM/SVO/SMO interfacial model than for SFM, suggesting a reduced thermodynamic constraint for the potential-determining step associated with the modified local electronic environment. The subsequent $*O \rightarrow *OO$ and $*OO \rightarrow *O_2$ segments are also slightly stabilized on SFM-V, suggesting a more balanced adsorption strength for oxygenated intermediates and an easier O–O bond formation/release process.

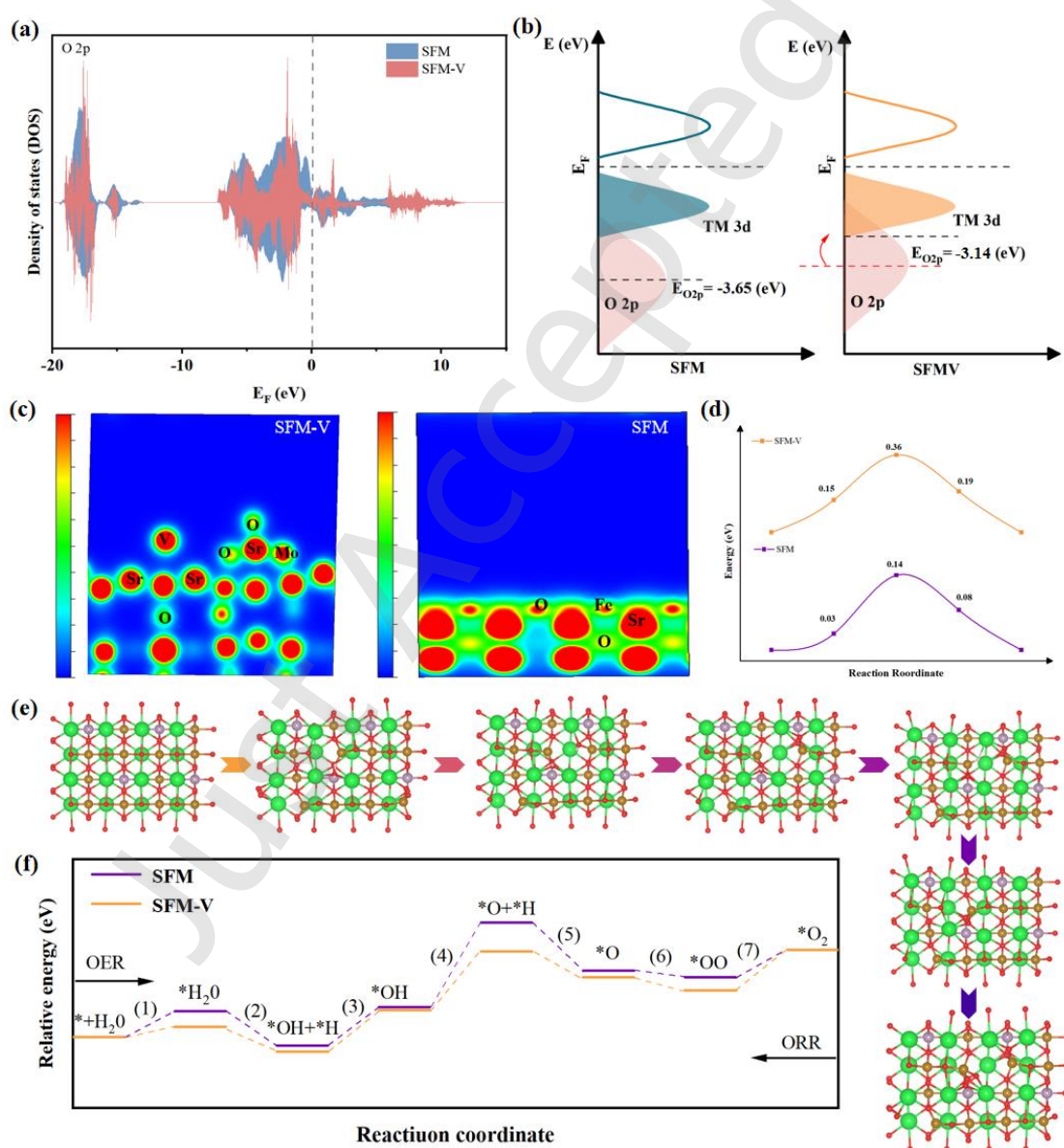


Fig. 6. DFT calculations regarding mechanisms on the air electrodes of R-PCECs. a) Schematic energy-level diagrams of O 2p. b) DOS of O 2p states near the Fermi level. c) Two-dimensional charge-density distributions of pristine SFM and the SFM/SVO/SMO interfacial model. d) comparison migration energy of SFM and

SFM-V. e) Geometric structures diagrams of the OER process on the surfaces of SFM. f) Calculated free-energy profiles of the OER and ORR on SFM and SFM-V

4. Conclusion

In summary, Sr capture in SFM-V functions as a dual-functional regulator, electronically activating the perovskite lattice while kinetically stabilizing Sr species. The results highlight that Sr capture is an active process involving electronic and defect-structural reconfigurations driven by the interfacial interactions between SFM and the in-situ formed SrVO_3 phase, reshaping oxygen-vacancy energetics, electronic hybridization, and reaction thermodynamics. This is further amplified by the upward shift of the O 2p band center, which strengthens M 3d–O 2p hybridization, reduces the vacancy formation penalty, and enhances coupled electron–ion mobility. The interface optimizes the adsorption of oxygenated intermediates, flattening the ORR/OER free-energy landscape and accelerating both oxygen reduction and evolution kinetics. Simultaneously, the Sr-capture-induced gradient structure increases the Sr migration barrier, mitigating long-term surface segregation and enhancing electrochemical stability. This integrated modulation of defect chemistry, electronic structure, and reaction thermodynamics is central to the improved bifunctional performance and long-term durability of SFM-V, providing valuable insights for the design of advanced electrocatalysts for energy conversion applications.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

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