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Enhancing Direct Electrochemical CO_2 Electrolysis by Introducing A-Site Deficiency for the Dual-Phase Pr(Ca)Fe (Ni) $O_{3-\delta}$ Cathode

Wanhua Wang, Haixia Li, Ka-Young Park, Taehee Lee, Dong Ding* 💿, and Fanglin Chen* 💿

High-temperature CO₂ electrolysis via solid oxide electrolysis cells (CO₂-SOECs) has drawn special attention due to the high energy convention efficiency, fast electrode kinetics, and great potential in carbon cycling. However, the development of cathode materials with high catalytic activity and chemical stability for pure CO₂ electrolysis is still a great challenge. In this work, A-site cation deficient dual-phase material, namely $(Pr_{0.4}Ca_{0.6})_xFe_{0.8}Ni_{0.2}O_{3-\delta}$ (PCFN, x = 1, 0.95, and 0.9), has been designed as the fuel electrode for a pure CO2-SOEC, which presents superior electrochemical performance. Among all these compositions, $(Pr_{0.4}Ca_{0.6})_{0.95}Fe_{0.8}Ni_{0.2}O_{3-\delta}$ (PCFN95) exhibited the lowest polarization resistance of 0.458 Ω cm² at open-circuit voltage and 800 °C. The application of PCFN95 as the cathode in a single cell yields an impressive electrolysis current density of 1.76 A cm^{-2} at 1.5 V and 800 °C, which is 76% higher than that of single cells with stoichiometric Pr_{0.4}Ca_{0.6}Fe_{0.8}Ni_{0.2}O_{3-δ} (PCFN100) cathode. The effects of A-site deficiency on materials' phase structure and physicochemical properties are also systematically investigated. Such an enhancement in electrochemical performance is attributed to the promotion of effective CO₂ adsorption, as well as the improved electrode kinetics resulting from the A-site deficiency.

1. Introduction

The increasing concentration of carbon dioxide (CO_2) in the Earth's atmosphere, primarily attributed to anthropogenic activities, has sparked a global imperative to combat climate change and transition toward a sustainable energy future.^[1,2] Numerous effective measures have been undertaken to curtail CO_2 emissions, such as improving energy efficiency,^[3] developing clean energy,^[4] and employing chemical engineering techniques to capture and utilize CO_2 .^[5] The electrochemical method has garnered significant research interest as a promising strategy

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to mitigate CO_2 levels. Through the electrochemical reduction of CO_2 into valued carboncontaining chemicals, such as carbon monoxide (CO), methane, and methanol, not only are CO_2 emissions reduced, but the electrical energy produced from clean and renewable alternative energy sources is also stored.^[6–8]

High-temperature CO₂ electrolysis using solid oxide electrolysis cells (SOECs) presents a promising avenue for directly converting CO₂ to CO with remarkable energy efficiency, holding significant potential for practical application in the future. The architecture of SOECs consists of a porous cathode, a dense electrolyte, and a porous anode. Firstly, the CO2 molecules are electrochemically reduced to CO and oxygen ions on the cathode, then oxygen ions traverse the dense electrolyte layer to reach the anode, where O_2 is produced and released, or oxygen ions react with other chemicals such as methane to produce value-added chemicals such as ethylene.^[9] As the place where CO₂ reduction reaction (CO₂RR) takes place, the cathode generally plays the core role in the overall electrochemical processes since CO2RR demands a

substantially higher activation energy compared to the oxygen evolution reaction.^[10] However, the harsh and complex working conditions in the cathodes make the development of suitable cathode catalysts a great challenge.^[11] An excellent cathode material should possess not only high catalytic activity but also enduring durability over extended periods of operations under a redox environment at elevated temperatures. Traditionally, Ni-based cermet electrodes (e.g. Ni-yttria stabilized zirconia, Ni-YSZ), where Ni serves as both an electrocatalyst and an electronic conductor, are the most widely applied cathode materials since their high electrical conductivity and excellent catalytic activity for CO2 reduction.^[12,13] Nonetheless, utilizing Ni-based cermet for the electrolysis of pure or concentrated CO₂ proves challenging due to Ni oxidation problems encountered during operation. This issue arises from the exposure of Ni particles to a concentrated CO2 atmosphere during the open-circuit condition at elevated temperatures, where the elevated oxygen partial pressure prompts the conversion of Ni into inactive and nonconductive NiO. This transform results in a serious degradation of the electrolysis performance.^[14,15] It would be necessary to feed sufficient safe gas such as CO and/or H₂ to make the gas composition reducing over all parts of the electrode.^[16] Additionally, carbon deposition issue in the Ni-based electrode is another challenge, especially under high CO

concentration, contributing to the deterioration of catalytic activity and long term.^[17] Consequently, exploring alternative cathode materials with high catalytic activity and stability for pure CO_2 electrolysis is urgently desirable.

Recently, perovskite oxide exhibiting mixed oxygen ionic and electronic conductivities (MIEC) has attracted great interests due to their excellent redox stability and resistance to coking.^[11,18,19] Moreover, the structural characteristics of MIEC electrodes allow the active sites to expand to the entire electrode surface, greatly contributing to enhanced performance. Bidrawn et al. were the pioneers to introduce MIEC perovskite La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCrM) as a cathode for CO₂ electrolysis, demonstrating its catalytic activity on CO2 reduction reaction.^[16] Subsequently, researchers have further explored diverse modification strategies, including doping, impregnation, and composite electrode to improve the performance. For instance, Xie and coworkers discovered that the current density of La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_{3- δ} (LSCM) single cells for pure CO2 electrolysis was improved significantly from 0.30 to 0.66 A cm⁻² at 1.5 V and 800 °C by impregnating NiCu nanocatalysts onto LSCM cathode.^[20] Recent investigations have also highlighted A-site doped lanthanum orthoferrites $(La_{1-x}A_xFeO_{3-\delta})$ as exhibiting high catalytic activity and mixed ionic and electronic conductivities at reduced temperature. Compounds such $La_{0.3}Sr_{0.7}Fe_{0.7}Cr_{0.3}O_{3-\delta}$, La_{0.6}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-δ}, and as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ have been applied as cathode catalyst and demonstrated great stability for pure CO₂ electrolysis in SOECs without the addition of safe gas.^[21–23] Despite certain reported perovskite materials exhibiting improved current density and stability for pure CO₂ electrolysis when compared to the state-of-the-art Ni-YSZ cathode, their electrolysis performance remains insufficient for the commercial goals. As such, there remains a pressing need to develop superior cathode materials that can enable efficient pure CO₂ electrolysis.

Designing $La_{1-x}A_xFeO_{3-\delta}$ based perovskite materials as potential cathodes for high-temperature pure CO2 reduction proves to be challenging. The incorporation of divalent Sr to partially replace trivalent La has often been chosen to enhance catalyst performance by forming oxygen vacancies and/or oxidizing Fe to obtain the overall charge neutrality.^[24] However, the presence of Sr element introduces segregation issues on the electrode surface, especially when the Sr-based perovskite oxides are exposed in the acidic environment like CO2, leading to the formation of SrCO₃ and consequently severe performance degradation.^[25,26] It has been reported that introducing Ca into the Asite is more desirable than Sr doping in the perovskite because Ca has a smaller size compared with Sr, which can reduce the lattice parameters and enhance the lattice stability as the Ca-O bond is stronger than the Sr–O bond. $^{\left[27,28\right] }$ The use of Pr, with its ability to exhibit both 3+ and 4+ oxidation states, adds intriguing electrical properties when substituting La as a rare earth element. $^{\left[29\right]}$ Rojo and co-workers synthesized a series of nanosized $Pr_{1-x}\ Ca_xFe_{0.8}Ni_{0.2}O_{3-\delta}\ (0 < x < 0.9)$ materials by a single-step synthesis route. Their findings indicated that when the proportion of Ca is over 0.4, the material becomes a composite of perovskite and the brownmillerite-type structure $(Ca_2Fe_2O_5)$.^[30] They also found that the brownmillerite phase was beneficial in promoting the ionic conductivity and the composition $Pr_{0.4}Ca_{0.6}Fe_{0.8}Ni_{0.2}O_{3-\delta}$ displayed the best electrochemical performance under air. Recently, Rao group has reported that the nanostructured brownmillerite Ca₂Fe₂O₂ possesses good spontaneous CO2 capture ability due to the accommodation of abundant oxygen vacancy.^[31] Furthermore, it has been reported that the introduction of A-site deficiencies in perovskite structure can significantly improve the oxygen diffusivity and hence bolster

the catalytic activity. For example, an A-site deficient $(La_{0.5}Sr_{0.5})_{0.9}Fe_{0.9}Mn_{0.1}O_{3-\delta}$ cathode material shows 1.5 times higher current density than stoichiometric $La_{0.5}Sr_{0.5}Fe_{0.9}Mn_{0.1}O_{3-\delta}$ at 1.5 V and 800 °C due to the enhanced CO₂ adsorption ability.^[32]

Taking all these factors into consideration, in this work, dual-phase perovskite-brownmillerite structure featuring A-site deficient $(Pr_{0.4}Ca_{0.6})_xFe_{0.8}Ni_{0.2}O_{3-\delta}$ (named as PCFN, where x = 1, 0.95, and 0.9) materials were synthesized and applied as a fuel electrode for CO2-SOECs. The effects of A-site deficiency on the phase composition of PCFN and the electrochemical performance of the cells are studied in detail. It has been found that the high content calcium in PCFN can induce the formation of a third phase CaCO₃ after exposing the PCFN material in CO₂ atmosphere at elevated temperature. The electrochemical performance for CO₂ splitting is determined by the "synergistic action" of three phases of the perovskite, Ca2Fe2O5 brownmilleritephase, and CaCO3. In addition, it has been found that the surface kinetic of CO2 reduction is significantly improved on A-site deficient PCFN, resulting in higher CO₂ electrolysis performance.

2. Results and Discussion

2.1. Phase Structure and Morphology

The crystalline structures of the materials, both with or without A-site deficiency, were examined using the X-ray diffraction (XRD) analysis technique and the results are shown in Figure 1a. PCFN100 demonstrate a non-pure phase composition, consisting of two distinct crystalline phases: the primary perovskite-structured Pr(Ca)Fe(Ni)O₃ and the secondary brownmillerite-structured Ca2Fe2O5.This observation is consistent with the literature.^[30,33] There is no shift in peak positions and/or emergence of impurity peaks beyond the two main phases after the A-site is deficient, indicating that 5% and 10% A-site deficiencies do not trigger the change in the material's phases. To investigate the chemical stability of the three materials, the raw PCFN series materials underwent calcination under a CO2 atmosphere at 800 °C for 5 h. As shown in Figure 1b, one peak at around 28° corresponding to CaCO₃ can be found, indicating that the composite is not stable, and a third phase will co-exist in the CO₂ atmosphere under high temperatures. Significantly, the relative intensity of the CaCO₃ peak decreases with an increasing degree of the A-site deficiency, suggesting that the generated amount of CaCO3 varies and can be reduced through A-site deficiency. However, the CaCO₃ phase disappeared after calcining the composite again in air at 800 °C for 5 h, as shown in Figure 1c, indicating that the PCFN series composites possess self-recovery properties. To further elucidate the source of CaCO₃, a pure brownmillerite phase Ca₂Fe₂O₅ was synthesized and then treated with CO₂ atmosphere at 800 °C for 5 and 10 h, respectively. The corresponding XRD pattern profiles are presented in Figure 1d. No CaCO3 peaks are detected, implying that Ca₂Fe₂O₅ stays stable under a CO₂ atmosphere while the perovskite phase $Pr(Ca)Fe(Ni)O_3$ undergoes a reaction with CO_2 , resulting in the generation of CaCO₃. This observation is consistent with previous literature findings.^[26]

2.2. Electrochemical Performance Characterization

To evaluate the CO_2 electrolysis performance of PCFN cathodes, LSGM electrolyte supported button cells with a cell configuration of



Figure 1. a) XRD patterns of the as-prepared PCFN powder. b) XRD profiles of PCFN samples treated in pure CO_2 atmosphere at 800 °C for 5 h. c) XRD patterns of the PCFN100 powder were treated in CO_2 for 5 h and then treated in the air for 5 h again. d) XRD patterns of prepared and CO_2 -treated $Ca_2Fe_2O_5$ sample.

PCFN/LSGM/LSCF were fabricated and tested (Figure S1, Supporting Information). Figure 2a shows typical current-voltage (I-V) curves of the single cells with the three types of PCFN cathode at 800 °C for pure CO₂ electrolysis. The open-circuit voltage (OCV) of the three single cells is approximately 0.1 V at 800 °C, consistent with values reported in the literature.^[34,35] The electrolysis current density initially increases with the increase in the applied voltage but undergoes a decrease at the voltage range 0.25-0.35 V, and then a plateau is observed. When the applied voltage is over 0.8 V, the threshold voltage for electrolysis of pure CO₂,^[36] the current density increases again with the increase in the applied voltage. The CO₂ electrolysis performance is significantly improved by applying the A-site deficiency strategy for the PCFN cathode. At 1.5 V, the output current density of the PCFN95-based single cells is 1.76 A cm⁻², whereas PCFN100-based SOEC only generates around 1 A $\rm cm^{-2}$ under a similar testing condition. Remarkably, the electrocatalytic performance of PCFN100 is boosted by roughly 76% in PCFN95 with 5% of A-site deficiency. However, the CO2 reduction reaction performance decreases with further increase in the A-site deficiency. The change in electrochemical performance may be related to the relative content of each phase in the composite material, with the optimal performance achieved by the "synergistic effect" of the perovskite, brownmillerite, and CaCO3 phases. The 5% A-site deficient PCFN95 material displays the optimal three-phase content. Moreover, the pure CO₂ electrolysis performance of PCFN95 single cells is considerably higher than most of the previously developed CO₂-SOECs using different fuel electrodes under similar testing conditions (Table 1). The CO2 electrolysis performance of PCFN95-based SOECs at different temperatures was also evaluated and is presented in Figure S2a, Supporting Information. To further compare the electrochemical performance of the electrode materials before and after A-site deficiency, PCFN100 and PCFN95 three-electrode cells were performed to investigate the relationship of overpotential with applied current density. As shown in Figure S2b, Supporting Information, as the current densities increase, the overpotential also rises for both samples. Notably, the overpotential of the PCFN95 electrode is lower than that of the PCFN100 electrode at the same current density, indicative of lower activation losses. It can be seen that PCFN95 electrode has faster electrochemical reactions during CO₂ electrolysis. In addition, the electrolysis step test at different applied current densities of 0.1, 0.2, 0.3, and 0.4 A $\rm cm^{-2}$ at 800 °C was investigated for the single cells using PCFN95 cathode and the results are displayed in Figure 2b. The cell voltages remain stable during each stage, demonstrating repeatability after a single cycle, indicative of good short-term stability of the PCFN95 cathode.

As mentioned at the beginning of this section, the *I*–V curves of the single cells are "peculiar" at the voltage range OCV = 0.8 V, in which there was one inflection point at around 0.25 V for each *I*–V curve. This phenomenon has been reported in the literature, typically attributed to the impurity O₂ leakage or elemental reduction but with no detailed

characterization and analysis.^[36,44] In this study, cyclic voltammetry method and continuous linear scan voltammetry method employing different scanning rates were utilized to investigate this behavior more comprehensively. Firstly, a cyclic voltage from 0 to 1.6 V, followed by a returning scan from 1.6 to 0 V, was applied to the PCFN100 single cell and this procedure was repeated four times. The test results were shown in Figure 2c, and the obtained I-V curves are repeatable. This result can exclude the hypothesis about elemental reduction at low voltage. If it is caused by the element reduction at low applied voltage, such as Fe⁴⁺ to Fe³⁺, then this reaction should more easily happen at high voltage, meaning that the inflection point should become weaker and weaker at the second, third, and fourth cycles with the decrease of the concentration of Fe4+at the surface of the PCFN electrode. This contradicts the experimental results. Figure 2d shows the I-V curves at different scanning rates, ranging from 0.001 to 0.08 V s⁻¹. It can be found that the inflection point weakens as the scanning rate decreases, and it even disappears when the scanning rate falls below 0.01 V s^{-1} . Therefore, the scanning rate has a close relationship with the "peculiar" inflection point. Considering the possibility that this phenomenon is attributed to impurity oxygen, potentially originating from the testing setup such as a CO₂ source or sealing leakage, a plausible explanation may be that with a low applied voltage, impurity oxygen will undergo an electroreduction reaction and form O^{2-} , which is subsequently transported to the anode side through the LSGM electrolyte. The reaction rate is fast when the scanning rate is high, leading to a swift increase in current density. O2 in the testing setup will be consumed rapidly, causing the current density to



Figure 2. Electrochemical performance characterization. a) *I–V* curves of single cells with PCFN100, PCFN95, and PCFN90 cathodes at 800 °C under pure CO₂. b) Short-term pure CO₂ electrolysis of PCFN95 single cell at different applied current densities at 800 °C. c) Cyclic voltammetry test of PCFN100 single cell using 0.05 V s⁻¹ scan rate at 800 °C under a pure CO₂ atmosphere. d) Continuous linear scan voltammetry test of the PCFN100 single cell using different scanning rates at 800 °C.

subsequently decline until an equilibrium is reached. However, when the small scanning rate is applied, the electroreduction reaction for O_2 is slow and correspondingly, the current density will increase slowly until the equilibrium is reached. Therefore, the appearance of the inflection point is closely related to the impurity oxygen in the CO_2 electrolysis testing chamber. Fortunately, this issue can be mitigated by decreasing the scanning rate.

CO2 reduction by SOECs involves complex mass transport and electrochemical processes. To unravel the kinetic processes underlying CO₂ reduction, electrochemical impedance spectroscopy (EIS) was conducted on single cells with LSCF anode and different PCFN cathodes. Figure 3a shows the corresponding EIS plots of the single cells at 800 °C under open-circuit conditions. The ohmic resistance (R_{0}) is the intercept of the spectra with the real axis at the high frequency, predominately coming from the LSGM electrolyte, the contact resistances and lead wires. The distance between the low and high-frequency intercept with the real axis corresponds to the total polarization resistance (R_p) originating from both the cathode and anode. The polarization resistance is the critical parameter for evaluating the electrode catalytic activity, with lower R_p value indicating higher activity in electrochemical reactions. The R_0 values of the cells with different PCFN cathodes are nearly indistinguishable, while the Rp values were significantly reduced in A-site deficient samples. Rp decreases from 0.849 Ω cm² for single cells with PCFN100 cathode to 0.458 Ω cm² for single cells with PCFN95 cathode, suggesting that the catalytic activity of CO2-RR is significantly enhanced by the introduction of A-site deficiencies.

Since the total polarization resistance of the single cells is influenced by both PCFN fuel electrode and LSCF oxygen electrode, to better investigate the catalytic activity of the PCFN cathode affecting CO_2/CO conversion kinetics, symmetrical cells with the configuration of PCFN/LSGM/PCFN were prepared and measured using EIS in a pure CO_2 atmosphere. Figure 3b shows the Nyquist plots of PCFN symmetrical cells at different temperatures. The ohmic resistances were

Table 1. Performance comparison with literature works for pure CO_2 electrolysis at 1.5 V and 800 °C.

Cell configuration Cathode/ Electrolyte/Anode	Electrolyte thickness (μm)	Polarization resistance $(\Omega \text{ cm}^2)$ at OCV	Current density (A cm ⁻²) at 1.5 V	References
PSFM/LSGM/LSCF-SDC	220	_	0.71	[37]
LCFN-GDC/YSZ/LSCF-GDC	300	0.7	~0.8	[26]
LSF/LSGM/LSCF-SDC	240	1.31	0.76	[38]
LSCFN-GDC/YSZ/LSCFN-GDC	200	0.683	0.442	[39]
LSTMC/LSGM/LSM	350	0.311	1.24	[40]
SFMM-SDC/LSGM/SFMM-SDC	400	0.58	1.35	[41]
LSFT/LSGM/LSCF-GDC	_	_	1.11	[42]
SFM-YSZ/YSZ/LSM-YSZ	10	0.41	1.10	[43]
PCFN100/LSGM/LSCF	300	0.849	1.00	This work
PCFN90/LSGM/LSCF	300	0.689	1.61	This work
PCFN95/LSGM/LSCF	300	0.458	1.76	This work

 $\mathsf{PSFM}, \ \mathsf{Pr}_{0.4}\mathsf{Sr}_{0.6}\mathsf{Fe}_{0.875}\mathsf{Mo}_{0.125}\mathsf{O}_{3-\delta'}, \ \mathsf{LSFN}, \ \mathsf{La}_{0.6}\mathsf{Sr}_{0.4}\mathsf{Fe}_{0.8}\mathsf{N}_{0.2}\mathsf{O}_{3-\delta'}, \ \mathsf{GDC}, \ \mathsf{Ce}_{0.8}\mathsf{Sm}_{0.2}\mathsf{O}_{2-\delta'}, \ \mathsf{LSF}, \ \mathsf{La}_{0.8}\mathsf{Sr}_{0.2}\mathsf{Fe}_{0.3-\delta'}, \ \mathsf{SDC}: \ \mathsf{Ce}_{0.8}\mathsf{Sm}_{0.2}\mathsf{O}_{2-\delta'}, \ \mathsf{LSFN}, \ \mathsf{La}_{0.4}\mathsf{Sr}_{0.6}\mathsf{Co}_{0.2}\mathsf{Fe}_{0.7}\mathsf{Nb}_{0.1}\mathsf{O}_{3-\delta'}, \ \mathsf{LSTMC}, \ (\mathsf{La}_{0.2}\mathsf{Sr}_{0.3}\mathsf{Sm}_{0.3-\delta'}, \mathsf{LSFN}, \ \mathsf{La}_{0.4}\mathsf{Sr}_{0.6}\mathsf{Co}_{0.2}\mathsf{Fe}_{0.7}\mathsf{Nb}_{0.1}\mathsf{O}_{3-\delta'}, \ \mathsf{LSTMC}, \ \mathsf{La}_{0.4}\mathsf{Sr}_{0.6}\mathsf{Co}_{0.2}\mathsf{Fe}_{0.7}\mathsf{Nb}_{0.1}\mathsf{O}_{3-\delta'}, \ \mathsf{LSTMC}, \ \mathsf{La}_{0.4}\mathsf{Sr}_{0.5}\mathsf{O}_{0-\delta'}, \ \mathsf{LSTMC}, \ \mathsf{LST$



Figure 3. Electrochemical performance comparison of PCFN100, PCFN95, and PCFN90 materials. a) Impedance spectra of the three types of PCFN single cells under pure CO₂ at 800 °C and open-circuit voltage condition. b) Impedance spectra of PCFN100, PCFN95, and PCFN90 symmetrical cells under pure CO₂ at different temperatures. c) Corresponding DRT curves of the EIS plots at 800 °C in (b). d) The activation energy for the CO₂ reduction reaction of the three PCFN cathodes.

subtracted, and the first intercept with the real axis was normalized from zero to enable direct comparison of the R_p values. As expected, the R_p values of PCFN95 and PCFN90 symmetrical cells were obviously reduced compared to PCFN100 symmetrical cells at different temperatures. However, the overlapping polarization impedance arcs made it challenging to differentiate the impacts of various substeps. To address this, the distribution of relaxation time (DRT) technique was employed to analyze the Nyquist plots and isolate multiple time constants. Figure 3c presents the corresponding DRT analysis outcomes of the three symmetrical cells at 800 °C. Three response peaks can be obtained for all curves from high to low frequencies, identified as HF (high-frequency, 1-4 kHz), IF (intermediate-frequency, 10-400 Hz), and LF (low-frequency, 0.5-5 Hz), indicating three different sub-steps taking place on the electrode. As can be seen, the area of HF peaks is similar and relatively small for the cells with different electrodes, suggesting that HF peak is most likely attributed to the oxygen ion transportation process at the electrode-electrolyte interface.^[17] While the IF and LF peaks are related to the electrochemical surface reaction processes, based on the Alder-Lane-Steele model and previous studies,^[21,45,46] the intermediate-frequency peak may correspond to the charge transfer and oxygen exchange kinetics at the gas-solid interface and the low-frequency peak can be assigned to the gas activation conversion of CO_2 –CO.^[47] By comparing the area of each peak for the individual cell, it is easy to notice that the LF peak contributes the most to the total resistance, indicating that the CO₂ reduction reaction kinetics was rate-limited by the sub-step of LF, such as CO₂ adsorption. The DRT results conducted at other operating temperatures (Figure S3, Supporting Information) corroborate this finding as well, with the LF peak

predominating in the total Rp at each temperature. The smaller area of LF and IF peaks for PCFN95 and PCFN90 electrodes demonstrates that the electrode surface kinetics was enhanced by A-site deficiencies, leading to an improvement of electrolysis performance. This change may relate to the formation of CaCO₃ phase: excessive CaCO3 deposited on the perovskite surface not only occupies the active sites but also hinders the charge transfer, similar to the effects of SrCO3 formation.^[48] PCFN95 and PCFN90 electrodes generate smaller amounts of CaCO₃ than PCFN100 electrode in a CO₂ environment; this may be the reason why the area of LF and IF peaks for PCFN95 and PCFN90 is lower. Figure 3d shows the Arrhenius plots of overall Rp as a function of temperature the different symmetrical cells in pure CO₂.^[49] The activation energies of PCFN100, PCFN95, and PCFN90 are 1.37, 1.28, and 1.34 eV, respectively. The smaller activation energy of PCFN95 indicates higher electrochemical activity toward CO2 reduction reaction in an equilibrium state at lower temperatures.

2.3. Physicochemical Properties

Carbon dioxide adsorption capability of the cathode materials plays a critical role for CO_2 -RR in SOECs at elevated temperatures.^[40,50]

To find out the reasons for the enhancement of CO₂ electrolysis performance by A-site deficiencies, the CO2 adsorption characteristics on PCFN series powder were measured by TG and CO₂-TPD. A comparative assessment of TG was conducted for PCFN series powder samples under air-CO2-air exchange gases. The obtained TGA profiles were shown in Figure 4a. As it can be seen, the CO₂ capacities of 3.03%, 1.81%, and 0.68% were achieved using PCFN100, PCFN95, and PCFN90, respectively, indicating that PCFN100 has the highest CO₂ adsorption capacity, but it will be reduced by A-site deficiency. It has to be noted that all three samples recovered immediately after the CO₂ gas was turned off, implying that the weight increase in CO2/N2 mixture gas is mainly coming from chemical adsorption. CO2-TPD behaviors of the three samples were further measured to compare the CO₂ adsorption ability. Figure 4b presents the TPD curves in the CO₂ atmosphere from room temperature to 900 °C. Generally, the peaks at high temperatures (over 200 °C) are caused by strong chemical desorption behavior and could be ascribed to the bidentate or bridged carbonates desorption peaks, which are the decomposition products of surface carbonates.^[51] The intensity of the desorption peak of PCFN90 and PCFN95 increased compared to that of PCFN100, suggesting that A-site deficient samples have better CO₂ desorption capacity. Significantly, the peak of PCFN95 shifts to a higher temperature, 698 °C, indicating enhanced bonding of the adsorbed CO2. It looks contradictory when combining the results of CO2-TGA and CO2-TPD together. A possible reason lies in the production of CaCO3. For most perovskite materials, A-site is occupied by the alkaline earth elements and the basic A-O layer is stronger than the B-O layer, which will make the A-O layer lower surface



Figure 4. a) Thermogravimetric analysis curves of PCFN100, PCFN95, and PCFN90 samples. b) Temperature-programmed desorption profiles for CO_2 on the surface of PCFN100, PCFN95, and PCFN90 powders.



Figure 5. High-resolution XPS spectra of Ca2p peaks. (left) As-prepared samples, (right) CO_2 -treated samples.

energy and more easily exposed.^[48] When exposing the PCFN100 sample in a CO2 atmosphere, part of the Ca-O layer may react with CO2, forming CaCO3, and the amount of produced CaCO3 will decrease with the reduction of the Ca-O layer. This is the reason of why the trend CO_2 adsorption capacity is PCFN100 > PCFN95 > PCFN90 and this trend is consistent with the XRD results shown in Figure 1b (the intensity of CaCO₃ peak decreases with the increase of A-site deficiency). However, after combining CO₂-TPD information, a conclusion can be drawn that this type of adsorption by forming CaCO₃ maybe not an effective adsorption for CO2-RR. Because most of the formed CaCO3 is stable and the carbonate species $\text{CO}_2^{\delta-}$ cannot be rapidly reduced to the gaseous CO under cathodic overpotential. Unfortunately, the generated stable CaCO₃ may accumulate and cover the active sites of the catalysts. Therefore, the A-site deficient PCFN95 and PCFN90 electrodes present better CO2-RR performance than the PCFN100 electrode.

The electronic structure of the catalysts plays a critical role in CO₂RR kinetics. X-ray photoelectron spectroscopy (XPS) was conducted to characterize the near-surface region of asprepared and CO2-treated PCFN series samples to determine the chemical environment of surface elements. Figure 5 shows the highresolution Ca2p spectra to analyze the chemical environment and the surface compositions of the as-prepared (left) and CO₂-treated (right) PCFN samples. For the as-prepared materials, the P1 peak of Ca2p1/2 at around 350.5 eV binding energy and the P3 peak of $Ca2p_{3/2}$ at around 346.9 eV binding energy can be assigned to the perovskite Ca.^[52] The brownmillerite Ca corresponds to the P2 peak and P4 peak, whose binding energy is about 348.9 eV for $Ca2p_{1/2}$ and 345.5 eV for $Ca2p_{3/2}$, respectively.^[53] After the treatment in CO₂, a small portion of the perovskite Ca would react with CO₂ to form CaCO₃, whose binding energy for the Ca element is close to the perovskite Ca. Therefore, the P1 and P3 peaks of the CO2-treated materials also contain Ca in CaCO₃.^[54] The detailed parameters for the deconvolution of Ca2p spectra are displayed in Table S1, Supporting Information. To compare the relative amount of the perovskite phase, brownmillerite phase, and CaCO3 phase, the ratios of the relative area of (P1 + P3)/(P2 + P4) were calculated and are summarized in Table 2. Firstly, it can be found that the relative content of brownmillerite Ca₂Fe₂O₅ reduced with the increase of A-site deficiency. After the CO₂ treatment, the relative content of P1 and P3 peaks increased markedly, and correspondingly, the percentage of (P2 + P4)decreased. It can be noted that PCFN95 has the smallest change (5.59%) in the amount of the brownmillerite phase compared to PCFN100 (16.41%) and PCFN90 (8.5%), indicating that PCFN95 has a more stable surface structure than PCFN100 and PCFN90.

XPS characterization methods were also performed on the O1s spectra, as shown in Figure 6 and Table S1, Supporting Information. There exist two fitting peaks, indicating the presence of two types of oxygen species. The peak at approximately 528.7 eV corresponds to lowenergy lattice oxygen (O_L) and the other peak at around 531.2 eV can be assigned to high-energy adsorbed oxygen species (O_A) such as O^{2-} and carbonates, etc.^[55] All three as-prepared samples have abundant adsorbed oxygen, which is favorable for CO₂-RR. However, an interesting phenomenon appeared after treating the three samples under a CO₂ atmosphere. As depicted in Table 3, the adsorbed oxygen species of CO2-treated PCFN100 increased by 5.18%, in contrast, the OA of PCFN90 decreased by 5.66%. PCFN95 has the smallest change, which is consistent with the above result of Ca2p. The ratio of adsorbed oxygen of PCFN95 is close to the data in the literature,^[33] which claims a better electrochemical performance. Although PCFN100 presents the greatest amount of adsorbed oxygen species, it may be caused by an

Table 2. Comparison of Ca 2p XPS peak deconvolution results before and after the treatment of CO_2 .

	Ratio of (P1 + P3):(P2 + P4)	Change in the percentage of (P2 $+$ P4) after CO ₂ treatment
PCFN100	57.79%: 42.21%	16.41%↓
PCFN100-CO ₂	74.20%: 25.80%	
PCFN95	59.64%: 40.36%	5.59%↓
PCFN95-CO ₂	65.23%: 34.77%	
PCFN90	63.23%: 36.77%	8.5%↓
PCFN90-CO ₂	71.73%: 28.27%	

excess of calcium carbonate, which would cover the active site of the electrocatalyst and have an adverse effect on the CO_2 –RR performance. Although the A-site deficiency method can reduce the formation of CaCO₃, excessive A-site deficiency will lead to a large reduction of adsorbed oxygen, such as for PCFN90. This may explain why PCFN95 shows the best CO₂ electrolysis performance among the three materials studied.

2.4. Durability for Direct CO₂ Electrolysis

To evaluate the long-term stability of the electrolysis cells with different PCFN electrodes, a constant current of 500 mA cm⁻² was carried out, and the cell voltage was monitored as a function of time. As shown in **Figure 7**a, at 800 °C, the cell voltage of PCFN100 single cells rapidly increased during the operation, indicating a serious degradation of CO_2 electrolysis performance. While for the A-site deficient PCFN95 and PCFN90 single cells, the durability for CO_2 electrolysis was greatly enhanced, and the performance of single cells with PCFN95 cathode is fairly stable. Figure 7b shows the cross-sectional SEM image of the PCFN95 single cell after the stability test; no obvious delamination is



Figure 6. High-resolution XPS spectra of O1s peaks. (left) As-prepared samples, (right) CO_2 -treated samples.

observed between the LSGM electrolyte and PCFN95 electrode, indicative of excellent thermal matching performances of PCFN95 electrode with LSGM electrolyte at high operating temperatures.

3. Conclusion

In summary, A-site deficient dual-phase composites PCFN95 were successfully synthesized and studied as the fuel electrode for direct CO₂ electrolysis in SOECs. Physicochemical characterization has revealed that A-site deficiency can mitigate formation of CaCO3 on the perovskite surface, consequently enhancing the CO₂ electrolysis performance. PCFN95 has achieved a favorable balance of perovskite, brownmillerite and CaCO₃ three phases under a high-temperature CO₂ environment, resulting in the improvement of effective CO₂ adsorption, as well as the promoted electrode surface kinetics. LSGM electrolyte-supported single cell with PCFN95 cathode achieved high CO2-RR performance with a cell current density of 1.76 A at 1.5 V and 800 °C, which is 76% higher than that of SOEC with non-deficient PCFN100 cathode under similar testing conditions. Single cells with PCFN95 cathode also show good stability for direct CO2 electrolysis. The underlying mechanism of the relationship between the performance variation and the composition content of each phase needs to be further studied in the future.

4. Experimental Section

Material synthesis: The $(Pr_{0.4}Ca_{0.6})_xFe_{0.8}Ni_{0.2}O_{3-\delta}$ (where x = 1, 0.95, and 0.9, denoted as PCFN100, PCFN95, and PCFN90, respectively) powders were synthesized by a combustion method.^[46] Stoichiometric amounts of $Pr(NO_3)_3$ ·GH₂O (purity 99.9%), Ca $(NO_3)_2$ ·4H₂O (purity 99.0%), Fe $(NO_3)_3$ ·9H₂O (purity 99.95%), and Ni $(NO_3)_2$ ·6H₂O (purity 99.9%) were dissolved in deionized water first. Next, citric acid (purity 99%) and glycine (purity 99%) at a molar ratio of 1:1.5:2 for total metal ions/citric acid/glycine were added to the solution acting as chelating agents and combustion agents. The mixed solution was stirred using a magnetic bar at 200 °C on a hot plate for about 2 h to form a gel and then heated at

500 °C for about 10 min where the gel spontaneously burned to generate the precursor powders. The target materials were obtained after calcining the precursor powders at 1000 °C for 5 h under an air atmosphere. Ca₂Fe₂O₅ powder was synthesized using the same method. La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3- $\delta}$ (LSGM) electrolyte powder and (La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3- $\delta}$} (LSCF) anode powder were purchased from Fuel Cell Materials, USA.}

Material characterization: The crystallographic structure of the synthesized powders was investigated by powder X-ray diffraction (PXRD, Rigaku MiniFlex II) with Cu Ka radiation at room temperature. The diffraction patterns were collected with a scan rate of 2° min⁻¹ and a step size of 0.02° in the range of 20-80°. The microstructure and morphology of the PCFN powder were examined using scanning electron microscopy (SEM, Zeiss Gemini500 FESEM). The microstructure of the single cells was also characterized by SEM. XPS (PHI VersaProbe III) was applied to characterize the chemical environment of surface elements of the samples. CO2 desorption behavior and capability were examined by temperatureprogrammed desorption of CO2 (CO2-TPD) (Micromeritics, AutoChem II). The detailed experimental conditions can be referred to a previous work.[46] Thermogravimetric analysis (TGA, NETZSCH STA 449

Table 3. Comparison of O1s XPS peak deconvolution results before and after the treatment of CO_2 .

	Ratio of O _A :O _L	Change in the percentage of O _A after CO ₂ treatment
PCFN100	69.52%: 30.48%	5.18%↑
PCFN100-CO ₂	74.70%: 25.30%	
PCFN95	67.71%: 32.29%	0.48%↓
PCFN95-CO ₂	67.23%: 32.77%	
PCFN90	66.49%: 33.52%	5.66%↓
PCFN90-CO ₂	60.83%: 39.17%	





F3) was performed to evaluate the adsorbed CO₂ content of PCFN series samples. 25 mg of PCFN powder was placed on an alumina sample holder and then heated from room temperature to 800 °C at a ramping rate of 10 °C min⁻¹ in an air/N₂ mixture. When the temperature reached 800 °C, the sample was kept at 800 °C for 2 h in air/N₂. Subsequently, the gas was switched to CO_2/N_2 , and the sample was kept at 800 °C for 3 h under CO_2/N_2 . Finally, the gas was switched back to air/N₂, and the sample was kept at 800 °C for 2 h in air/N₂. For testing the electrical conductivity of the different PCFN materials, the PCFN powders were uniaxially pressed in a rectangular mold under 300 MPa and the samples were sintered at 1250 °C for 5 h.

Cell fabrication: CO_2 electrolysis performance with PCFN series material as cathode was evaluated by LSGM electrolyte-supported single cells, with the cell configuration of PCFN/LSGM/LSCF, where LSCF was used as the air electrode. LSGM electrolyte substrates were prepared by uniaxially dry-pressing LSGM powder under 200 MPa for about 1 min to form green pellets, followed by

sintering at 1450 °C in the air for 10 h to obtain dense electrolyte pellets with a thickness of approximately 300 μ m. The PCFN and LSCF electrode slurries were prepared by dispersing the corresponding powder in ethanol with high-energy ball milling for 15 min. The slurry was then mixed with Heraeus binder V006 at a weight ratio of 1:1.5 and transformed into a thick slurry by using a planetary centrifugal mixer (Thinky mixer ARE-310). PCFN cathode slurry and LSCF anode slurry were subsequently brush-painted onto the two sides of the LSGM pellet, followed by calcinating at 1000 °C for 2 h to form a single cell with a 0.33 cm² active area. For the fabrication of symmetrical cells, both sides of the LSGM electrolyte were painted with PCFN slurry, and the active area was kept the same as that of the single cells. A thicker LSGM electrolyte (around 1 mm) was used to prepare three-electrode cells. Both sides of the LSGM electrolyte were brushed with PCFN electrode slurry as the working and counter electrode, and the edge of the electrolyte was brushed with Au paste as the reference electrode.

Electrochemical performance measurements: Single cells were measured in a homemade cell-testing setup with pure CO_2 fed into the cathode while the anode was exposed to atmosphere air. Firstly, the gold paste was brushed onto the surface of the cathode and anode as the current collector with silver wire as the lead wire. Then sealing the single cell onto the alumina tube using a conductive paste (DAD-87, Shanghai Research Institute of Synthetic Resins, China) and heat-treated at 200 °C for 2 h to dry the conductive paste. Subsequently, a layer of ceramic adhesive (552-1105, Aremco, USA) was applied to the periphery of the attached cells to ensure sealing. Pure CO2 was supplied into the fuel electrode side with a flow rate of 30 mL min $^{-1}$, and the LSCF air electrode side was exposed to the ambient air. The electrochemical performance of the single cells was tested using a Versa STAT MC electrochemical workstation. The current-voltage relationship (I-V curves) was obtained by performing linear sweep voltammetry from 0 to 1.6 V with a step change of 50 mV. EIS spectra were measured at an OCV with a frequency ranging from 1 MHz to 0.01 Hz and an AC amplitude of 10 mV. The durability of the single cell was examined using a galvanostatic with a constant current density of 500 mA cm⁻² at 800 °C.

Symmetrical cells were placed in a pure CO₂ atmosphere and tested at 650–800 °C by electrochemical impedance spectra with a signal amplitude of 10 mV in the frequency range of 1 MHz–0.01 Hz to check the interfacial polarization resistance of the electrode. The corresponding DRT analysis was performed using DRT tools.^[S657]

Three-electrode cells were used to evaluate the overpotential of the electrode materials. ElS measurement concerning the CO_2 reduction reaction was executed in a pure CO_2 environment at 800 °C, with different DC currents applied. The electrode overpotential (?) can be calculated by integrating the obtained polarization resistance over current densities. The details about this measurement can be referred to Zhang et al. and Jin and Huang.^[58,59]

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Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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A-site deficiency, cathode material, CO_2 adsorption, direct CO_2 electrolysis, solid oxide electrolysis cells

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