Conversion of methane to ethylene with high yield remains a fundamental challenge due to the low ethylene selectivity, severe carbon deposition and instability of catalysts. Here we demonstrate a conceptually different process of in situ electrochemical oxidation of methane to ethylene in a solid oxide electrolyzer under ambient pressure at 850 °C. The porous electrode scaffold with an in situ-grown metal/oxide interface enhances coking resistance and catalyst stability at high temperatures. The highest C₂ product selectivity of 81.2% together with the highest C₂ product concentration of 16.7% in output gas (12.1% ethylene and 4.6% ethane) is achieved while the methane conversion reaches as high as 41% in the initial pass. This strategy provides an optimal performance with no obvious degradation being observed after 100 h of high temperature operation and 10 redox cycles, suggesting a reliable electrochemical process for conversion of methane into valuable chemicals.
Conversion of natural gas, mainly CH₄, into transportable fuels and chemicals has been largely driven for several decades by emerging industrial trends, including the rising demand for H₂ to upgrade lower-quality oils and a global shortage of aromatics caused by shifting refinery targets toward gasoline⁶. Light olefins, mainly C₂H₄, as key chemical feedstocks and building blocks, are currently produced through multistage processes from syngas to methanol and then to olefins, although there is some ongoing research of direct conversion of syngas to olefins. This syngas-to-olefin route is dominant in current and near-term industry production⁷⁻⁸; however, the carbon-atom efficiency is normally below 50% in addition to the significant amount of CO₂ emission. This mainly arises since the removal of oxygen in carbon monoxide consumes hydrogen and generates water.

Direct conversion of CH₄ to C₂H₄ is potentially more economically and environmentally friendly, but it is a more challenging route. CH₄ is a small and stable molecule that exists in nature, and it has strong C–H bonds, negligible electron affinity, large ionization energy, and low polarizability. The direct-oxidation route can be realized through either oxidative coupling or direct nonoxidative conversion in a heterogeneous catalysis process⁹. It is effective to activate the C–H bond of CH₄ with oxygen to generate C₂H₄; however, over-oxidation of CH₄ remains unavoidable, leading to lower carbon atom efficiency. Furthermore, the low CH₄ conversion with low selectivity of C₂H₄ is another huge challenge⁹,¹⁰. Nonoxidative conversion is a process of dehydrogenation of highly stable CH₄ together with selective C–C coupling, and a recent work has represented the highest methane conversion (48.1%) and ethylene selectivity (48.4%) at 1090 °C.⁸ In terms of reaction mechanism, the cleavage of a C–H bond with oxygen to generate C₂H₄ involves the key step of the first cleavage of C–H bonding in CH₄ and then the selective coupling of C–C bonding for C₂H₄ generation through a gaseous electrochemical process in the porous anode. The electrochemical pumping of O²⁻ ions from the cathode to the anode is indeed a process of generating active oxygen species for CH₄ activation and oxidation in the presence of suitable catalysts. Electrochemical oxidation of CH₄ with O²⁻ ions is also a charge-rebalancing process while the transformation of O²⁻ ions to the active interfaces in the anode would involve different types of oxygen species including O²⁻ and O⁻ ions to initiate the CH₄ oxidation process¹³⁻¹⁹. Active metal–oxide interfaces at nanoscale would be ideal to accommodate these oxygen species especially in the form of O⁻ ions. These active oxygen species are one kind of the key active radicals at the confined metal–oxide interfaces to activate CH₄ while the electrochemical pumping of O²⁻ ions would continuously oxidize CH₄ in conjunction with gaseous selective coupling to generate C₂H₄ in the presence of suitable interface catalysis. Electrochemical pumping of active oxygen species to the porous anode would facilitate the oxidative removal of deposited carbon on the electrode scaffold and therefore enhance the coking resistance during the CH₄ cracking process. The applied potentials would split the oxygen-containing molecules such as gaseous O₂, H₂O, or CO₂ in the cathode to generate O²⁻ and simultaneously transport them to the anode. This feature provides the unique advantage of directly electrolyzing H₂O or CO₂ to H₂ or CO to generate oxygen species in conjunction with selective oxidation of CH₄ to C₂H₄ in the anode.

The incorporation of metal nanoparticles on oxide scaffold has been widely proven to be quite effective to enhance catalytic conversion of CH₄ to C₂H₄ and the typical metal nanocatalysts, such as iron nanoparticles are normally considered to be suitable to construct metal–oxide interfaces with strong interactions to facilitate the catalysis conversion²⁰⁻²¹. These metal–oxide interfaces are usually prepared by directly loading metal nanoparticles on porous substrates through an impregnation method. However, long-term stability of metallic nanoparticles simply loaded on oxide surface remains a major challenge. The severe agglomeration and sintering of these nanoparticles lead to catalysts performance degradation especially at high temperature. An alternative method is to dope the iron element in the host lattice of oxide scaffold during the catalyst synthesis in air and then in situ grow the metallic nanoparticles on oxide...
surface through a phase decomposition process under reducing conditions\textsuperscript{19,13,22–23}. The metal nanoparticles directly embedded on porous oxide backbones particularly exhibit enhanced high-temperature stability and coking resistance, which may be due to the strong metal–oxide interactions at the unique interface architectures at nanoscale. Strong interface interactions are also highly favorable for the transfer of oxygen species especially in the form of oxygen ions in this work. These active oxygen species are expected to in situ electrochemically activate and oxidize CH\textsubscript{4}, and even remove the deposited carbon if present at metal–oxide interfaces in the cathode.

Here, we utilize redox-reversible layered perovskite Sr\textsubscript{2}Fe\textsubscript{1.5}\textsubscript{−}\textit{δ}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}} (SFMO) anode to electrochemically oxidize CH\textsubscript{4} to C\textsubscript{2}H\textsubscript{4} in an oxide-ion-conducting solid oxide electrolyzer. Ceramic SFMO is a mixed conductor with rich oxygen vacancies and we have already shown its excellent activity and coking resistance toward CH\textsubscript{4} oxidation\textsuperscript{25–27}. We firstly in situ construct metal–oxide interfaces at nanoscale on porous SFMO scaffold by synergistic control of nonstoichiometry and doping of Sr\textsubscript{2}Fe\textsubscript{1.5+\textit{x}}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}} (\textit{x} = 0–0.1). We then tailor the amount of excess iron to grow iron nanoparticles with different metal nanoparticle distribution on the SFMO scaffold through a phase decomposition process in reducing atmospheres. We then investigate the electrochemical pumping of oxygen species from air in the cathode to the anode for the selective electro–oxidation of CH\textsubscript{4} to C\textsubscript{2}H\textsubscript{4}. We finally study the electrochemical oxidation of CH\textsubscript{4} to chemicals in the anode in conjunction with electrolysis of CO\textsubscript{2} to CO in the cathode.

**Results**

**Growth of exsolved interfaces.** Figure 2\textsuperscript{a} shows the X-ray diffraction (XRD) patterns of the oxidized Sr\textsubscript{2}Fe\textsubscript{1.5}\textsubscript{−}\textit{δ}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}} (\textit{x} = 0–0.1) samples while the excess iron element is doped into the oxide lattice to form a series of homogeneous solid solutions. The chemical formulas of Sr\textsubscript{2}Fe\textsubscript{1.5}\textsubscript{−}\textit{δ}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}}, Sr\textsubscript{2}Fe\textsubscript{1.5}\textsubscript{−}\textit{δ}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}}, Sr\textsubscript{2}Fe\textsubscript{1.5}\textsubscript{−}\textit{δ}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}}, Sr\textsubscript{2}Fe\textsubscript{1.5}\textsubscript{−}\textit{δ}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}}, and Sr\textsubscript{2}Fe\textsubscript{1.5}\textsubscript{−}\textit{δ}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}} are denoted as SFMO, 0.025Fe–SFMO, 0.050Fe–SFMO, 0.075Fe–SFMO, and 0.100Fe–SFMO, respectively. The presence of excess iron in the host oxide lattice would result in metallic iron nanoparticles on the SFMO scaffold after reduction, producing the electrochemically active metal–oxide interfaces through a phase decomposition process. The iron in the host lattice is mainly present in the form of Fe\textsuperscript{3+}/Fe\textsuperscript{4+} oxidation state as shown in the X-ray photoelectron spectroscopy (XPS) in Supplementary Fig. 1. The oxidized sample has a porous microstructure with clean scaffold surface as shown in Supplementary Fig. 2, and the lattice spacing of 0.288 nm in the transmission electron microscopy (TEM) is in accordance with (002) plane. Figure 2\textsuperscript{b} shows the XRD of Sr\textsubscript{2}Fe\textsubscript{1.5}\textsubscript{−}\textit{δ}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}} (\textit{x} = 0–0.1) after reduction, confirming the presence of metallic iron phase that arises from the exsolution of excess iron dopant in the oxide lattice upon reduction. We further determine the oxygen nonstoichiometry of Sr\textsubscript{2}Fe\textsubscript{1.5}\textsubscript{−}\textit{δ}Mo\textsubscript{0.5}O\textsubscript{6−\textit{δ}} (\textit{x} = 0–0.1) before and after reduction using iodometric titration and summarize the results in Supplementary Table 1. For the SFMO sample, the oxygen storage capacity is 0.2465 mol after reduction, indicating that the reversible oxygen loss may be mainly from the valence change of Fe/Mo in the lattice, while no iron nanoparticle exsolution is observed in this process. After reduction, the excess iron (\textit{x} = 0.025–0.1) has been transformed into metallic iron nanoparticles while the left iron remains unchanged in a fully oxidized state. The exsolution of iron nanoparticles further leads to oxygen loss which shows a strong dependence of oxygen nonstoichiometry on the exsolution of iron metal as shown in Supplementary Table 1, which again validates the exsolution of up to 95–100% excess iron from the oxide lattice through a phase decomposition process during reduction. Figure 2\textsuperscript{c} shows the uniform metallic iron...
nanoparticles with diameters of ~25 nm anchoring on the SFMO oxide surface after reduction in hydrogen atmosphere, which confirms the in situ growth of metal–oxide interfaces through a phase decomposition process. Figure 2d shows the in situ grown metal–oxide interfaces with the iron nanoparticles deeply embedded on the SFMO substrate, which demonstrates a clear heterojunction interface that is anticipated to produce strong interfacial interaction. At high temperature, the strong interfacial interactions at nanoscale would provide enhanced thermal stability against nanoparticle agglomerations and carbon deposition from CH$_4$ pyrolysis.

SOEs with porous SFMO anodes are constructed while the cell microstructures are shown in Supplementary Fig. 3. We use La$_{0.9}$Sr$_{0.1}$Ga$_{0.3}$Mg$_{0.7}$O$_{3-δ}$ (LSGM) electrolyte with dimension of 1 mm in thickness and 20 mm in diameter. LSGM is an excellent oxygen-ion-conducting electrolyte with high ionic conductivity at intermediate to high temperatures and we conduct CH$_4$ oxidation at 850 °C to enhance the C$_2$H$_4$ yield. The electrochemical oxidation of CH$_4$ in the anode is conducted in conjunction with O$_2$ electrolysis from air in the cathode at 850 °C. The CH$_4$/O$_2$ fuel cell mode is a mode of electrochemical oxidation of CH$_4$ with O$_2$ gas toward CO$_2$ generation driven by the oxygen gradient across the electrode polarization resistance is as low as ~0.4 Ω cm$^2$ for the different anodes at the applied voltages of 1.6 V, indicating the significantly enhanced electrode process at higher applied voltages. Figure 3b shows the short-term operation of CH$_4$ oxidation at different voltages, which again confirms the significantly enhanced electrochemical process with metal–oxide interfaces in the anodes. Figure 3c summarizes the electrode polarizations of the electrochemical oxidation of CH$_4$ with different cathodes at 1.2–1.6 V at 850 °C. It is observed that the reduction of electrode polarization resistances strongly depends on the growth of metal–oxide interfaces in the electrode while higher applied voltage facilitates the electrochemical process and therefore enhances the electrode reaction kinetics. It should be noted that the overall electrode activity is enhanced with the growth of metal–oxide interfaces; however, more attentions need to be paid to the conversion of CH$_4$ to C$_2$H$_4$ with less over-oxidation of CH$_4$ to CO$_2$ in the porous anodes.

Methane conversion at interfaces. The properties of CH$_4$ explain the exceptionally high molecule stability which therefore leads to the difficulties of CH$_4$ activation and conversion. A limitation with most existing heterogeneous catalysts is that the initial C–H bond cleavage is the rate controlling step. It is widely accepted that the oxidation reaction of CH$_4$ to C$_2$H$_4$ is usually initiated on the surface of solid catalyst by reacting CH$_4$ with surface oxygen

![Figure 3](https://example.com/figure3.png)

**Figure 3** Electrochemical oxidation of CH$_4$ at the anode in conjunction with O$_2$ electrolysis. **a** The current density-voltage (I–V) relationship clearly reveals the superior performance with up to 100% enhancement of the SFMO cathodes with nanoscale metal–oxide interfaces in comparison to the bare cathode. The optimal chemical composition of the anode is found to be 0.075Fe–SFMO. The growth of metal–oxide interfaces drastically improves the current densities to ~1 A cm$^{-2}$ at 1.6 V with the presence of optimum length of metal–oxide interfaces in the porous SFMO scaffolds. Supplementary Fig. 5 shows that the electrode polarization resistance is as low as ~0.4 Ω cm$^2$ for the different anodes at the applied voltages of 1.6 V, indicating the significantly enhanced electrode process at higher applied voltages. Figure 3b shows the short-term operation of CH$_4$ oxidation at different voltages, which again confirms the significantly enhanced electrochemical process with metal–oxide interfaces in the anodes. Figure 3c summarizes the electrode polarizations of the electrochemical oxidation of CH$_4$ with different cathodes at 1.2–1.6 V at 850 °C. It is observed that the reduction of electrode polarization resistances strongly depends on the growth of metal–oxide interfaces in the electrode while higher applied voltage facilitates the electrochemical process and therefore enhances the electrode reaction kinetics. It should be noted that the overall electrode activity is enhanced with the growth of metal–oxide interfaces; however, more attentions need to be paid to the conversion of CH$_4$ to C$_2$H$_4$ with less over-oxidation of CH$_4$ to CO$_2$ in the porous anodes.
species to form methyl radicals with the first C–H bond cleavage, and then it continues in a gas-phase coupling step involving the coupling of methyl radicals to CH2, followed by dehydrogenation to C2H4. In our work, the oxygen species are continuously produced and transported to the anode while the metal–oxide interfaces at nanoscale would be highly favorable to accommodate these active oxygen species to react with CH4 to initiate the first C–H bond cleavage under external applied potentials. Here the theoretical calculations are tentatively conducted to understand the cleavage of C–H bond in CH2, especially at the nanoscale metal–oxide interfaces. We firstly study the CH4 activation over the (Fe/Mo)O2 termination on the SFMO (001) surface as shown in Supplementary Fig. 6. In this step, a CH4 molecule from the feed gas dissociatively adsorbs on a metal site and a neighboring oxygen atom, forming a hydroxyl group with O on the surface and releasing a methyl radical. As shown in Fig. 3d and Supplementary Fig. 7, our calculations suggest that molecular adsorption of CH4 on one Fe site with the bond length of 3.263 Å is energetically unfavorable. After the C–H bond cleavage of CH4, the CH3 radical adsorbs on surface metal Fe with the bond length of 2.146 Å and the H atom binds with the O atom of SFMO surface forming O–H bond (0.987 Å). And the energy barrier of hydrogen abstraction reaction is up to 1.0 eV on the SFMO (001) surface, indicating an energetically unfavorable process for CH4 activation. In contrast, for the Fe/SFMO system, the CH4 mainly adsorbs at the interface between Fe clusters and SFMO surface. The adsorption energy of CH4 is −0.26 eV, where the CH4 binds with the Mo atom (3.734 Å) of the SFMO surface and together with the Fe atom (3.545 Å) of Fe clusters. After the first C–H bond cleavage of CH4, the CH3 radical adsorbs on the Fe atoms of Fe clusters with the bond lengths of 2.027 and 2.093 Å while the H atom binds with the O atom at the Fe/SFMO interface forming O–H bond (0.980 Å). The cleavage of C–H bond in CH4 at the metal–oxide Fe/SFMO (001) interface is highly favorable with the energy barrier as low as only 0.46 eV. At this stage, active oxygen at metal–oxide interfaces would be present in the form of new oxygen species (Oads) to initiate the cleavage of C–H bond in CH4. The energy barrier of oxygen transfer process through oxygen vacancy site is only 0.34 eV, as shown in Supplementary Fig. 8. Of course, the oxygen deficiency in SFMO would be favorable for CH4 activation and oxidation. As we know, the charge transfer from adsorbed CH4 molecule to catalyst surface may be another key factor in CH4 activation. In the anode, the adsorbed CH4 coupled with active oxygen species would continuously donate free electron to external circuit under electrochemical potentials and thus facilitates CH4 activation at the metal–oxide interfaces. It can be therefore concluded that the metal–oxide interface with active oxygen species would be effective to accommodate the reaction of C–H bond cleavage under externally applied potentials in the porous anode.

Figure 4 shows the product analysis result of electrochemical oxidation of CH4 with different composite anodes while the oxide ions are ionically pumped to the anodes from air in the cathode. CH2 with 100% concentration is supplied to the anode and the products from the anode exhaust stream are analyzed using an online gas chromatography. We firstly investigate the thermal splitting of CH4 to C2H4 without externally applied voltage and find that only ~0.4% C2H4/C2H6 is generated with H2 of around 1.6%, as shown in Supplementary Fig. 9. We also observe slight carbon deposition in this process if without electrochemical pumping oxygen ions to the anodes. When voltages are applied to the cell, it is observed that both applied voltages and metal–oxide interfaces on the anode scaffold impact the electrochemical process. C2H4 has been formed and its concentrations show a strong and positive dependence on the applied potentials, which confirms the successful conversion of CH4 to C2H4 using this electrochemical approach. C2H6 has also been formed through

![Fig. 4](https://example.com/figure4.png)

**Fig. 4** CH4 conversion and C2 selectivity in conjunction with O2 electrolysis. a The product analysis of electrochemical oxidation of CH4 with different anodes. b C2 selectivity and CH4 conversion. c The product analysis of electrochemical CH4 oxidation with composite anodes. d CH4 conversion and C2 selectivity after cycling the output gas.
the oxidative coupling of CH₄ in the electrochemical conversion process while its concentrations are ~1/3 of the C₂H₄ concentrations. The by-products are mainly H₂ together with small amount of CO₂; however, their concentrations are in a close decreasing trend with the C₂ (C₂H₄ + C₂H₆) product generations. We show that the C₂ products reach 16.7% (11.5% C₂H₄ + 5.2% C₂H₆) with 82.2% C₂ selectivity while the CH₄ conversion ratio is approaching as high as 40.5% in Fig. 4b at ambient pressure and 1.6 V. This represents the highest C₂H₄ yields and C₂ selectivity in the reported catalytic conversion of CH₄ including non-oxidative and oxidative conversion processes. The C atom efficiency is reaching ~98–100% with negligible over oxidation of CH₄ to CO₂, which further indicates the exceptionally high efficiency for CH₄ conversion in this electrochemical process. The SFMO itself is an oxygen-nonstoichiometric catalyst and the iron species with unsaturated oxygen coordination at the SFMO surface would deliver catalytic activity. In contrast, redox stable La₀.75Sr₀.25Co₀.5Mn₀.5O₃₋δ (LSCM) electrode without iron dopant in the lattice shows negligible catalysis activity toward C₂H₄ generation. It is also observed that the metal–oxide interfaces enhance C₂ product generation by ~50–100%, indicating the favorable cleavage of C–H bond at metal–oxide interfaces.

Here the electrochemical processes are therefore dominated by the synergistic effect of the applied voltages and metal–oxide interfaces in the anodes. We further cycle the output gas for the electrochemical oxidation process and confirm that CH₄ conversion has been enhanced to ~81.1% in Fig. 4c; however, the main products are syngas while the C₂ selectivity remains ~41% (Fig. 4d). This indicates that the direct electrochemical oxidation of CH₄ dominates the C₂H₄ generation, and the cycling oxidation degrades the C₂ selectivity with the increase of syngas generation. We further conduct control experiment of electrochemical oxidation of C₂H₆ in the anode and we observe that the dominant products are C₂H₄, CH₄, and H₂ even without applied voltages as shown in Supplementary Fig. 10. This may be due to the thermal splitting of C₂H₆; however, significant coking is present in this process. When we apply voltage, the concentration of hydrocarbon product is slightly increased but the serious coking problem leads to rapid degradation of the cell performance. We therefore believe that the cycling oxidation increases syngas generation with enhanced CH₄ conversion, while the C₂ selectivity generally remains unchanged, indicating that the dominant C₂ selectivity comes from the initial electrochemical oxidation process.

This simultaneous electrochemical process involves ionically pumping oxide ions from the cathode, across the electrolyte, to the anode for CH₄ conversion. This feature provides an opportunity to convert oxygen-containing molecules, such as CO₂ into CO while the CH₄ conversion in the anode is maintained. Figure 5a shows the current–voltage (I–V) relationship of CO₂ electrolysis in the cathode in conjunction with CH₄ oxidation in the anode in a simultaneous process. The growth of metal–oxide interfaces in the porous electrode scaffolds also improves the current densities while the optimum composition is 0.075Fe–SFMO in which the content of metal nanoparticle dominates the metal–oxide interface length. Figure 5b gives the dependence of CO generation from CO₂ electrolysis both on metal–oxide interfaces and applied voltages, which indicates that the higher voltages facilitate CO₂ reduction while optimum composition is the 0.075Fe–SFMO composite with proper interface length. Figure 5c shows the CH₄ conversion toward chemicals in the anode while the CO₂ electrolysis is simultaneously performed in the cathode. Similar phenomenon has been observed for the performance dependence on the synergy of

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![Fig. 5](https://example.com/fig5.png)

**Fig. 5** Electrochemical oxidation of CH₄ in conjunction with CO₂ electrolysis. **a** The current–voltage (I–V) relationship of CO₂ electrolysis with CH₄ oxidation at 850 °C. **b** CO production in the cathode at various voltages. **c** The product analysis in the anode. **d** The long-term performance of the 0.075Fe–SFMO–SDC electrode for CH₄ oxidation with CO₂ electrolysis at 850 °C.
applied voltages and metal–oxide interfaces on the anode scaffold. The C\textsubscript{2} products reach 2.04\% (C\textsubscript{2}H\textsubscript{4} – C\textsubscript{2}H\textsubscript{6}) with 75.6\% C\textsubscript{2} selectivity while the CH\textsubscript{4} conversion ratio reaches 6.02\% at 1.6 V. This lower performance of CO\textsubscript{2}/CH\textsubscript{4} conversion in contrast to LSGM electrolyte, indicative of the strong interface interaction that facilitates catalytic conversion using FeO\textsubscript{x}–SrTiO\textsubscript{3}–TiO\textsubscript{2}–MnO\textsubscript{2} substrates. The catalytically active Fe or Ni can be directly doped into the lattice of the oxide substrate during materials synthesis, and then the metal nanoparticles would be grown to anchor on the oxide surface after reduction. These metal–oxide interfaces with enhanced stability and coking resistance could have broad potential applications in many other catalysis fields.

Discussion
In conclusion, we demonstrate a conceptually different approach of highly efficient conversion of CH\textsubscript{4} to C\textsubscript{2}H\textsubscript{4} with exceptionally high C\textsubscript{2}H\textsubscript{4} yield and C\textsubscript{2} selectivity in a solid oxide electrolyzer. The growth of metal–oxide interfaces at nanoscale with strong interactions in the porous electrode scaffolds possess not only improved activity of CH\textsubscript{4} activation but also enhanced coking resistance and thermal stability. Electrochemical oxidation of CH\textsubscript{4} in the anode in conjunction with O\textsubscript{2} electrolysis in the cathode shows the highest C\textsubscript{2} yields of 16.7\% (11.5\% C\textsubscript{2}H\textsubscript{4} + 5.2\% C\textsubscript{2}H\textsubscript{6}) with 82.2\% C\textsubscript{2} selectivity and exceptionally high durability even after 100 h of high temperature operation. Another efficient process with high C\textsubscript{2} yields has also been demonstrated with electrochemical oxidation of CH\textsubscript{4} in the anode in conjunction with CO\textsubscript{2} electrolysis in the cathode. The active oxygen species electrochemically pumped to the confined metal–oxide interface in the anode scaffold enable both carbon removal and CH\textsubscript{4} activation. This strategy provides a reliable and efficient electrochemical process for conversion of CH\textsubscript{4} into valuable chemicals. The growth of the metal–oxide interfaces can also lead to an interfacial interaction that facilitates catalytic conversion using FeO\textsubscript{x}–SrTiO\textsubscript{3}–TiO\textsubscript{2}–MnO\textsubscript{2} substrates. The catalytically active Fe or Ni can be directly doped into the lattice of the oxide substrate during materials synthesis, and then the metal nanoparticles would be grown to anchor on the oxide surface after reduction. These metal–oxide interfaces with enhanced stability and coking resistance could have broad potential applications in many other catalysis fields.

Methods
Synthesis
Synthesis of SFMO. 0.025Fe–SFMO, 0.050Fe–SFMO, and 0.10Fe–SFMO, and 8.10Fe–SFMO (SrFe\textsubscript{x}Mo\textsubscript{0.1}O\textsubscript{4−δ}, x = 0–0.1) were carried out by a microwave-assisted combustion method\textsuperscript{14,15}. The C\textsubscript{2}H\textsubscript{2}Mo\textsubscript{0.1}O\textsubscript{4} (SDC) powders were synthesized using a combustion method\textsuperscript{14}. LSGM was prepared by using a traditional solid-state reaction method\textsuperscript{12,14}.

Characterization.
XRD (Miniflex 600, Japan) and XPS (ESCALAB 250Xi, USA) were used to analyze the phase formation of samples and elemental states before and after reduction. The oxygen nonstoichiometry of SrFe\textsubscript{x}Mo\textsubscript{0.1}O\textsubscript{4−δ}, (x = 0–0.1) before and after reduction was determined using iodo-metric titration\textsuperscript{10}. The microstructures of the samples and the exsolution of nanoparticles were analyzed using scanning electron microscopy (SEM; SU-8010, Japan) and high-resolution transmission electron microscopy (HRTEM; Tecnai F20, USA).

Electrochemical measurements:
The SrFe\textsubscript{x}Mo\textsubscript{0.1}O\textsubscript{4−δ} (x = 0–0.1) and SDC powders were mixed with a weight ratio of 65:35 and a suitable amount of cellulose and α-terpineol were added to prepare electrode slurry. The 1-mm-thick LSGM disks were used as the electrolyte support to assemble single cells with different electrodes (1 cm\textsuperscript{2}) using a brush printing method followed by heat treatments at 1100 °C for 3 h in air. The silver current collector with 0.18 mm in diameter was coated on the electrode surfaces and then heat-treated in air at 530 °C for 0.5 h. For electrochemical tests of CH\textsubscript{4} oxidation, the in situ AC impedance, long-term stability tests and the current density voltage curve (I–V curve) were recorded using an electrochemical workstation (Zahner IM6, Germany). The CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and H\textsubscript{2} in the output gas were analyzed using an online gas chromatograph (GC; Shimazu, 2014, Japan).

Theoretical calculations.
Spin-polarized DFT+U theory calculations were performed using a plane wave basis set Vienna Ab-initio Simulation Package (VASP) code\textsuperscript{18,19}. The generalized gradient approach (GGA) was used including Perdew–Burke–Ernzerhof (PBE) functional to describe exchange and correlation. The interaction between core and valence electrons was described with the projector augmented wave (PAW) method. The energies and residual forces were converged to 10\textsuperscript{−8} eV and 0.02 eV Å\textsuperscript{−1}, respectively. The plane wave cut-off used for energy calculations was set to 800 eV and the U−J value for Fe was set to 4.0 eV while no U−J parameter was used for Mo. The SrFe\textsubscript{x}Mo\textsubscript{0.1}O\textsubscript{4−δ} cubic supercells of bulk SFMO with different distributions of Mo atoms were optimized with a 4 × 4 × 4 k-point grid and only the (Fe/Mo)O\textsubscript{2} terminated surfaces were considered because they were expected to be more catalytically active than the SrO terminated surface. By comparison of stability, the (Fe/Mo)O\textsubscript{2} terminated surface model constructed from the plane diagonal-Mo bulk structure (a = b = c = 7.8717 Å).
Received: 14 August 2018 Accepted: 18 February 2019
Published online: 12 March 2019

References
1. Schwach, P., Pan, X. L. & Bao, X. H. Direct conversion of methane to value-added chemicals over heterogeneous catalysts: challenges and prospects. Chem. Rev. 117, 8497–8520 (2017).
2. Zhong, L. S. et al. Cobalt carbide nanoprisms for direct production of lower olefins from syngas. Nature 538, 84–87 (2016).
3. Torres Galvis, H. M. & de Jong, K. P. Catalysts for production of lower olefins from synthesis gas: a review. ACS Catal. 3, 2130–2149 (2013).
4. Jiao, F. et al. Shape-selective zeolites promote ethylene formation from syngas via a ketene intermediate. Angew. Chem. Int. Ed. 57, 4692–4696 (2018).
5. Jiao, F. et al. Selective conversion of syngas to light olefins. Science 351, 1065–1068 (2016).
6. Schwach, P. et al. Structure sensitivity of the oxidative activation of methane over MgO model catalysts: II. Nature of active sites and reaction mechanism. J. Catal. 329, 574–587 (2015).
7. Noon, D., Seubai, A. & Senkan, S. Oxidative coupling of methane by van der Waals Correction was calculated using the equation of $E_{\text{ads}} = E_{\text{bond}} - E_{\text{substrate}} - E_{\text{CH}_4}$, where $E_{\text{ads}}$ is the total energy of the adsorption system, $E_{\text{substrate}}$, and $E_{\text{CH}_4}$ are the energy of the system without adsorption and the energy of the CH$_4$ in gas phase, respectively. The climbing-image nudged elastic band (CI-NEB) method was employed to calculate the energy barrier of oxygen vacancy transfer and the C–H bond cleavage in CH$_4$ reaction processes.

Acknowledgements
K.X. acknowledges the National Key Research and Development Program of China (2017YFA0700102), the Natural Science Foundation of China (91845202), Dalian National Laboratory for Clean Energy (DNL180404) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20000000). F.C. acknowledges the U.S. National Science Foundation (DMR-183206).

Author contributions
C.Z., S.H. and J.L. conducted the experiments. X.H. conducted the calculations. F.C. provided useful discussion and polished the English. K.X. supervised the work. All authors were involved in the data analysis and discussion.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-019-09083-3.

Competing interests: The authors declare no competing interests.

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Journal peer review information: Nature Communication would like to thank the anonymous reviewer for their contribution to the peer review of this work. Peer review reports are available.

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