Electrochemical Methane Conversion

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Abstract:
Methane, as an earth-abundant C1 resource, is a green-house gas as well as a key building block in chemical industry. Electrochemical conversion of methane into fuels and valuable chemicals represents an attractive promise toward carbon neutralization and reducing CO2 emission in industrial methane reforming. To overcome the catalyst degradation and energy cost problems, it is critical to activate the C−H bonds in methane effectively in order to operate under ambient conditions, while without at the cost of product selectivity. In this review, we focus on catalyst structures and system design strategies in recent developments of electrocatalytic methane conversion progresses. The combination of electro-, thermo- and photo- catalytic methods can enable complementary and enhanced activities as well as new insights in reaction conditions and mechanisms.

Keywords: methane oxidation, electrocatalysis, photocatalysis, thermocatalysis, catalyst design
Introduction

Methane (CH$_4$) is the side product of oil exploitation and widely exists in natural gas, shale gas, and combustible ice. Attributed to its nature of abundance and low price, methane is becoming a critical precursor of chemicals and fuels for replacing coal and oil.[1] The utilization of CH$_4$ offers attractive potentials to decarbonize current petroleum industries. Although the extent of methane emissions is smaller than carbon dioxide (CO$_2$), CH$_4$ is more potent as a heat-trap gas absorbing and emitting infrared radiation, with 86 times per mass unit as much as CO$_2$.[2] Thus, compared to direct combustion or emissions of methane, the large-scale methane conversion into value-added chemicals benefits both environment and economy.

The tetrahedral configuration of methane shows a high symmetry and a low polarity. Meanwhile, the dissociation energy of the C–H bond is up to 439.3 kJ·mol$^{-1}$. Compared to its valuable products (such as CO, CH$_3$OH, C$_2$H$_4$), the selective conversion of methane under ambient conditions has been attracting substantial interests from both academia and industry.[3] The direct methane conversion in industry needs harsh reaction conditions (high temperature > 900 K and pressure > 2.5 bar) that are both energy- and capital-intensive.[4] It is possible to directly oxidize CH$_4$ into oxygenated products at temperatures below 500 K, while expensive oxidants, such as H$_2$O$_2$, NO$_x$ and oleum, are needed.[5] The in-situ generation of active oxidizing species in the electrochemical procedure is an alternative solution. In this review, we focus on the strategy of electrochemical CH$_4$ activation and corresponding catalyst designs. The main article includes three sections that introduce current progresses and challenges of the electrochemical CH$_4$ conversion (Figure 1). In the first section, we introduce the CH$_4$ conversion at low temperatures by elaborating catalyst designs and system
selection. In the second section, we discuss the CH$_4$ usage at high temperatures combining thermocatalysis and electrocatalysis together to pursue high conversion rates and large current densities. In the third section, we focus on photochemical methods applied to electrochemical CH$_4$ oxidation to bring complementary advantages and new insights.

**Low-temperature methane electro-conversion**

Breaking C–H bond(s) requires a large activation energy that does not take place spontaneously.$^{[6]}$ Energy input, as well as oxidants and high-valent metal ions, can facilitate this process.$^{[7]}$ The redox intermediate is required to meet two demands: (i) strong activity to break C–H bond(s); and (ii) limited side reactions with solvent and products. The recent representative research progress in methane electro-conversion was summarized in Table 1. Concentrated sulfuric acid is widely chosen for its broad electrochemical window that is compatible with high-valent metals. For example, Pd$_{2}^{II,III}$ complex was generated in concentrated sulfuric acid electrolyte via electrochemical oxidation methods,$^{[8]}$ which presented a low C–H activation energy (25.9 kcal·mol$^{-1}$) and a high turnover frequency (TOF) of 2000 h$^{-1}$ at 140 ºC and 500 psi of methane. The formation of di-nuclear Pd$_{2}^{III}$ complex followed a mechanism involving an initial electron transfer, a chemical step, and a subsequent electron transfer (Figure 2a)$^{[8]}$. Pd$^{II}$ was first oxidized to Pd$^{III}$, and then coupled to another Pd$^{II}$ forming the key intermediate of M–M bonded Pd$_{2}^{II,III}$ species, which were further oxidized into Pd$_{2}^{III}$. The structure of Pd$_{2}^{III}$ dimer was a Pd–Pd bonded center with 5-coordinated oxygen atoms of H$_{x}$SO$_{4}^{(x-2)}$ for each Pd atom.$^{[9]}$ CH$_{3}$OSO$_{3}$H and CH$_{3}$SO$_{3}$H were the major products of methane oxidation, attributed to the polarity effect preventing further oxidation. The H$_{x}$SO$_{4}^{(x-2)}$
ligand from Pd$_{2}^{III}$ dimer attracted H atom from CH$_4$ to generate methyl radical (CH$_3$•), which acted as the rate limiting step (Figure 2b).$^{[10]}$ CH$_3$• could recombine with Pd$_{2}^{II,III}$ center and produce CH$_3$OSO$_3$H after reductive elimination, or CH$_3$• reacted with SO$_3$ to form CH$_3$SO$_3$H. Liu et al. reported that vanadium (V)-oxo dimer reduced the activation energy to 10.8 kcal·mol$^{-1}$, and achieved a high TOF of 1336 h$^{-1}$ at 3 bar of methane.$^{[11]}$ The structure of V$_2^{V,V}$ was a dimer with two terminal O atoms connected by a bridging oxo and two HSO$_4^{−}$ ligands. In the process of methane activation, the limiting step was the removal of the first electron from O $2p$ orbital from the HSO$_4^{−}$ ligand (Figure 2c). CH$_3$• was generated by the same ligand from CH$_4$, similar to the radical mechanism, but with a lower energy barrier.

As the usage of concentrated sulfuric acid can raise problems in equipment corrosion and products separation, more ambient electrolytes may benefit post-processing and product purification. For instance, Park et al. incorporated Co$_3$O$_4$ into ZrO$_2$ nanotubes for methane electro-oxidation in 0.5 M Na$_2$CO$_3$ at room temperature, and an yield of 2,416 µmol·g$_{cat}$·h$^{-1}$ (1-propanol and 2-propanol) was obtained at 1.6 V (vs. reversible hydrogen electrode, RHE) after 12 h.$^{[12]}$ In this system, a ZrO$_2$ structure with large surface area was capable of good adsorption ability of carbonate ions, and Co$_3$O$_4$ with rich surface oxygen vacancies could generate carbonate radical (CO$_3^{−}$•), which compared to hydroxyl radical (OH•) with a lower energy barrier. Acetaldehyde (CH$_3$CHO), although was not detected in the product, was a crucial intermediate for the production of 1-propanol and 2-propanol. CO$_3^{−}$• broke the C−H bond to form CH$_3$•, which subsequently combined with CH$_3$CHO. Nucleophilic addition between CH$_4$ and aldehyde group led to produce 2-propanol, and the radical addition generated 1-propanol (Figure 2d).$^{[13]}$ Furthermore, Park et al. also synthesized a ZrO$_2$:NiCo$_2$O$_4$ quasi-solid solution, and the methane oxidation efficiency remained at 47.5% after 20
Compared to CH₄, 1-propanol and 2-propanol were prone to be oxidized, and were converted into propionic acid and acetone within 20 h of electrochemical test (Figure 2c). Propionic acid was the final main product with the rate of 1,173 µmol·g⁻¹cat⁻¹·h⁻¹.

Another approach was to use electron-rich organometallic compounds to break C–H bonds. While the low-valent metal centers seemed incompatible with O₂ and prevented catalytic air oxidation of methane, an electrochemical regenerating strategy was developed using silicon nanowire arrays to employ O₂ gradient. At the bottom of silicon nanowire arrays, O₂ was consumed and the RhⅡ complex catalyst was regenerated from RhⅢ complex by electrochemistry.[15] RhⅡ complex reacted with dissolved CH₄ and formed RhⅢ catalyst-CH₃ complex. The RhⅡ catalyst-CH₃ complex was sensitive to O₂ and further oxidized to CH₃OH and RhⅢ complex (Figure 3a) in the bulk solution. Through solution catalytic cycle, RhⅡ tetramesityl porphyrin metalloradical with 0.1 M tetrabutylammonium perchlorate in 1,2-difluorobenzene reached a turnover number (TON) up to 52,000 in 24 h.

The direct conversion of CH₄ to CO₂ has been widely investigated in low-temperature methane fuel cells to generate electricity. Pt is an active transition metal catalyst under ambient conditions. The reaction mechanism and active sites of Pt have been studied,[16] and the CH₄ electro-oxidation is sensitive to the applied potentials. Although the CH₄ electro-oxidation was possible to take place at potentials more positive than 0.17 V vs. RHE, within the H UPD region (0.05–0.40 V vs. RHE), the adsorbed hydrogen may significantly block active sites on Pt surface so that the CH₄ oxidation cannot proceed. By sweeping potentials to more positive range, the oxidation peak centered at 0.75 V vs. RHE corresponded to the stripping of CO*, an intermediate in CH₄ oxidation (Figure 3b). CO* was eliminated by the OH* adsorption and CO–OH coupling. Density functional theory (DFT)

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calculations were conducted to estimate the binding energies of OH*, CO*, CH₃*, H*, and the CH₄ activation energy. The CH₃* and H* binding energies and the methane activation energy were linear functions of the CO* binding energy. Catalysts with strong CO* binding and weak OH* binding energies were proposed to be desirable for methane electro-oxidation. Trewyn et al. reported that atomically dispersed active Pt organometallic complexes boosted methane fuel cell performances.[17] Supported by ordered mesoporous carbon, a maximum power of 403 µW·mg⁻¹Pt was obtained at 80 °C. The single Pt site was coordinated by 2,2'-bipyridyl ligands and two chlorine (Cl) atoms or phenyl (Figure 3c). Various 2,2'-bipyridyl served as anchors, and the substitution of Cl or phenyl was critical to the performance. Phenyl linked complex provided a power of 101 µW·mg⁻¹Pt, which rose sharply to 278 µW·mg⁻¹Pt by replacing with Cl. Compared to phenyl, Cl maintained Pt in the +2 state, and the heterolytic cleavage between Pt–Cl broke the C–H bonds in methane efficiently.

Another strategy is to use a potential bias to trigger the surface property change. Sekine et al. reported that electric field could facilitate proton hopping on the surface.[18] Using 10 wt% Ni–10wt%Mg–La₀.₁Zr₀.₉O₂₋ₓ, the incorporation of Mg formed NiO–MgO solid solution on Mg–La₀.₁Zr₀.₉O₂₋ₓ, which suppressed the reduction of NiO at low temperatures by making it more cationic. The reforming process did not happen without the electric field. With an input current of 3.0 mA, CH₄ reforming using CH₄, H₂O, CO₂, and O₂ mixture was managed to operate at 473 K, and the apparent activation energy was 8.2 kJ·mol⁻¹.

**High-temperature methane electro-conversion**

The C–H cleavage is facilitated at high temperatures, in which CH₄ is prone to be fully oxidized...
to CO₂. Solid oxide fuel cells (SOFCs) were able to conduct O²⁻ through oxygen vacancies over 500 °C,[19] generating electric power to fully use the combustion energy. Y-stabilized ZrO₂ (YSZ) is commonly used as anode materials with excellent performance,[20] while the Ni-based materials tend to be deposited with carbon. Material degradation at high temperatures is also a serious problem, which can be improved by forming alloys. For instance, a porous NiO–Sm₀.₂Ce₀.₈O₂₋δ anode was prepared by incorporating SnCl₂ through infiltration.[21] After calcination and reduction, Sn–Ni inter-metallic compound was formed. Without the Sn incorporation, the cell had a lifetime less than 10 h in 3% H₂O−H₂. By 1 wt% introduction of Sn, the cell lifetime was increased to over 230 h at 0.8 V and 700 °C, with a peak power density of 0.28 W·cm⁻².

The SOFC operation in dry CH₄ can result in coking on the catalyst, and thus mixing CH₄ with O₂ and H₂O is critical to prevent the coking issue. Meanwhile, carbon coking can be consumed to refresh surface of catalysis. Controlling the supply mode of CH₄ to balance fuel consumption, power can be continuously generated and fuels can be fully utilized. For instance, a cycle with seven steps was applied, namely, anode reduction, Ar purging, supplement of CH₄, operation in CH₄, Ar purging, consuming coking, and anode re-reduction (Figure 4a).[22] The cell output energy was 394 mW·cm⁻² in the stage operating in CH₄, with high current density of 625 mA·cm⁻². The step of consuming coking was a key stage, in which the O²⁻ flux oxidized carbon as well as the catalysts. After approximately 30 min, the potential reduced to zero with a constant current density of 41.7 mA·cm⁻². The flux of protective gas had a mild influence on the time duration, but the increase of current density dramatically shortened the span. Compared to only 18 min of stable operation with continuous fuel supply, the anode with coking consumption showed much better redox stability and maintained its original activity after 6 cycles in 90 min.
Metallic state species, such as Ni and Pt, are sensitive to poisoning and coking. Loading Ni on oxides that prefer adsorbing O\textsubscript{2} can alleviate coking. For example, Moon et al. reported that Ni-gadolinium-doped ceria present a stability over 500 h\textsuperscript{[23]} with 1.35 and 0.74 W·cm\textsuperscript{-2} of energy density at 650 and 550 °C, respectively. In addition, enclosing metal catalysts into inorganic shells can prevent coking outside the shell, and maintain mass transport as the shell is gas permeable. For example, Jung et al. coated Pt nanoparticles with 1.5 nm-thick Al\textsubscript{2}O\textsubscript{3} shell, and the electrode activity was raised by 300 times\textsuperscript{[24]} The use of perovskite-type oxides is an alternative means against coking. Perovskite structures can tolerate large cation distortion and are rich in oxygen vacancies. Yang et al. reported that Sr\textsubscript{2}FeNb\textsubscript{0.2}Mo\textsubscript{0.8}O\textsubscript{6-δ} double perovskite exhibited coking-resistance and a rigid structure under reducing conditions\textsuperscript{[25]} The electrocatalytic performance was not compromised at 800 °C, achieving a power density of 380 mW·cm\textsuperscript{-2}.

Incorporating CH\textsubscript{4} reforming catalysts can help to alleviate the coking problem. Perovskite La\textsubscript{0.7}Sr\textsubscript{0.3}Fe\textsubscript{0.8}Ni\textsubscript{0.2}O\textsubscript{3-δ} (LSFN) was reported to be sprayed onto 8 mol% NiO-YSZ anode as catalysts, and in-situ reduced into Fe\textsubscript{0.64}Ni\textsubscript{0.36}, SrLaFeO\textsubscript{4}, and La\textsubscript{2}O\textsubscript{3} with uniformly dispersed FeNi alloys\textsuperscript{[26]} The catalyst first transformed CH\textsubscript{4} into syngas, which was further oxidized on YSZ. This type structure of SOFC was able to operate in two types of fuels, i.e., 97% CH\textsubscript{4}–3% H\textsubscript{2}O and 30% CH\textsubscript{4}–70% air. At 800 °C, the maximum power output was 0.343 W·cm\textsuperscript{-2}, and the stability was obtained over 100 h with the incorporation of catalysts in both type of fuels. Without the LSFN catalysts, the activity decay was observed in 12 h using CH\textsubscript{4}–air, or in 3 h using CH\textsubscript{4}–H\textsubscript{2}O. By rational design and screening, Liu et al. reported Ce\textsubscript{0.90}Ni\textsubscript{0.05}Ru\textsubscript{0.05}O\textsubscript{2} as a catalyst to reform CH\textsubscript{4} to H\textsubscript{2} and CO, showing 99% H\textsubscript{2} selectivity and 97% CO selectivity\textsuperscript{[27]} The anode was designed as a layer-by-layer structure. A BaZr\textsubscript{0.1}Ce\textsubscript{0.7}Y\textsubscript{0.1}Yb\textsubscript{0.1}O\textsubscript{1.8} catalyst was prepared and mixed with coking tolerating materials
Ce_{0.8}Sm_{0.2}O_2, and on the top of them was the reforming catalyst. At a relatively low temperature of 500 °C, a power density of 0.37 W·cm^{-2} was generated using 3.5% H_2O–CH_4 fuel.

In addition to the full oxidation into CO_2, CH_4 is also a critical C_1 resource. Thus, great efforts have been made toward the CH_4 partial (or selective) oxidation to value added products. Industrial hydrogen is mainly obtained from the methane steam reforming. For example, Ni–CeO_2/γ–Al_2O_3–MgO was reported to lower the operating temperature, and 96.4% CH_4 conversion and 75.3% H_2 selectivity were achieved at 600 °C and 4.5 A.[28] Since CO_2 is another important C_1 resource, the solid oxide electrolyzer cells (SOECs) provide feedstocks for Fischer-Tropsch synthesis by converting both CH_4 and CO_2 into syngas, thus eliminating these two kinds of green-house gases simultaneously. For example, Sr_2Fe_{1.5}Mo_{0.5}O_{6−δ}–Sm_{0.2}Ce_{0.8}O_{1.9} was reported as both the anode and cathode, assembling a symmetrical cell.[29] At 850 °C and 0.3 V, the current density reached 242 mA·cm^{-2}. Xie et al. chose redox-stable perovskite-type La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3−δ} in a symmetrical cell (Figure 4b), and CuNi was doped into perovskite lattice and reduced to metal nanoparticles.[30] H_2O in the stream was dissociated at the metal-oxide interfaces, and *OH reacted with carbon to form *COH that subsequently decomposed to *CO and *H. The *OH group also helped to remove carbon.

However, the conversion of CH_4 to hydrocarbon in SOECs has rarely been reported, due to its low selectivity. The catalysts need to efficiently break C–H bond(s) and favor the C–C coupling, as well as inhibit the CO_2 formation. A Fe-doped Sr_2Fe_{1.5}Mo_{0.5}O_{6−δ} anode was reported to convert methane to 11.5% C_2H_4 and 5.2% C_2H_6 under nonoxidative conditions.[31] The conversion ratio of CH_4 was 40.5% and the combined C_2H_4+C_2H_6 selectivity was 82.2% (Figure 4c). The CH_4 conversion rate and C_2H_4 concentrations were dependent on the applied potentials, suggesting C_2H_4
was further transformed from C$_2$H$_6$. Tang et al. achieved C$_6$–C$_8$ through CH$_4$ reforming on Fe–Al/SiO$_2$.[32] Incorporating that material in SOEC fostered equilibrium to CH$_4$ conversion, as the byproduct H$_2$ was exhausted. At 1050 °C, the CH$_4$ conversion rate reached 15.62%, and the selectivities were 40.08%, 27.37%, and 10.72% for C$_2$, benzene-toluene-xylene, and naphthalene respectively (Figure 4d).

**Photo-electrochemical methane conversion**

Photocatalysts can absorb ultraviolet–visible (UV–vis) light to produce electrons and holes. Meanwhile, the bandgaps need to match the redox potentials of CH$_4$ oxidation.[33] The challenge of photo-conversion of CH$_4$ is the kinetic sluggish of breaking C–H bonds. When both thermo- and photo- methods are combined, the inert C–H activation step can be managed to operate at enhanced rates. Steam reforming of methane into H$_2$ and CO$_2$ is thermodynamically preferred at lower temperatures, while at higher temperatures only CO/H$_2$ mixture can be obtained. For example, under air-mass (AM) 1.5G illumination, a Pt/blackTiO$_2$ catalyst on a light-diffuse-reflection-surface achieved a H$_2$ yield of 185 mmol·h$^{-1}$·g$^{-1}$ and 60% quantum efficiency at 500 °C, which was 1,000 times larger than state-of-art performance at room temperature.[34]

Efforts have also been made to reduce the catalyst deactivation and high energy consumption at high temperatures. Using an Ag-decorated ZnO nanostructure, a quantum yield of 8% (< 400 nm) and over 0.1% (~ 470 nm) were achieved to quantitatively convert CH$_4$ to CO$_2$ at room temperature.[35] Due to its wide bandgap, pure ZnO only showed UV absorption. With 0.1 wt% Ag decoration, the absorption was extended to visible light region, attributed to the surface plasmon resonance of Ag.
nanoparticles (Figure 5a). In-situ electron paramagnetic resonance (EPR) indicated the existence of electron trapping sites (Zn\(^{+}\)) and surface defects (O\(^{-}\)) under illumination. CH\(_4\) was converted through a two-step mechanism. Initially, surface O\(^{-}\) radical ions attracted H from CH\(_4\), generating •CH\(_3\). Meanwhile, •CH\(_3\) was further oxidized into CO\(_2\) by radicals, such as •OH (O\(^{-}\) reacting with OH\(^{-}\)) and O\(_2^{-}\) (Zn\(^{+}\) reacting with O\(_2\)). Instead of converting CH\(_4\) to CO\(_2\), Zn species could also oxidize CH\(_4\) to CO through methyl carbonates intermediates. Khodakov et al. reported that a ternary composite of Zn, H\(_3\)PW\(_{12}\)O\(_{40}\) and TiO\(_2\) showed a quantum efficiency of 7.1\% at 362 nm with 84\% CO selectivity.\(^{[36]}\)

The CO formation rate was 0.02 mmol·g\(^{-1}\)·h\(^{-1}\) without Zn, and increased by 20 times to 0.429 mmol·g\(^{-1}\)·h\(^{-1}\) with the Zn incorporation. After exposure to pure methane, Zn\(^{2+}\) was changed to Zn\(^{0}\), which could be re-oxidized to Zn\(^{2+}\) by air. In-situ Fourier-transform infrared (FTIR) spectroscopy study presented signals of bidentate carbonate (CO\(_3\)), H\(_2\)O (O–H) and carbonate ester (C–O), suggesting a mechanism of carbonate and its ester formation (Figure 5b). Applying \(^{12}\)CH\(_4\), O\(_2\) and \(^{13}\)CO\(_2\) atmosphere, both \(^{13}\)CO and \(^{12}\)CO were detected, implying that a partial of CO\(_2\) was converted to CO. The formation of CO was ascribed to the decomposition of surface methyl carbonates under illumination. In the presence of water, ZnO exhibited selectivity toward methanol and formaldehyde under mild light irradiation at room temperature. Ye et al. reported ZnO loaded with 0.1 wt\% of Au catalyst presented 125 μmol\(_{\text{oxygenates}}\)·h\(^{-1}\) rate with ~ 95\% selectivity.\(^{[37]}\) Surface plasmon resonance had little contribution to photocatalytic performance, because no products were detected under visible light. Without adding water, the over-oxidized product (i.e., CO\(_2\)) was detected. By increasing water amount, both the yield and selectivity of oxygenates were promoted. Loading Au onto ZnO boosted •CH\(_3\) and •OH formation, indicating Au functioned as co-catalysts. As described above, •CH\(_3\) was produced by ZnO, and subsequently combined with •OOH to form CH\(_3\)OOH in the
pathway to oxygenates (Figure 5c). The existence of water helped to protonate O₂ to •OOH on the Au co-catalyst, and facilitated single-electron-coupled proton reduction of CH₃OO•. CH₃OOH was the precursor of CH₃OH through photo-reduction procedure, and might directly decompose into HCHO (Figure 5d). Similarly, Yi et al. investigated a CuO/ZnO nanocomposite. In spite of a smaller bandgap of CuO than ZnO, the photocurrent response of CuO was negligible compared to ZnO, suggesting the fast recombination of electrons and holes in CuO. The electrons enriched in the conduction band of CuO were further transferred to the conduction band of ZnO, thus fostering oxygen activation and leading to an enhanced activity.

Another potential photo-catalyst is BiVO₄ with a bandgap 2.4 eV, which can typically convert CH₄ directly to CO₂. When a low concentration (0.5 − 5 mM) of nitrite ions, the undesired CO₂ formation was inhibited and the production of CH₃OH was increased, with a high selectivity of CH₃OH over 90%. In the UV range, NO₂⁻ had three separated optical absorption bands, which worked as UV filter slightly preventing water photolysis. More importantly, NO₂⁻ acted as •OH scavengers balancing •OH concentration, thus cutting off the pathway of CH₃OH over-oxidation toward CO₂. Meanwhile, •CH₃ was excited from CH₄ and •OH, and the reduction of •OH decreased •CH₃, blocking the generation of ethane from two •CH₃ radicals coupling. Andreu et al. reported a BiVO₄/V₂O₅ co-dispersed beta zeolite as a visible light photocatalyst for transforming CH₄ into CH₃OH. The introduction of Bi and V decreased the acidity of OH groups controlling the surface oxidation, and extended the absorption spectrum to longer wavelengths. Compared to pure beta zeolites that produced CO₂ with a yield of 59.8 µmol·h⁻¹, the incorporation of both Bi and V allowed to reduce the CO₂ yield to 23.0 µmol·h⁻¹. The yield of CH₃OH remained unchanged around 10 µmol·h⁻¹·g⁻¹. Because of the blocking of OH group, the amount of •CH₃ was reduced, leading to the
C₂H₆/CH₃OH ratio from 1.43 to 0.23.

The photoelectrochemical strategy has also been emerging for CH₄ transformation at room temperatures. The energy input for CH₄ activation is supplied by light, and the intrinsic activity can be regulated by applied potentials, resulting in various partial oxidized products. For example, a TiO₂ photoelectrode was reported as a photo-electrochemical CH₄ catalyst in 1.0 M NaOH under UV light with CH₄ bubbling.[41] The applied potential bias was in the range of 0.4 – 1.2 V vs. RHE. The combined CO and O₂ production added up to 80 – 90% of Faradaic efficiency (FE), and the CO selectivity varied at different potentials (Figure 6a). At an applied potential of 0.4 V vs. RHE, the highest FE for producing CO was reported as 81.9%, which dramatically decreased to 24.7% at 1.2 V vs. RHE. The mechanism of TiO₂ activating CH₄ was proposed as the charge separation forming Ti³⁺−O•−, and the subsequent attacking CH₄ by O•−. After yielding Ti−O−CH₃ and subsequent Ti−O=CH₂, the CO pathway was diverged from carbonate. The Ti³⁺ site was crucial in the CO production pathway, in which enriched Ti³⁺ sites tended to form Ti³⁺−C bond to promote CO formation. Otherwise, the Ti−O−C structure led to form carbonate.

To overcome the low solubility of CH₄ in water, triple-phase boundary has also been adopted in photoelectrochemical process (Figure 6b). For example, Takenaka et al. reported using WO₃, with a bandgap of 2.7 eV and absorbing blue light, to covert CH₄ to C₂H₆.[42] With an applied voltage, the electron-hole recombination was reduced. The porous n-type semiconductor WO₃ was dispersed on Ti microfiber to conduct excited electrons, and the photogenerated positive holes on WO₃ oxidized CH₄ to •CH₃, accelerating coupling to C₂H₆. At 1.2 V applied voltage, a photon-to-current conversion efficiency of 11% and a C₂H₆ selectivity of 54% (Figure 6c) were recorded. The ratio of CH₄/H₂O feeding stream needed to be strictly controlled, otherwise oxygen evolution reaction could dominate.
Outlook and Perspectives

In this review, we summarized the development of electrochemical CH₄ conversion in both mild conditions and SOFC/SOEC systems. The combination of thermo-, electro- and photo- strategies has provided new insights in the activation of C–H bonds as well as the stability control of intermediates. Despite great efforts made to pursue high CH₄ conversion rates and selectivities, several substantial challenges still exist in these fields toward practical CH₄ utilizations.

First, for the low-temperature CH₄ electro-conversion. In order to avoid the competing reactions of oxygen evolution, the electrolyte requires a larger stability window. Strategies applying high valent metal catalysts (Pt, Pd and V complex) focus on the use concentrated sulfuric acid and SO₃/H₂SO₄. Although high TOFs, yields and stabilities have been reported, substantial challenges existed in the separation of products from electrolytes. Meanwhile, the usage of concentrated sulfuric acid is also capital costing and adds strict requirement on the equipment. Electrolysis in less corrosive electrolyte is more attractive, such as using CO₃•⁻/CO₃²⁻ as the redox pair to break C–H bonds. Non-noble metal (Co, Ni, V) oxide and RuO₂ are emerging as electrocatalysts in water-based electrolyte. It needs further exploration of more suitable redox pairs that can break C–H bonds and are compatible with water. In addition, although alcohols and acids with multiple carbon atoms can be generated, the yields have generally remained low for practical applications, and the over-oxidation of products are still severe.

Second, for the high-temperature CH₄ electro-conversion. As the cleavage C–H bond is easier at higher temperatures, the current density can reach at 200 – 400 mA·cm⁻² with reasonably good CH₄
conversion rates. Simultaneous utilization of both anode and cathode reactions to convert CH₄ and CO₂ to syngas and hydrocarbon is an attractive strategy applying Ni, Pt, Cu, Fe and their alloy as catalysts. Meanwhile, the coking and deactivation of catalysts still remain as a major problem impacting the cell lifetime. High-performance coking resistant catalysts that is metal free or with metal/oxide interfaces are urgently needed. SrFeMoOₓ and SmCeOₓ based coking resistant materials are under development. The operating time region of cells can be around hundreds of hours, because coking and deactivation are prominent at high temperature (800 °C). The operating temperature is needed to be reduced but not compromise electro-conductivity. Solid electrolytes with rich O vacancies can conduct O²⁻ at lower temperature (~ 300 °C) to reach sufficient ionic conductivity, which can be further explored.

Third, for the photo-electrochemical methane conversion. The photo-generated radicals and holes can help to break C–H bonds at ambient conditions. The major products generally reported are CO and CO₂, suggesting that the selective oxidation of CH₄ into alcohols and hydrocarbons remains as a big challenge. In addition, the UV light is often needed to initiate the methane activation for photocatalysts (e.g. TiO₂, ZnO and BiVO₄), also limiting the applications. The potential of using longer wavelengths and lower photoenergies can help to prevent product over-oxidation, while the yields and quantum efficiencies still remain at a low level. Thus, substantial efforts in developing and adopting smaller bandgap materials and hierarchical structures to improve light absorption, as well as incorporation of co-catalysts (such as Au, Ag, Pt and Pd) to reduce energy barriers are needed. Furthermore, the rational design and regulating the electrolyte compositions to increase selectivity are also worth of exploration.
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References

[1] a) Z. Zakaria, S. K. Kamarudin, *Renewable Sustainable Energy Rev.* 2016, 65, 250-261; b) K. Huang, J. B. Miller, G. W. Huber, J. A. Dumesic, C. T. Maravelias, *Joule* 2018, 2, 349-365.

[2] a) R. B. Jackson, M. Saunois, P. Bousquet, J. G. Canadell, B. Poulter, A. R. Stavert, P. Bergamaschi, Y. Niwa, A. Segers, A. Tsuruta, *Environ. Res. Lett.* 2020, 15, 071002; b) P. V. L. Reddy, K.-H. Kim, H. Song, *Renewable Sustainable Energy Rev.* 2013, 24, 578-585.

[3] a) X. Meng, X. Cui, N. P. Rajan, L. Yu, D. Deng, X. Bao, *Chem* 2019, 5, 2296-2325; b) J. Jang, K. Shen, C. G. Morales-Guio, *Joule* 2019, 3, 2589-2593; c) X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng, M. Wei, *Science* 2014, 344, 616-619.

[4] a) D. C. Upham, H. H. Kristoffersen, Z. R. Snodgrass, M. J. Gordon, H. Metiu, E. W. McFarland, *Appl. Catal., A* 2019, 580, 102-110; b) P. Schwach, X. Pan, X. Bao, *Chem. Rev.* 2017, 117, 8497-8520; c) X. Zhang, C. Pei, X. Chang, S. Chen, R. Liu, Z. J. Zhao, R. Mu, J. Gong, *J. Am. Chem. Soc.* 2020, 142, 11540-11549.

[5] a) X. Cui, H. Li, Y. Wang, Y. Hu, L. Hua, H. Li, X. Han, Q. Liu, F. Yang, L. He, X. Chen, Q. Li, J. Xiao, D. Deng, X. Bao, *Chem* 2018, 4, 1902-1910; b) Y. Kwon, T. Y. Kim, G. Kwon, J. Yi, H. Lee, *J. Am. Chem. Soc.* 2017, 139, 17694-17699.

[6] J. C. Fornaciari, D. Primc, K. Kawashima, B. R. Wygant, S. Verma, L. Spanu, C. B. Mullins, A. T. Bell, A. Z. Weber, *ACS Energy Lett.* 2020, 5, 2954-2963.

[7] A. H. Bagherzadeh Mostaghimi, T. A. Al-Attas, M. G. Kibria, S. Siahrostami, *J. Mater. Chem. A* 2020, 8, 15575-15590.

[8] M. E. O'Reilly, R. S. Kim, S. Oh, Y. Surendranath, *ACS Cent. Sci.* 2017, 3, 1174-1179.
[9] R. S. Kim, E. C. Wegener, M. C. Yang, M. E. O'Reilly, S. Oh, C. H. Hendon, J. T. Miller, Y. Surendranath, *J. Am. Chem. Soc.* **2020**, *142*, 20631-20639.

[10] R. S. Kim, A. Nazemi, T. R. Cundari, Y. Surendranath, *ACS Catal.* **2020**, *10*, 14782-14792.

[11] J. Deng, S. C. Lin, J. Fuller, 3rd, J. A. Iniguez, D. Xiang, D. Yang, G. Chan, H. M. Chen, A. N. Alexandrova, C. Liu, *Nat. Commun.* **2020**, *11*, 3686.

[12] M. Ma, B. J. Jin, P. Li, M. S. Jung, J. I. Kim, Y. Cho, S. Kim, J. H. Moon, J. H. Park, *Adv. Sci.* **2017**, *4*, 1700379.

[13] M. Ma, C. Oh, J. Kim, J. H. Moon, J. H. Park, *Appl. Catal., B* **2019**, *259*, 118095.

[14] B. S. Natinsky, S. Lu, E. D. Copeland, J. C. Quintana, C. Liu, *ACS Cent. Sci.* **2019**, *5*, 1584-1590.

[15] M. J. Boyd, A. A. Latimer, C. F. Dickens, A. C. Nielander, C. Hahn, J. K. Nørskov, D. C. Higgins, T. F. Jaramillo, *ACS Catal.* **2019**, *9*, 7578-7587.

[16] M. Joglekar, V. Nguyen, S. Pylypenko, C. Ngo, Q. Li, M. E. O'Reilly, T. S. Gray, W. A. Hubbard, T. B. Gunnoe, A. M. Herring, B. G. Trewyn, *J. Am. Chem. Soc.* **2016**, *138*, 116-125.

[17] T. Yabe, K. Yamada, T. Oguri, T. Higo, S. Ogo, Y. Sekine, *ACS Catal.* **2018**, *8*, 11470-11477.

[18] A. Hauch, R. Kungas, P. Blennow, A. B. Hansen, J. B. Hansen, B. V. Mathiesen, M. B. Mogensen, *Science* **2020**, *370*, eaba6118.

[19] B. Shri Prakash, S. Senthil Kumar, S. T. Aruna, *Renewable Sustainable Energy Rev.* **2014**, *36*, 149-179.

[20] Q. Yang, J. Chen, C. Sun, L. Chen, *Int. J. Hydrogen Energy* **2016**, *41*, 11391-11398.
[22] Y. Jiao, L. Zhang, W. An, W. Zhou, Y. Sha, Z. Shao, J. Bai, S.-D. Li, *Energy* **2016**, *113*, 432-443.

[23] D. Lee, J. Myung, J. Tan, S.-H. Hyun, J. T. S. Irvine, J. Kim, J. Moon, *J. Power Sources* **2017**, *345*, 30-40.

[24] J. Seo, N. Tsvetkov, S. J. Jeong, Y. Yoo, S. Ji, J. H. Kim, J. K. Kang, W. Jung, *ACS Appl. Mater. Interfaces* **2020**, *12*, 4405-4413.

[25] H. Ding, Z. Tao, S. Liu, Y. Yang, *J. Power Sources* **2016**, *327*, 573-579.

[26] X. Lv, H. Chen, W. Zhou, F. Cheng, S.-D. Li, Z. Shao, *Renewable Energy* **2020**, *150*, 334-341.

[27] Y. Chen, B. deGlee, Y. Tang, Z. Wang, B. Zhao, Y. Wei, L. Zhang, S. Yoo, K. Pei, J. H. Kim, Y. Ding, P. Hu, F. F. Tao, M. Liu, *Nat. Energy* **2018**, *3*, 1042-1050.

[28] Q. Lu, Y. Hou, S. R. Laraib, O. Khalifa, K. Li, W.-l. Xie, M.-s. Cui, Y.-p. Yang, *Fuel Process. Technol.* **2019**, *192*, 57-64.

[29] Y. Wang, T. Liu, L. Lei, F. Chen, *J. Power Sources* **2017**, *344*, 119-127.

[30] J. Lu, C. Zhu, C. Pan, W. Lin, J. P. Lemmon, F. Chen, C. Li, K. Xie, *Sci. Adv.* **2018**, *4*, eaar5100.

[31] C. Zhu, S. Hou, X. Hu, J. Lu, F. Chen, K. Xie, *Nat. Commun.* **2019**, *10*, 1173.

[32] K. Liu, F. Meng, D. Zhu, Z. Wang, S. Lou, J. Zhao, H. Xiao, Y. Tang, *Chem. Eng. Technol.* **2020**, *43*, 2007-2014.

[33] a) H. Song, X. Meng, Z.-j. Wang, H. Liu, J. Ye, *Joule* **2019**, *3*, 1606-1636; b) D. Hu, V. V. Ordomsky, A. Y. Khodakov, *Appl. Catal., B* **2021**, 286.

[34] B. Han, W. Wei, M. Li, K. Sun, Y. H. Hu, *Chem. Commun.* **2019**, *55*, 7816-7819.
[35] X. Chen, Y. Li, X. Pan, D. Cortie, X. Huang, Z. Yi, Nat. Commun. 2016, 7, 12273.

[36] X. Yu, V. De Waele, A. Lofberg, V. Ordomsky, A. Y. Khodakov, Nat. Commun. 2019, 10, 700.

[37] H. Song, X. Meng, S. Wang, W. Zhou, X. Wang, T. Kako, J. Ye, J. Am. Chem. Soc. 2019, 141, 20507-20515.

[38] Z. Li, X. Pan, Z. Yi, J. Mater. Chem. A 2019, 7, 469-475.

[39] S. Murcia-Lopez, K. Villa, T. Andreu, J. R. Morante, Chem. Commun. 2015, 51, 7249-7252.

[40] S. Murcia-López, M. C. Bacariza, K. Villa, J. M. Lopes, C. Henriques, J. R. Morante, T. Andreu, ACS Catal. 2017, 7, 2878-2885.

[41] W. Li, D. He, G. Hu, X. Li, G. Banerjee, J. Li, S. H. Lee, Q. Dong, T. Gao, G. W. Brudvig, M. M. Waegele, D. E. Jiang, D. Wang, ACS Cent. Sci. 2018, 4, 631-637.

[42] F. Amano, A. Shintani, K. Tsurui, H. Mukohara, T. Ohno, S. Takenaka, ACS Energy Lett. 2019, 4, 502-507.
Figure 1. a) Methane conversion by the combination of electro-, thermo- and photo- strategies. b) Schematic of an energy diagram for methane activation breaking the first C–H bond.
Figure 2. a) Summary of the Reactions between Pd$^{II}$, Pd$_2^{III}$, Pd$^{III}$, and Pd$_2^{II,III}$. Reproduced with permission.$^{[9]}$ Copyright 2020 American Chemical Society. b) The electrophilic C–H activation by a bound bisulfate (HSO$_4^-$) ion. Reproduced with permission.$^{[10]}$ Copyright 2020 American Chemical Society. c) Calculated frontier orbitals involved in the turnover-limiting step and the proposed transition state of C–H activation step (left panel) and proposed catalytic cycle (right panel). Reproduced with permission.$^{[11]}$ Copyright 2020 Deng et al., under a CC BY license. d) Nucleophilic addition reaction of methane and acetaldehyde to form 2-propanol (up) and free radical addition reaction of methane and acetaldehyde to form 1-propanol (down). Reproduced with permission.$^{[13]}$ Copyright 2017 Ma et al., under a CC BY license. e) Production rate of propionic acid, 1-propanol, 2-propanol, acetone and acetic acid after 5 h, 12 h and 20 h (left panel), and product selectivity after 5 hours (right panel). Reproduced with permission. This article is protected by copyright. All rights reserved.
h, 12 h and 20 h of electrochemical CH4 oxidation by 0.5-ZrO2:NiCo2O4 (right panel) in 0.5 M Na2CO3 at 298 K. Reproduced with permission.\textsuperscript{[14]} Copyright 2019 Elsevier B.V.
Figure 3. a) The reactivities of Rh\textsuperscript{II} metalloradical with CH\textsubscript{4} and O\textsubscript{2} (left panel) and schematic of the proposed catalytic cycle (right panel). Reproduced with permission\textsuperscript{[15]} Copyright 2019 American Chemical Society. b) Argon background subtracted chronoamperometry during the methane activation phase in 0.5 M perchloric acid (left panel) and cyclic voltammetry showing the oxidation feature after the electrode potential hold when purging with methane compared to the inert argon purge (right panel). Reproduced with permission\textsuperscript{[16]} Copyright 2019 American Chemical Society. c) Schematic representation of the general synthetic procedure for ordered mesoporous carbon-tethered single-site catalysts. Reproduced with permission\textsuperscript{[17]} Copyright 2016 American Chemical Society.
Figure 4. a) A successive seven-step process of an SOFC operated on dry methane and deposited carbon at 800°C. Reproduced with permission.\cite{22} Copyright 2016 American Chemical Society. b) The schematic of electrochemical CO₂/CH₄ reforming process in SOEC to produce syngas. CO₂ electrolysis in the cathode, CH₄ electrochemical oxidation in the anode. Reproduced with permission.\cite{30} Copyright 2018 Lu et al., under a CC BY license. c) The product analysis of electrochemical oxidation of CH₄ with different anodes. (1- SFMO, 2- 0.025Fe-SFMO, 3-0.050Fe-SFMO, 4- 0.075Fe-SFMO, 5- 0.100Fe-SFMO) Reproduced with permission.\cite{31} Copyright 2019 Zhu et al., under a CC BY license. d) Catalyst lifetime test at 1000°C, 1 bar. The selectivities of different products were displayed over the reaction time. Reproduced with permission.\cite{32} Copyright 2020 WILEY-VCH.
Figure 5. a) Metallic nanostructures functioning as both a co-catalyst and a light-harvesting medium. Reproduced with permission.\textsuperscript{35} Copyright 2016 Chen et al., under a CC BY license. b) Reaction steps in methane photo-oxidation over Zn, H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} and TiO\textsubscript{2} ternary composites. Reproduced with permission.\textsuperscript{36} Copyright 2019 Yu et al., under a CC BY license. c) Yields and selectivities of liquid products under simulated sunlight irradiation. d) The proposed reaction mechanism for photocatalytic CH\textsubscript{4} oxidation to CH\textsubscript{3}OOH, CH\textsubscript{3}OH, and HCHO. Reproduced with permission.\textsuperscript{37} Copyright 2019 American Chemical Society.

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Figure 6. a) Schematic illustration of selective CH$_4$ oxidation to CO on a TiO$_2$ photoelectrode (left panel) and dependence of the CO efficiency and selectivity on the applied potentials (right panel). Left-axis: efficiency; right-axis: selectivity of CO over all carbonaceous products. Reproduced with permission.[41] Copyright 2018 American Chemical Society. b) Photoelectrochemical system for gas-phase CH$_4$ activation. c) Time course of product formation in the photoanode compartment. Reproduced with permission.[42] Copyright 2019 American Chemical Society.

Table 1. Summary of representative research progress of methane electro-conversion.
### Table of Contents

Electrochemical conversion of methane into fuels and valuable chemicals represents an attractive promise toward carbon neutralization and reducing carbon dioxide emission in methane reforming. The combination of electro-, thermo- and photo-
catalytic methods can enable complementary and enhanced activities as well as new insights in reaction conditions and mechanisms.