



Review Article

Challenges in the selective electrochemical oxidation of methane: Too early to surrender

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**Abstract**

The selective electrochemical oxidation of methane to value-added chemicals has been pursued for decades without breakthroughs and developments beyond academic research. Main setbacks encountered in virtually every report are poor methane conversion rate and selectivity. For tangible progress, research should focus on tackling CH₄ mass transport and concentration limitations. At the same time, harmonized research protocols must be developed, e.g. to define standard control experiments and key metrics. This will facilitate data comparison and accelerate electrocatalyst discovery, which so far remained challenging due to inconsistent data-reporting practices. Fundamental research on model (well-defined) electrocatalysts should also be intensified, along with in-situ spectroscopic investigations to understand the reaction mechanism and design catalysts to prevent overoxidation.

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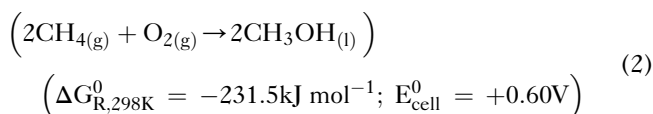
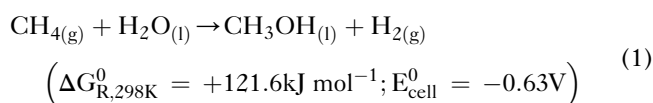
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Methane conversion, Electrocatalysis, Selective oxidation, Methanol, Active oxygen species.

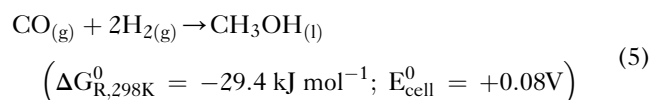
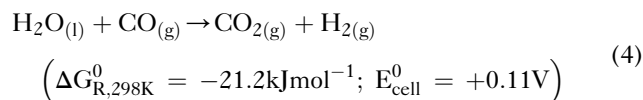
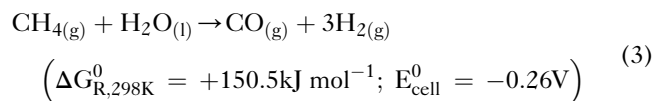
Methane valorization by partial oxidation: Do we need it?

The controlled activation of the C–H bond in methane (CH₄) is considered a “holy grail” in chemistry and catalysis due to the industrial relevance of value-added chemicals that could be directly produced by selective

CH₄ oxidation [1]. The direct conversion of CH₄ to methanol (CH₃OH), according to reactions 1 or 2, is of great interest because the produced CH₃OH could be used as feedstock for chemical syntheses and as an energy source [2]. Such direct CH₄-to-CH₃OH route is, however, hampered by the chemical inertness of CH₄, in which C–H bonds are weakly polarized, sterically hindered, and hence very stable, making it difficult to react CH₄ partially and not fully to CO and CO₂.



While an efficient direct route remains unviable, the chemical industry produces large amounts of CH₃OH from synthesis gas through an indirect process via steam methane reforming (SMR) and the water-gas shift reaction, according to reactions 3–5:



This route is energy-intensive and causes CO₂ emissions of about 300 million tons per annum (MTPA), corresponding to ca. 10% of the total CO₂ emissions of the chemical sector [3]. In the last decade, CH₃OH production has nearly doubled to 98 MTPA and will

potentially rise to 500 MTPA by 2050 [3]. The reliance on SMR is incongruent with global ambitions to phase out fossil fuels and reach net-zero carbon emissions by 2050. The increasing demand for CH₃OH underscores its relevance for the chemical industry and society, but the associated CO₂ emissions, projected to skyrocket, call for the development of alternative technologies for CH₄ valorization and CH₃OH production. In line with the ongoing electrification of the chemical industry, electrochemical conversion processes appear to be a renewable pathway for selective CH₄ oxidation, ideally directly to CH₃OH, in a decentralized fashion, and powered by green electricity (from wind and solar), hence potentially with zero carbon emission [4].

Interestingly, the motivation provided by academic literature on selective electrochemical oxidation of methane (SEOM) mainly revolves around conceiving alternatives to CH₄ flaring (combustion of CH₄ on offshore oil drilling platforms causing CO₂ emissions) and avoiding atmospheric CH₄ emissions. However, oil producers have available options to reduce flaring by up to 95% within 2030 [5]. Likewise, CH₄ emissions by the energy sector (accounting for 35% of the global CH₄ emissions—the remainder being associated with microbial processes, ruminants, wetlands, etc. [6]) will likely be reduced by 30–60% in the coming years, achieving zero emissions by 2050 [7].

Research efforts on SEOM remain, in our opinion, primarily justified by the need for alternatives to SMR, hence, to reduce CO₂ emissions, even if newly developed technologies would rely on fossil CH₄. Nevertheless, biogenic sources can be considered as a nonfossil feedstock for CH₄ valorization and toward carbon circularity. In fact, the current world production of biomethane through anaerobic digestion, landfill, and gasification technologies is at around 35 MTPA (3% of total bioenergy demand, 0.1% of natural gas demand), and the production is projected to increase to around 720 MTPA (stated policies scenario) or 2000 MTPA (sustainable development scenario) by 2040 [8,9].

Selective electrochemical oxidation of methane—we need orchestrated research efforts

The SEOM has attracted scientific interest since the 1960s. However, the research community is growing slowly compared to what is seen for H₂O electrolysis or the electrochemical CO₂ reduction reaction (CO₂RR). The lack of a critical mass of researchers investigating this subject is a first hurdle to advance in the field—this may originate from the earlier disillusion of the heterogeneous catalysis community that invested huge efforts on direct CH₄ conversion without making a breakthrough. From 2014 to 2022, about 4'000 articles were published worldwide on the electrochemical CO₂RR

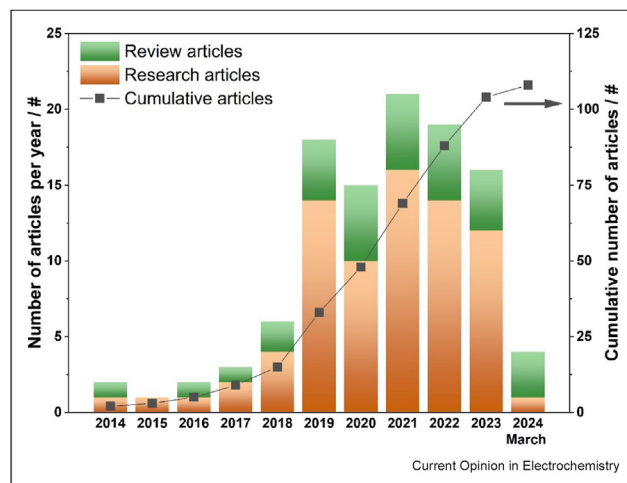
[10] and >20'000 patents were filed on H₂O electrolysis [11]. In contrast, only about 110 articles have been published on the SEOM in the last ten years, as shown in Figure 1—herein, we limit ourselves to low-temperature electrochemical processes. Interestingly, out of these publications, about 30 articles are reviews. It is surprising that so many reviews have been published in a field that stagnates since decades, and hence remains still in its infancy. While with the present opinion we are shifting the balance further in favor of review articles, we hope to provide a constructively critical analysis of the state of the art and encourage intensified and orchestrated research efforts to advance in the field.

(Electro)chemical methane activation mechanisms—in essence

Although discussed in various articles and reviews [12–15], a brief recap of the mechanisms of electrochemical CH₄ activation is provided in the following to substantiate the content of the following sections. While mechanistic details have yet to be fully uncovered, it is common to encounter in the recent literature two main pathways for the cleavage of the C–H bond [15]:

In the *direct pathway*, adsorption of CH₄ on the electrocatalyst surface (anode) is a key step to enable polarization of the C–H bond. This lowers the activation barrier for proton abstraction or for nucleophilic attack by a surface-adsorbed oxygen species generated electrochemically in the vicinity of the adsorbed CH₄ molecule. CH₄ is found to overoxidize to CO and CO₂ on noble-metal electrocatalysts (typically, platinum-group metals [PGMs]) [16]. The community seems to

Figure 1



Number of review and research articles on selective electrochemical oxidation of methane between 2014 and March 2024. Within research articles, we also included those on photoelectrochemical approaches and density functional theory calculations.

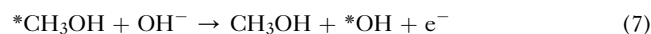
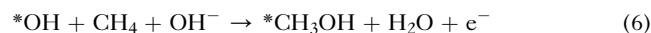
not have reached yet a consensus on the main cause of methane full oxidation, i.e., whether it results from the ease of adsorption of methane and its oxidation intermediates on the electrocatalyst surface, leading to consecutive proton abstraction steps, or from formation of adsorbed oxygenated species (by partial oxidation) that rapidly oxidize further due to a low redox potential (discussed in the next session). In contrast, metal oxide anodes have been proven not only to adsorb CH₄ moderately but also to mediate its reaction with adsorbed oxygen species (by so called “water discharge”), thereby forming CH₃OH [17]*.

In the *indirect pathway*, CH₄ homogeneously reacts in the electrolyte, more likely nearby the electrode surface, with an oxidizing agent produced locally, i.e., on the electrode surface. Once converted into its reduced form, the oxidizing agent regenerates electrochemically, i.e., via a Faradaic process at the electrode surface. This pathway implies a non-Faradaic oxidation of CH₄. Oxidizing agents can be reactive oxygen species (ROS) generated through partial oxidation of H₂O [18] or through partial reduction of O₂ [19]**. Metal complexes (of Ag^I/Ag^{II} [20], Pd^{II}/Pd^{III} [21], Pt^{II}/Pt^{IV} [22], Rh^{II}/Rh^{III} [23]) and surface-adsorbed chlorine intermediates (*Cl [24]), have also been successfully used as redox mediators for CH₄ activation. In homogeneous catalysis, complexes based on high-valent metal ions were found to be able to activate the methane’s C–H bond [25,26]. Their application in an electrochemical system, where their regeneration (reoxidation) would take place electrochemically (via a Faradaic process at the electrode surface), might be a promising approach to explore. Nevertheless, since the application of such redox mediators requires downstream separation steps, the use of water as the redox mediator, i.e., via formation of ROS, remains a most preferred approach. In addition, in general, the *indirect pathway* currently appears more promising than developing electrode surfaces capable of selective conversion of CH₄ (i.e., via *direct pathway*), as electrocatalysts that can generate ROS efficiently have meanwhile been developed

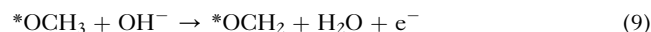
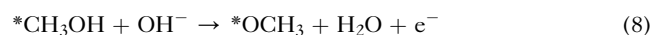
In the following, we briefly discuss the mechanism of two selected electrocatalytic systems presented in recent literature on the SEOM.

The mechanism for the SEOM via *direct pathway* was studied by density functional theory (DFT) calculations for transition metal (oxy)hydroxide electrocatalysts [17]—e.g., considering a CoOOH-model surface, with focus on the pathway to CH₃OH and CO₂. It was proposed that, in the potential range of 0.5–1.5 V vs. standard hydrogen electrode (SHE) under alkaline pH conditions, the selectivity to CH₄ or CO₂ is potential-dependent, as outlined in the following reactions scheme (reactions 6–10). The asterisks (*) indicate surface-adsorbed species.

Selective CH₄ oxidation to CH₃OH in the potential window of 0.5–1 V vs. SHE:



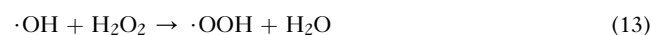
Overoxidation of CH₄ to CO₂ above 1 V vs. SHE:



The first reaction step combines the electrochemical activation of the C–H bond of CH₄ with OH[−] of the CoOOH surface and the concerted rebinding of the CH₃ fragment with a surface-adsorbed OH (*OH) (6). The formed adsorbed *CH₃OH on the surface has two options: (i) the CH₃OH can desorb, and the hydroxyl group on the surface can be replenished electrochemically by hydroxyl ion to give back the initial catalyst (CoOOH) (7); and (ii) the *CH₃OH can further oxidize to *OCH₃ (8). At 1 V vs. SHE, the thermodynamic favorability of the two reactions switches and (8) becomes more favorable. *OCH₃ then oxidizes to *OCH₂, a step again thermodynamically favorable (9). These are the first steps toward the overoxidation of CH₄ to CO₂. The other favorable oxidation steps after *OCH₂ were not explicitly calculated (10).

For the *indirect pathway* of the SEOM, ROS can be generated cathodically over a carbon-based electrode toward the production of HCOOH [19]. The proposed mechanism proceeds according to the following reactions (11–18):

ROSs formation:



CH₄ activation:



CH₃OOH formation:



CH₃OH formation:



HCOOH formation:



In such a reaction mechanism, first O₂ is reduced to H₂O₂ on the electrode, then the ROSs are formed by electrochemical reduction of H₂O₂ or chemical reaction between H₂O₂ and the previously formed radicals [11–13]. Second, ·OH radicals activate CH₄ to produce CH₃· radicals in the electrolyte [14]. Then, CH₃OOH is generated by a reaction between CH₃· and ·OOH radicals [15]. Subsequently, CH₃OH is generated by electrochemical reduction of CH₃OOH or radical reaction between CH₃· and ·OH [16–17]. Finally, HCOOH is formed in the presence of ·OH radicals [18].

In general, for a catalyst to perform well in the SEOM, it must effectively lower the activation barrier for C–H bond cleavage and prevent overoxidation. The C–H bond activation—as exemplified earlier—can occur directly through methane adsorption on the catalyst surface or indirectly via regenerable in-situ generated oxidizing agents such as peroxocarbonates or hydroxy radicals. In nonelectrochemical methane oxidation, the involvement of reactive oxygen species suggests a homolytic cleavage pathway [27]. However, for transition-metal catalysts, the pathway (homolytic or heterolytic) remains debated due to the lack of definitive spectroscopic evidence, making both routes plausible [28–31]. Preventing overoxidation is particularly challenging as the activation barriers for subsequent oxidation steps are lower once methane is activated. Therefore, it is crucial to ensure that methanol can be efficiently transported away from the reaction sites, thus avoiding its further oxidation. Future research should focus on improving in-situ characterization techniques (to provide clearer mechanistic insights), and developing catalysts with precise control over the nature and surface concentration of active sites and reactor designs to avoid overoxidation.

Few achievements, many challenges—what are promising directions?

Most reports on SEOM deal with producing CH₃OH in aqueous electrolytes, using three-electrode or H-cell configurations, at atmospheric pressure and close-to-ambient conditions [14]. Analyzing the results, it emerges that virtually every study reports small current densities (total current densities in the 1 mA cm⁻²

regime or lower) and low CH₃OH production rates (in the 0.1–1 nmol s⁻¹ cm⁻² regime). Moreover, the tested electrode materials often feature complex compositions with poor scalability perspectives. In other words, no breakthrough has yet been achieved in the field. Why is this so? We outline in the following crucial factors that, in our view, hamper progress in SEOM and provide our opinion on most promising directions to pursue.

• Poor selectivity—undesired methanol oxidation

The *direct pathway* for SEOM is challenging from both thermodynamic and kinetic standpoints. The standard CH₄ oxidation potential to methanol (reaction 19) is +0.63 V vs. SHE (see Figure 2). This potential is less positive than that for the water oxidation reaction (WOR, +1.23 V vs. SHE—reaction 20). In principle, in the 0.63–1.23 V potential range, CH₄ can be activated without competition from WOR. In practice, however, slow CH₄ conversion kinetics are typically observed. Operating at larger overpotential to accelerate the CH₄ conversion is counterproductive as WOR begins to compete.

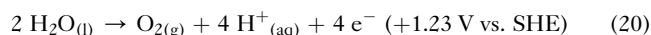
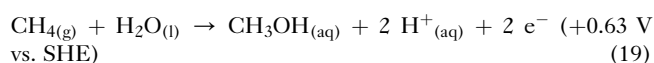
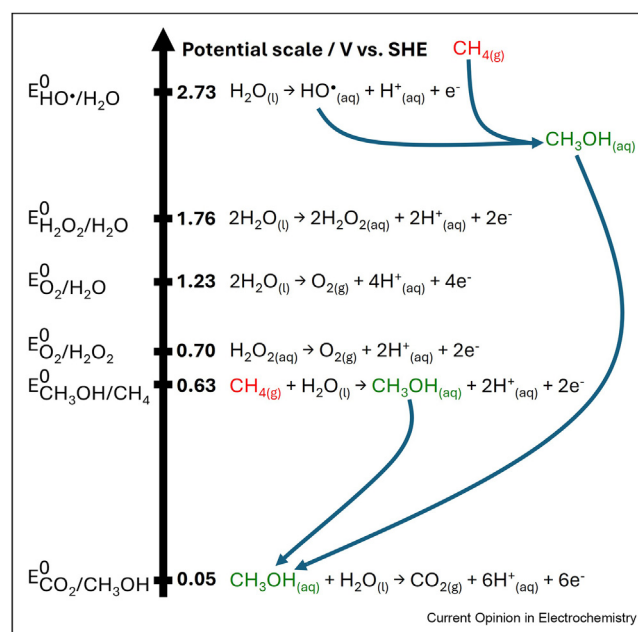
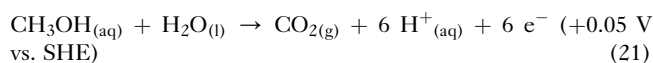


Figure 2

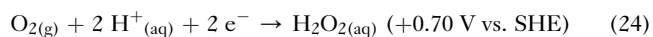
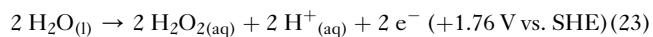
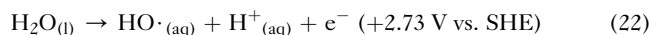


Thermodynamic potentials relevant for selective electrochemical oxidation of methane and competing reactions. The different equilibria are written as oxidation reactions.

Most importantly, even if the kinetics of CH₄ activation in the +0.63 to 1.23 V potential range was favorable, the CH₃OH - CO₂ redox potential is of (ca.) 0.05 V vs. SHE (reaction 21), i.e., it is less positive than that of CH₄. CH₃OH is more strongly polarized and less sterically hindered than CH₄, leading to a higher susceptibility of the former to electrophilic and nucleophilic attacks, i.e., a more pronounced reactivity. Hence, the formed CH₃OH can easily oxidize at the electrode surface to CO and CO₂, leading to poor selectivity and product yields, and a low Faradaic efficiency (FE) to CH₃OH [1]. This is the real culprit of the SEOM—often not highlighted in the literature.



In the *indirect pathway*, ROSs are usually generated (anodically) at more positive potentials than CH₃OH oxidation (reactions 22–24). However, due to the lack of in-situ mechanistic studies, it is unclear whether the oxidation of CH₃OH to CO₂ proceeds homogeneously in solution through ROS, or heterogeneously through the adsorption of CH₃OH on the electrode surface. To minimize CH₃OH oxidation and losses in FE, we would need an electrocatalyst that is efficient towards ROS generation but lousy in CH₃OH oxidation. Boron-doped diamond is known to oxidize CH₃OH indirectly through ROS and not on the electrode surface [32]—based on a similar concept, SnO₂ might also be promising.



Based on what is mentioned earlier, accumulation of CH₃OH in the electrolyte, by simply increasing the electrolysis time, cannot be achieved, independent of a *direct* or *indirect pathway*. Product removal from the electrolyte, on the other hand, is challenging as CH₃OH is highly soluble in aqueous electrolytes and thus, it is difficult to remove in the case of batch electrolysis. Therefore, batch operation is not ideal if the electrocatalyst is not selective. A promising approach to remove CH₃OH from the electrode surface is to opt for a flow cell.

While *direct* and *indirect pathways* are often mentioned in SEOM literature, we still have poor understanding of the reaction mechanism and little evidence with respect to which reaction intermediates form. Unfortunately, a limited number of studies is devoted to such aspects, more likely because the reaction complexity, in terms of variety of intermediates and time scales, along with operating conditions (e.g., gas concentration or pressure, mass

transport), makes the application of in-situ and operando spectro-electrochemical techniques challenging [33].

As discussed in the following, the main roadblock remains to achieve reasonable conversion rates for the SEOM. Most studies have dealt with developing new electrocatalysts, whereas the main obstacles toward high current densities are the low solubility and poor mass transport of CH₄ in aqueous electrolytes (regardless of the *direct* or *indirect pathway*)—hence, the community should deal with cell and process engineering aspects too.

- *Low CH₄ concentration and mass transport*

The solubility of CH₄ in water at room temperature and atmospheric pressure is 1.4 mM only [34]. This limits the kinetics of SEOM in aqueous electrolytes. Higher CH₄ concentrations can be achieved in organic solvents, e.g. up to 24 mM in tetrahydrofuran [35]. Besides concerns associated to their toxicity and volatility, organic solvents might be more reactive than CH₄ itself, and hence undergo degradation—nonetheless, it remains worth exploring organic solvents at least at the lab scale [23,36,37], e.g., using rotating-(ring)-disk electrode setups (R(R)DE).

To improve substantially the solubility of CH₄ in water (by a factor 10–100), an approach can be increasing the pressure up to 10–100 bar [38]. A proof of concept has been demonstrated, leading to a 220-fold increase in the yield compared to atmospheric pressure [39]*. Note, however, that the CH₄ solubility reached at 20 bar in water is comparable to that of CO₂ at atmospheric pressure (34 mM) [34].

For both *direct* and *indirect pathways* to achieve high conversions, it is necessary to enable efficient CH₄ mass transport to the electrode surface. This can be attained by flowing CH₄ through a porous electrode, the so-called gas diffusion electrode (GDE, consisting of a porous transport layer/gas diffusion layer and a catalyst layer) [40]*. In general, the use of GDE-based cell has received minor attention for SEOM, whereas we and other authors [41,42] advocate for intensifying the research efforts in this direction. Research on such applied and engineering aspects could attract the interest of the industry, hence strengthening the research capabilities by public—private partnerships.

When operating with GDEs, gas-flow rate and pressure can be controlled to tune the reaction kinetics and achieve an optimal tradeoff between high conversion (low flow rates) and high selectivity (high flow rates). Temperature can be controlled too. When operating with a liquid electrolyte, the solubility of CH₄ increases with decreasing the electrolyte temperature. However, when operating with a humidified CH₄ feed [43], the

increase of temperature could be beneficial to tune the $\text{CH}_4:\text{H}_2\text{O}$ molar ratio (i.e., partial pressures), hence providing an additional knob that together with pressure and gas-flow rate could enable control over reaction kinetics and product distribution.

For SEOM, worth mentioning are the three GDE-based cell configurations shown in Figure 3. Cell configurations presented in Figure 3-left (the so-called microfluidic cell) and in Figure 3-middle (zero-gap cell) have been successfully applied in PEM water electrolysis and fuel cells, and in CO_2RR . From an engineering point of view, these technologies can be promising to advance the field of SEOM, not only in electrolysis mode but also considering the perspective selective oxidation of methane when used as fuel in fuel cells [44]. The hollow-fiber electrode, shown in Figure 3-right, represents an emerging concept [45]. Selective oxidation of propylene has been achieved with such electrode and cell configuration [46], but beneficial effects of enhanced mass transport were not evident from this study. Being still a relatively novel approach, it needs first to be further explored for processes that are better understood and developed at a higher technology readiness level (TRL) before considering its suitability for the SEOM. Regardless of the cell or electrode configuration, the SEOM should initially be paired with well-known half-cell processes (indicated with “?” in Figure 3), e.g., the hydrogen or oxygen evolution reactions in the case of anodic and cathodic SEOM, respectively.

A final point: out of the few reports available on GDEs for SEOM, most of them use carbon-based materials.

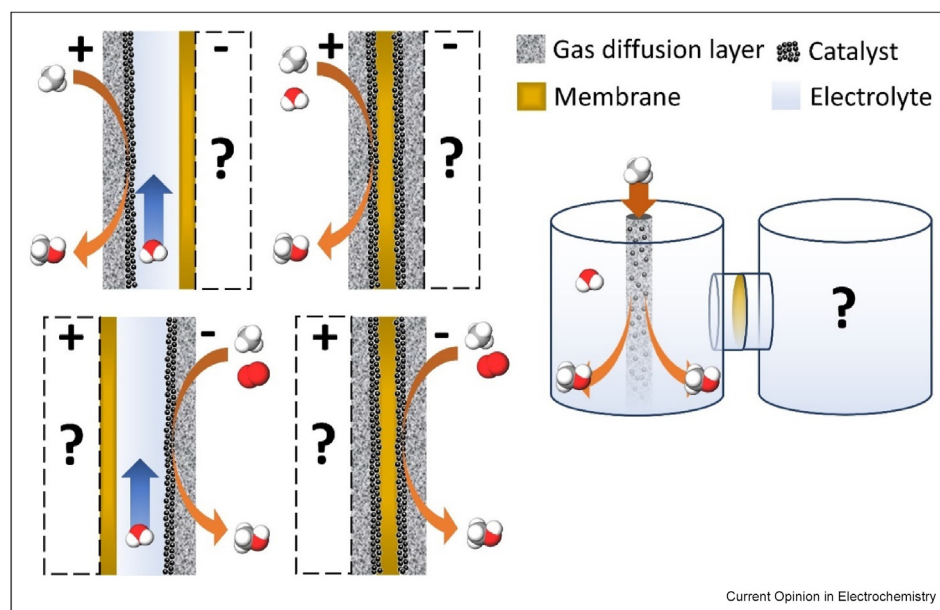
This choice is questionable due to the potential instability of carbon electrodes, particularly when used as anodes or, in general, when exposed to ROS. Moreover, their degradation can lead to formation of CO and CO_2 and can affect and falsify the estimation of conversion rates, product yields and FEs. The use of metal-based materials as gas-diffusion layers/porous transport layers (frits, felts, meshes, foams, etc.) is recommended, as frequently applied in water electrolyzers [47].

- *Questionable selection and characterization protocols of electrocatalysts*

Practical formation rates of CH_3OH , or value-added products in general, are in the range of or below background levels of $0.1 \text{ nmol cm}^{-2} \text{ s}^{-1}$ (equal to $0.002 \text{ ppb cm}^{-2} \text{ s}^{-1}$ or $10 \mu\text{A cm}^{-2}$ partial current density), whereas ultrahigh purity CH_4 gas (99.999%) has hydrocarbon impurity levels in the 0.5- to 2-ppm range (this can already easily lead to false positives). Such low yields (ascribed to low currents and poor selectivity as discussed above) make material discovery challenging.

In dealing with the issue of low product formation rates, the community studying the electrochemical dinitrogen reduction to ammonia has set a virtuous example by agreeing that ammonia production rates can be considered significant only if above $10 \text{ nmol cm}^{-2} \text{ s}^{-1}$ [48]. In addition, quantitative isotope labeling and control experiments (e.g., under inert gas atmospheres, etc.) became a must-include in publications. Such modus

Figure 3



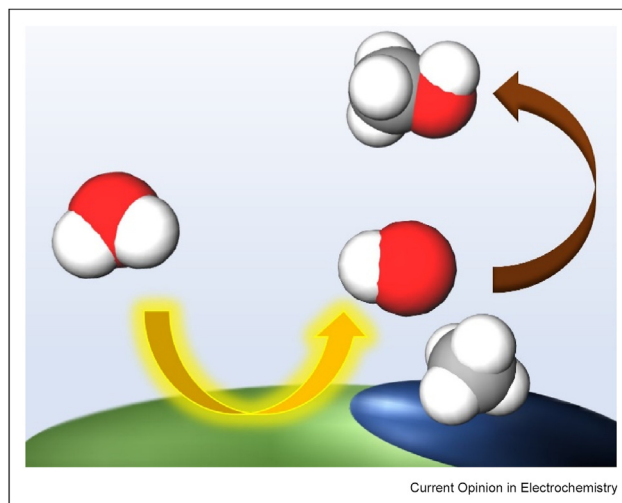
The use of gas-diffusion (left and middle) and hollow-fiber (right) electrodes enables increased mass transport of CH_4 to the reaction sites.

operandi is still not a standard protocol within the SEOM community. Consequently, it is difficult to judge if products identified and reported formation rates are significant or instead due, e.g., to decomposition of carbon-based current collectors, membranes, or impurities. This is worsened by the often-incomplete description of experimental conditions adopted for the electrochemical tests—we believe the more the details the better! There is also no consensus on how to normalize and report product formation rates. Both $\text{nmol cm}^{-2} \text{s}^{-1}$ and $\text{mmol h}^{-1} \text{g}_{\text{catalyst}}^{-1}$ are commonly used. We also recognized a trend in reporting the electrocatalysts' performance as mass-specific current or product formation rate (e.g. $\text{mmol g}_{\text{cat.}}^{-1}$ or $\text{mA mg}_{\text{cat.}}^{-1}$). These nonharmonized figures complicate data comparison across different labs and publications—in fact, the electrocatalyst loading on electrodes (e.g., mg cm^{-2}) and the electrode surface area are often not reported. Thus, the SEOM community would clearly benefit from more harmonized, thorough, and rigorous research protocols and data-reporting metrics to make tangible progress.

Finally, we noted that several studies deal with complex catalysts with poorly defined composition, morphology, and structure. In fundamental research to screen and test working electrodes (i.e., in a three-electrode cell, RDE setups, etc.), we advocate for the use of defined (model) electrode surfaces [49], such as single crystals, physical-vapor-deposited or chemical-vapor-deposited (PVD or CVD) films and highly-defined layers of nanoparticles [50]. This is particularly relevant to discover active catalysts for CH_4 activation by the *direct pathway* (where CH_4 surface adsorption is a key step). For the *indirect pathway*, bifunctional electrocatalysts as depicted in Figure 4 should be investigated, e.g., electrodes consisting of well-known materials for efficient partial water oxidation (to ROS), surface-modified with metals (e.g., nanoparticles) to enable CH_4 surface adsorption—this approach could facilitate the SEOM kinetics by bringing in close vicinity ROS and CH_4 . In general, materials investigated as working electrodes must be selected bearing in mind scalability perspectives and should be based on carbon-free materials (to avoid degradation and false positives) and tested under controlled CH_4 mass transport conditions, that is, by using R(R)DE setups [17]. Even more ideal would be closed gas-tight R(R)DE setups that could operate under high- CH_4 -pressure conditions [39].

Selected promising electrocatalysts should then be tested at relevant currents and examined in view of their stability in a full-cell configuration, e.g. using GDE-based cell designs outlined earlier. Before doing so, however, a first step should be to test the chosen cell design and process parameters to validate that CH_4 oxidation can be operated at relevant conversion rates and currents. For this, PGM electrocatalysts can be a suitable choice, even if the main product is CO_2 .

Figure 4



Proposed mechanism of selective electrochemical oxidation of methane on a bifunctional electrocatalyst for the *indirect pathway* mediated by anodically generated reactive oxygen species from H_2O .

- *Additives—electrolyte composition*

Tuning the electrolyte composition and the formation of solid–electrolyte interface (SEI) provide additional knobs to steer selectivity in electrochemical conversion processes. For example, in the oxidative decarboxylation of acetic acid—the so-called Kolbe oxidation process—a passivating organic layer is formed on PtO_x electrodes, which prevents undesired formation of oxygen in favor of ethane formation with substantial FEs. Interestingly, when the (local) carbonate concentration is increasing, the selectivity of acetic acid (acetate) oxidation changes from ethane toward the formation of CH_3OH , the so-called Hoefer Most reaction. Although the exact reason for the change in selectivity in high local carbonate concentrations is not yet fully understood, these observations could be exploited for the selective conversion of CH_4 . For example, addition of specific amounts of acetate or carbonate to the electrolyte, or mixtures thereof, could be used to determine how surface modification affects the conversion of CH_4 [51]. Evidently, this requires isotopic labeling studies to discriminate whether ethane or CH_3OH would form by partial oxidation of CH_4 or stem from acetate. Moreover, the formation of an SEI might increase the local concentration of the gaseous reactant (CH_4 in this case) at the electrode surface—a concept successfully applied in the lithium-mediated electrochemical reduction of dinitrogen gas to ammonia [52].

To summarize the discussion above, we provide in Table 1 factors and experimental parameters that influence the SEOM.

Table 1

Relevant factors and experimental parameters for the selective electrochemical oxidation of methane.

Factor/experimental parameter	Benefits	Drawbacks
Batch-type cell (H-cell) configurations	Easy to use (assembling, operating, cleaning); Widely used and commercially available; Moderate cost	Accumulation of CH ₃ OH in the electrolyte, by increasing the electrolysis time, cannot be achieved (due to CH ₃ OH oxidation); Product removal is challenging; Difficult to achieve high CH ₄ concentration and mass transport
Flow-cell configurations	Product removal from the electrode surface	Commercially available for, e.g., water or CO ₂ electrolysis, hence the design might require modification/customization; More sophisticated design, operation and cleaning compared to batch cell; Higher cost
Direct pathway	The standard CH ₄ oxidation potential to methanol is less positive than that for the water oxidation reaction, CH ₄ can be activated without competition from WOR; The direct, one-step reaction, might be easier to understand from a mechanistic viewpoint	Slow CH ₄ conversion kinetics; Operating at larger overpotential is counterproductive as WOR begins to compete; CH ₃ OH has an oxidation potential less positive than that of CH ₄ : the formed CH ₃ OH can easily oxidize at the electrode surface to CO and CO ₂
Indirect pathway (anodic)	Can be efficient with an electrocatalyst that is efficient towards ROS generation but lousy in CH ₃ OH oxidation	ROS are usually generated at more positive potentials than CH ₃ OH oxidation, i.e., the formed CH ₃ OH can easily oxidize at the electrode surface to CO and CO ₂
Indirect pathway (cathodic)	Electrode potential can be lower than the oxidation potential of CH ₃ OH	Co-feeding of O ₂ and CH ₄ to the electrode can be complicated
Aqueous electrolyte	Available; cheap; nonhazardous; nontoxic; most commonly used solvent; easy for upscaling	Solubility of CH ₄ in H ₂ O at room temperature and atmospheric pressure (1.4 mM) is lower than in organic solvents
Nonaqueous/organic/electrolyte	Toxicity and volatility; organic solvents might be more reactive than CH ₄ themselves; higher cost	Better solubility of CH ₄ hence higher CH ₄ concentrations can be achieved
Electrolyte additives	Formation of solid–electrolyte interface might increase the local concentration of the gaseous reactant at the electrode surface	Little is known about possible mechanism and solid–electrolyte interface contribution, which hence might be more difficult to understand and control
Atmospheric pressure	Easy to handle; No hazard	Low solubility of CH ₄ , limited concentration
High pressure	Higher solubility; higher concentration; 220-fold increase in the yield compared to atmospheric pressure	Requires special apparatus; more difficult to handle; more risk and hazard
Sheet electrode	Easy to handle; Wide choice of electrode materials; Easy to prepare; Cheap;	Limited mass transport of CH ₄ to the electrode surface; limited product removal; implies a nonzero gap configuration and hence (potentially) higher cell resistance compared to GDEs
Rotating-(ring)-disk electrode	Improved and tunable mass transport of CH ₄ to and product removal from the electrode surface	Requires disk-shaped electrodes hence limited choice of electrode materials/shape/geometry (non-disk-shaped electrodes require adapters); Requires special apparatus; Limited electrode geometric surface area; Expensive;
Gas-diffusion electrode	Gas flow rate and pressure can be controlled to tune the reaction kinetics and achieve an optimal tradeoff between high conversion (low flow rates) and high selectivity (high flow rates)	More difficult to produce and handle; Preparation is multistep process; Limited choice of materials to produce gas diffusion electrodes; Possible operation and stability issues (associated with degradation, flooding, etc.)
Quantitative isotope labeling	Crucial to avoid false positives	Expensive experiments
Control experiments under inert-gas atmospheres	Crucial to avoid false positives	N.A.
Complex composition of electrode material	Possibly higher product formation rate/better selectivity	Unknown reaction mechanism and nature of active component/sites; Poorly defined composition, morphology, and structure
Defined (model) electrode surfaces	Relevant to discover active catalysts/catalytically active sites for CH ₄ activation	Requires single crystals, physical or chemical vapor deposited films or defined nanoparticle systems

Conclusions

Despite many challenges, the concept of methane-to-methanol conversion remains a promising alternative to the energy-intensive and environmentally unfriendly SMR route. Currently, the SEOM is hampered by poor conversion rates and selectivity. The use of suboptimal process conditions such as low methane concentration and poor mass transport, common in a significant number of reports on the subject, makes the supply of reactant (CH₄) the main rate-limiting step. To ramp up conversion rates and to get insights into the mechanism of C–H activation and selective oxidation, research should be intensified in investigating a broader process-parameter space, e.g., by operating at high pressure, by tuning the electrolyte composition, or using nonaqueous media. This might enable operation at CH₄ concentrations that are orders of magnitude higher than in water at atmospheric pressure. Physical and chemical vapor deposition techniques have become a standard in electrode preparation for fundamental study on water and CO₂ electrolysis. We argue that the use of highly defined (model) electrocatalysts instead of the often-used complex and highly heterogeneous counterparts, in combination with in-situ spectroelectrochemical techniques, will advance the mechanistic understanding of selective methane electrochemical conversion and unleash the discovery of promising electrocatalyst materials. Moreover, we attribute the limited success also to the lack of control experiments, such as quantitative isotope labeling, which makes it complicated to assess if the identified products and reported yields originate from SEOM or, instead, are due to contamination or degradation of cell components. Similarly, unconventional and nonhomogenized reporting of figures of merit complicates comparing results across different publications and from different labs, whereas a more orchestrated research effort based on defined research protocols could accelerate progress in the field. Finally, we suppose that, even if not successful in achieving high currents and product yields, the publication of well-executed investigations with thorough descriptions of used methods and of experimental procedures can also be beneficial for the community.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Marco Altomare reports financial support was provided by Dutch Research Council. Georgios Katsoukis reports financial support was provided by Dutch Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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