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Clean Heat and Power from Hydrogen

CLEAN HEAT AND POWER FROM HYDROGEN

Grant agreement no.: 101137799
Start date: 01.01.2024 – **Duration**: 48 months.
Project Coordinator: Anders Ødegård, Sintef

DELIVERABLE REPORT

D3.4: PROX CATALYST FOR IMPROVED CHEMICAL CO OXIDATION DURING AIR BLEEDING	
Due Date	M12 2024
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Workpackage	3
Workpackage Leader	UFR
Lead Beneficiary	SINTEF
Date released by WP leader	28th February 2025
Date released by Coordinator	28th February 2025

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R	*Document, report*	X
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DEC	*Website*	
DMP	*Data management plan*	
OTHER	*Software, algorithms, models*	

SUMMARY	
Keywords	PROX, Preferential Oxidation Catalysts, CO Oxidation, CO removal, Impurity Tolerant Fuel Cell Catalysts, Contaminated Hydrogen
Abstract	This report discusses the integration of carbon monoxide preferential oxidation (CO-PROX) catalysts into the membrane electrode assembly (MEA) of a proton exchange membrane fuel cell (PEMFC) system. This integration is essential for improving the system's tolerance to CO impurities commonly present in industrial hydrogen. The report explores the different mechanisms behind CO-PROX to gain understanding about CO-PROX catalyst key factors including selectivity and efficiency. Special focus lies on commercially available catalysts, primarily noble metal-based systems like platinum, palladium, and gold. These catalysts offer high activity and selectivity for CO oxidation at low temperatures and are evaluated for their integration into PEMFCs, highlighting their catalytic properties, efficiency, and challenges. Additionally, cost-effective alternatives like base metal oxides are discussed, emphasizing their potential for commercialization despite certain limitations in stability and selectivity. The report also investigates important performance factors such as catalyst activity, stability, and resistance to deactivation. It provides an overview of various types of PROX catalysts, both noble metal-based and emerging alternatives. Special attention is given to the CO-PROX catalyst requirements in the context of catalyst layer (CL) integration. Furthermore, the role of commercial PROX catalysts and their integration into fuel cell systems is reviewed, alongside alternative catalyst designs aiming at improving selectivity and long-term performance. The findings seek to provide guidance for selecting suitable CO-PROX catalysts for anode CL integration, considering both performance and operational practicality for the hydrogen purification required in PEMFCs.
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D3.4 PROX CATALYSTS FOR IMPROVED CHEMICAL CO OXIDATION DURING AIR BLEEDING

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1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are at the forefront of clean energy technologies, offering high efficiency and minimal emissions by directly converting chemical energy into electricity. Using hydrogen as a fuel, PEMFCs enable applications in transportation, stationary power generation, and portable energy systems. Unlike traditional combustion-based systems, fuel cells produce only water as a byproduct, making them a key technology for achieving the global decarbonization goals.[1] However, the widespread adoption of PEMFCs is hindered by the insufficient purity of hydrogen fuel. These impurities can originate from hydrogen production, storage, or transmission through gas pipelines, introducing contaminants such as carbon monoxide (CO). CO is particularly detrimental, as it strongly adsorbs onto the active sites of the platinum-based fuel cell catalysts, significantly reducing system efficiency and lifespan.[2]

To ensure optimal fuel cell performance, CO levels in the hydrogen stream must be reduced below 10 ppm to impede degradation of the Pt anode catalyst.[3] Various purification methods, including pressure swing adsorption (PSA), membrane separation, and selective methanation, are employed. This however increases the capital expenditure of the PEMFC system and imposes additional challenges with respect to system integration.[4]

An alternative approach is the preferential oxidation (PROX) of CO, which selectively oxidizes CO to CO_2 while minimizing hydrogen consumption. By embedding CO-PROX catalysts directly into the catalyst layer of the fuel cell, the system's impurity tolerance can be improved without increasing the fuel cell stack size or requiring a separate CO-PROX unit.[4]

Current research focuses on the development of advanced PROX catalysts with the goal to improve catalytic activity, selectivity, and stability. The ongoing research and development in the field of PROX catalysis is critical for the purification of hydrogen, to comply with international purity standards and to ensure high performance and long-term operation of PEM fuel cells to deliver clean power and heat.[5]

2. SCOPE

This work aims to identify and evaluate **commercially available CO-PROX catalysts** suitable for integration into the catalyst layer of a PEM fuel cell, with the goal of enhancing system performance and ensuring long-term operation by effectively mitigating CO poisoning effects.

The discussion provides a framework for integrating PROX catalysts into the PEM fuel cell by exploiting the oxygen utilization through air bleeding. Air bleeding involves the intentional introduction of small amounts of oxygen or air into the anode gas feed to counteract CO adsorption on the catalyst surface. In PEM fuel cells, one possible source of oxygen is O_2 diffusion through the membrane, from the cathode to the anode side, also being referred to as **internal air bleed**.

At the active sites of the CO-PROX catalyst, CO can react with oxygen from the air bleed, forming CO_2 and thereby reducing CO contamination. While the effectiveness of CO removal depends on

the specific type of catalyst and the oxidation mechanisms employed, for long-term fuel cell operation, factors such as catalyst stability under typical operating conditions must be considered. This report extends beyond the selection of suitable CO-PROX catalysts for fuel cell integration, by offering research perspectives and outlining different potential integration approaches to advance the widespread use of PEM fuel cell systems that can operate on industrial hydrogen to comply with international standards for the hydrogen quality.

3. DISCUSSION

3.1 Brief introduction to CO-PROX

Hydrogen, as a clean energy carrier, is essential for the operation of proton exchange membrane fuel cells (PEMFCs). However, industrial hydrogen, often derived from hydrocarbon reforming or as a byproduct of chemical processes, usually contains impurities like carbon monoxide (CO), hydrogen sulphide (H_2S), and nitrogen compounds. These contaminants originate from various stages of hydrogen production, storage, and distribution, including incomplete hydrocarbon conversion during reforming or contamination in gas pipelines and storage facilities. Among these, CO poses a significant challenge for PEM fuel cells due to its strong adsorption onto the platinum-based catalyst being commonly used in the fuel cell system.[6]

The presence of even trace amounts of CO in the hydrogen feed severely impacts the functionality of PEMFCs. CO amounts even as low as 10 ppm can lead to a substantial performance decrease in low-temperature PEM fuel cells (operating below 120 °C). This is because of the strong interaction between the impurity molecules and the platinum-based catalyst, which is located at the heart of the fuel cell, the membrane electrode assembly (MEA). CO molecules can occupy active catalytic sites, thereby inhibiting the electrochemical oxidation of hydrogen and reducing overall fuel cell efficiency.[4] This phenomenon, known as catalyst poisoning, occurs because platinum has a stronger binding affinity for CO than for hydrogen, making the removal of CO from the catalyst surface particularly challenging.[7]

To mitigate CO poisoning, various hydrogen purification techniques have been developed, including pressure swing adsorption (PSA), membrane separation, water-gas shift (WGS) reaction, selective methanation (SMET), and CO preferential oxidation (CO-PROX). While effective for the large-scale purification of hydrogen, PSA suffers from low recovery rates and large space requirements. Membrane separation offers compactness and energy efficiency but relies on materials like palladium alloys, which are expensive and prone to degradation. Via the water-gas-shift (WGS) reaction, CO concentrations can be lowered significantly. However, thermodynamics limits the WGS reaction to around 0.5 – 2 vol.% CO, necessitating further cleanup steps.[6]

In contrast, CO-PROX stands out as a highly effective and selective purification method for fuel cell applications. It involves the selective oxidation of CO to CO_2 in the presence of excess hydrogen fuel by using oxygen or air as oxidant. Unlike other purification methods, the CO-PROX method combines simplicity, cost-effectiveness, and high selectivity. It can reduce CO concentrations to far below 10 ppm, meeting the stringent purity requirements for the hydrogen
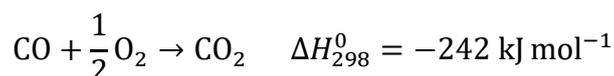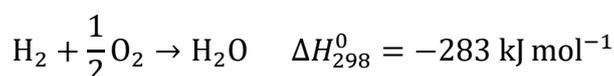
used in PEMFCs and thereby allowing for long-term catalyst stability, enhancing system performance under realistic operating scenarios.[6]

3.2 CO-PROX mechanisms

Understanding the different CO oxidation mechanisms is vital for assessing and selecting possible CO-PROX catalysts. Several mechanisms have been identified, depending on the type of catalyst as well as on the operating conditions:

- Langmuir-Hinshelwood (L-H) mechanism: commonly observed in noble metal catalyst systems like Pt, Pd, or Au.[8]
- Mars-van Krevelen (MvK) mechanism: particularly associated with catalysts featuring a high oxygen storage capacity (OSC), e.g. CuO/CeO$_2$-based catalysts.[8]
- Eley-Rideal (E-R) mechanism: found in catalytic systems where gaseous CO directly reacts with adsorbed oxygen species rather than competing for active sites.[9]
- Termolecular Eley-Rideal (TER) mechanism: observed in single-atom catalysts (SAC), such as Pt- or Fe-based SACs that offer high activity under specific conditions.[8]

In CO-PROX catalysis, one major challenge is the competing oxidation of hydrogen fuel. This reaction of hydrogen with oxygen decreases the overall efficiency of the CO-PROX reaction. Therefore, CO-PROX catalysts must exhibit high selectivity in favour of CO oxidation to CO$_2$ while minimizing the competing hydrogen oxidation reaction.[7]

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H_{298}^0 = -283 \text{ kJ mol}^{-1}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad \Delta H_{298}^0 = -242 \text{ kJ mol}^{-1}$$

A fundamental understanding of these mechanisms enables the rational design of CO-PROX catalysts featuring enhanced CO selectivity, stability, and long-term performance, which is essential for effective and prolonged PEM fuel cell operation.

3.2.1 Langmuir-Hinshelwood mechanism

The Langmuir-Hinshelwood (L-H) mechanism is one of the most widely studied pathways for catalytic CO oxidation. This mechanism is particularly relevant in noble metal catalysis such as Pt, Pd, and Au, which are interesting for CO oxidation because of their good stability and high catalytic activity. The L-H mechanism describes the reaction progressing entirely on the surface of the catalyst, where both, CO and O$_2$ molecules, competitively adsorb on adjacent active sites of the catalyst.[8]

The fundamental steps of the L-H mechanism include adsorption, reaction, and desorption processes. First, CO and O$_2$ molecules adsorb onto the active catalytic sites, typically the metal

or metal oxide surface. Following adsorption, the oxygen molecules subsequently dissociate into individual oxygen species, which can then react with the surface-bound CO to form CO_2. Finally, the produced CO_2 desorbs from the surface, leaving behind active sites that are available for following CO-PROX reactions.[7]

$$1.\ CO +\ ^* \rightarrow CO^*$$

$$2.\ O_2 + 2\ ^* \rightarrow 2\ O^*$$

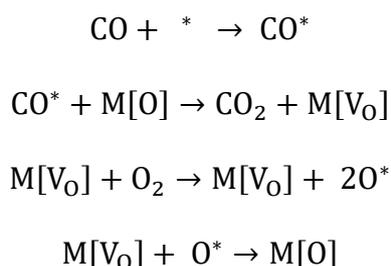$$3.\ CO^* + O^* \rightarrow CO_2 + 2\ ^*$$
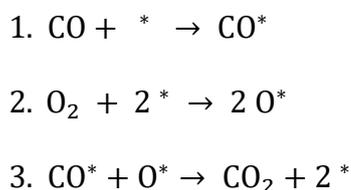
Here, * denotes an active site. Because CO and O_2 compete for active sites, the relative adsorption energies and the site availability are critical factors for the efficiency of the reaction. One advantage of the L-H mechanism is its reliance on surface reactions, which allows precise control over the catalytic activity through careful catalyst design. However, the mechanism also introduces challenges, including competitive adsorption between CO and H_2. Since H_2 may also react with O_2 to produce unwanted by-product water, the oxidation of hydrogen results in decreased selectivity which adversely affects CO-PROX efficiency.[8]

Catalysts employing the L-H mechanism are designed to maximize CO adsorption while minimizing interaction with H_2. For instance, Pt-based catalysts are often modified with dopants or alloyed with other metals, such as Au or Pd, to fine-tune the adsorption properties and improve selectivity toward high CO oxidation.[8]

3.2.2 Mars-van Krevelen mechanism

The Mars-van Krevelen (MvK) mechanism is a cornerstone model for CO-PROX reactions. It describes the reaction of CO with lattice oxygen from the catalyst or catalyst support, rather than proceeding via adsorbed molecular oxygen species. Here, the catalytic cycle progresses with the formation of CO_2 which leaves behind an oxygen vacancy. This vacancy is then replenished by molecular oxygen from the gas phase to regenerate the catalyst surface.[10]

The MvK mechanism follows distinct steps, starting with CO adsorption on the catalyst surface. The adsorbed CO reacts with lattice oxygen to form CO_2. Removal of CO_2 leaves behind an empty oxygen vacancy (V_O) as described below[7]:

$$CO +\ ^* \rightarrow CO^*$$

$$CO^* + M[O] \rightarrow CO_2 + M[V_O]$$

$$M[V_O] + O_2 \rightarrow M[V_O] + 2O^*$$

$$M[V_O] + O^* \rightarrow M[O]$$

Here, M[O] represents a metal site adjacent to lattice oxygen and M[V_O] denotes a metal site with an oxygen vacancy. Adsorbed oxygen can fill the vacancy to restore the lattice oxygen, completing the catalytic cycle.

This mechanism mainly relies on the catalyst's capability to take up and release oxygen, a property which is known as oxygen storage capacity (OSC). Reducible oxide supports, such as cerium oxide (CeO_2) and its composites are particularly following the MvK mechanism due to their high OSC and ability to sustain oxygen vacancies without facing the issue of structural degradation.[10]

Catalysts employing the MvK mechanism typically exhibit strong metal-support interactions (SMSI), that ease oxygen vacancy formation and reoxidation. One prominent example is CuO/CeO_2-based catalysts which have been studied extensively due to their ability to activate lattice oxygen even at temperatures as low as 50 °C. The interface between CuO and CeO_2 plays a pivotal role, as synergistic effects reduce the activation energy for oxygen vacancy formation allowing efficient CO oxidation.[7]

Recent research has highlighted the formation of oxygen vacancies as rate-determining step in the MvK mechanism. The rate-determining step involves the reduction of metal sites and breaking of the metal-oxygen bond, which can be modified by dopants or alloying. For example, the addition of Pd or Cu to CeO_2-ZrO_2 systems was found to significantly improve the kinetics of oxygen vacancy formation, leading to enhanced catalytic performance of the CO oxidation reaction.[10]

One advantage of the MvK mechanism with respect to CO-PROX is its ability to mitigate the competitive adsorption of H_2 and CO on the catalyst's surface. Unlike the Langmuir-Hinshelwood mechanism, the MvK pathway directly involves lattice oxygen and as a result reduces the likelihood of unwanted H_2 oxidation. By optimizing the interaction between CO and lattice oxygen, selectivity towards CO oxidation via the MvK mechanism can be even increased further.[11]

3.2.3   Eley-Rideal mechanism

The Eley-Rideal (E-R) mechanism presents another CO-PROX reaction pathway. It describes a suprafacial reaction in which a gaseous reactant directly reacts with an adsorbed species, however without significant movement of either species along the catalyst surface. This mechanism is distinct from other processes that focus on surface-bound species (e.g. Langmuir-Hinshelwood or Mars-van Krevelen mechanism), as it does not rely on the adsorption of both reactants. Instead, CO oxidation proceeds by leveraging the interaction of a gaseous CO molecule with pre-adsorbed oxygen (O*) on the catalyst surface.[12]

The first step in the E-R mechanism is the adsorption of molecular oxygen (O_2) onto the catalyst surface. This implies that the catalytic surface must provide active sites (*) to which O_2 can bind and subsequently dissociate. In this case, one O_2 molecule interacts with two neighbouring active sites that enable the dissociation into two reactive oxygen atoms. The efficiency of this step

strongly depends on the adsorption energy of O_2, which itself depends on the composition and electronic properties of the catalyst.[9]

$$O_2 + 2\,^* \rightarrow 2\,O^*$$

Once the oxygen molecules dissociated into adsorbed O^* species, the next step is the reaction of a gaseous CO molecule with one of these adsorbed oxygen atoms. In this step, the gaseous CO molecule directly reacts with the pre-adsorbed oxygen atom to form CO_2, which then desorbs into the gas phase. The active site * is freed and becomes available for another cycle of adsorption and reaction. The direct interaction avoids the necessity of CO and O_2 occupying the surface simultaneously, distinguishing the Eley-Rideal mechanism from the Langmuir-Hinshelwood mechanism.[9]

$$CO + O^* \rightarrow CO_2 + {}^*$$
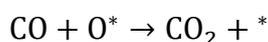
The direct reaction of gaseous CO with adsorbed oxygen minimizes site competition, making this mechanism particularly suitable for systems where H_2 selectivity is crucial, as is the case for PEM fuel cells. Additionally, the E-R pathway complements other mechanisms like the L-H and MvK mechanism as these reaction pathways often take place simultaneously in mixed catalyst systems to give enhanced overall performance of the CO-PROX reaction.

3.2.4 Termolecular Eley-Rideal mechanism

The Termolecular Eley-Rideal (TER) mechanism represents an advanced and less common pathway for CO oxidation. It is relevant in high-performance single-atom catalysts (SACs) and specialized noble metal systems, where unique catalytic dynamics can enhance reaction rates and selectivity compared to conventional mechanisms such as Eley-Rideal or Langmuir-Hinshelwood pathway.[12]

The TER mechanism involves the simultaneous interaction of two adsorbed CO molecules with a single adsorbed O_2 molecule on the catalyst surface. This trimolecular interaction forms an intermediary species $(OCO-OCO)^*$, which can further dissociate to yielding two CO_2 molecules. Finally, CO_2 removal regenerates the active sites of the CO-PROX catalyst.[12]

$$2\,CO + O_2 + 3\,^* \rightarrow 2\,CO^* + O_2^*$$

$$2\,CO^* + O_2^* \rightarrow (OCO - OCO)^*$$

$$(OCO - OCO)^* \rightarrow 2\,CO_2 + 3\,^*$$
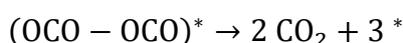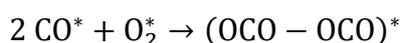
The TER mechanism is particularly interesting in SACs because of their unique electronic and spatial properties. SACs, such as Pt or Fe single atoms excel in performance by benefiting from the TER mechanism. Their well-defined active sites provide the necessary environment for the trimolecular interaction. Studies show that SACs exhibit lower energy barriers (as low as 0.20 eV

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for the rate-determining step) compared to conventional L-H or E-R pathways. Additionally, the trimolecular interaction, compared to bimolecular mechanisms, enables higher reaction rates due to its fast CO to CO_2 conversion kinetics.[13]

The unique TER reaction dynamics make it ideally suited for advanced CO-PROX applications. Its ability to operate highly efficient at low temperatures while being highly selective toward CO oxidation aligns well with the requirements for PEMFC systems. Moreover, compatibility with advanced SACs and noble metal systems make systems that rely on the TER mechanism highly relevant in next-generation CO-PROX catalysts.

3.3 Key performance factors

3.3.1 Temperature

The selectivity of the CO-PROX reaction, defined as the preference for CO oxidation over H_2 oxidation, is highly temperature dependent. The reaction temperature influences both, the kinetic but also thermodynamic characteristics of the catalyst, and directly affects the competing H_2 oxidation reaction.

At lower temperatures, many CO-PROX catalysts exhibit high selectivity towards CO oxidation as the activation energy for CO oxidation is lower than that for the H_2 oxidation.[14] For example, CuO/CeO_2 catalysts achieve complete CO conversion at 80°C with minimal H_2 oxidation. The superior performance at low temperatures is attributed to the CuO/CeO_2 interface, providing active sites that preferentially oxidize CO over H_2 as well as the oxygen transfer capability of CeO_2, enhancing the redox properties which promotes CO oxidation.[15]

Gold-based catalysts, such as AuCu bimetallic systems, also exhibit high selectivity within a low temperature regime (30 - 100°C) due to electronic interactions between Au and Cu. This increases CO adsorption, thereby levering CO conversion to CO_2 and suppresses H_2 dissociation, further contributing to increased selectivity.[16]

The strong temperature dependence of CO-PROX highlights the need for optimized reaction conditions which are tailored to the specific catalyst system. For Cu-based catalysts, it is crucial to operate below 100 °C for maintaining high CO selectivity, as higher temperatures lead to an increase of the competing H_2 oxidation. In particular, CuO/CeO_2 catalysts selectively oxidize CO between 50–100 °C, achieving efficient CO removal without significant hydrogen oxidation.[15]

Other catalysts such as AuCu bimetallic catalysts or platinum-group metals supported on CeO_2 offer a broader temperature window ranging from 30 °C to 100 °C, benefiting from synergistic metal interactions that suppress hydrogen oxidation.[16]

Summarized, CO-PROX catalysts must be selected according to the specific operating temperature of the fuel cell stack to ensure high CO oxidation activity as well as selectivity.

3.3.2 Support materials and metal-support interactions

The support material plays a critical role in the performance, selectivity, and stability of the CO-PROX catalyst. The catalyst support affects key catalytic properties, including catalyst dispersion (preventing sintering and improving active site availability), electronic interactions (modifying adsorption energies for CO and O_2), as well as redox behaviour and oxygen storage capacity (OSC) allowing for enhanced catalytic activity through participation of lattice oxygen.[17, 18]

The support material's ability to interact with the active metal catalyst is critical. The so-called metal-support interactions (MSI) is categorized into two primary types: strong metal-support interactions (SMSI) and electronic metal-support interactions (EMSI). SMSIs, first identified on TiO_2-supported metals, involve partial encapsulation of metal particles by the support under reducing conditions. In contrast, EMSIs rely on electron transfer between metal and support material, which modifies the electronic structure of the active metal and thereby influences CO adsorption and the reaction pathways.[7]

Well-known support materials for CO-PROX catalysts are reducible supports, like ceria (CeO_2). These are widely employed due to their high oxygen storage capability and good redox properties making them well-suited CO-PROX support materials. The high oxygen mobility at the metal-support interface enables the Mars-van Krevelen mechanism because lattice oxygen from the support can participate in the oxidation reaction of adsorbed CO to CO_2.[19] This makes reducible supports highly interesting materials for CO-PROX as it improves both, catalytic activity and selectivity.

Non-reducible supports like alumina (Al_2O_3) and silica (SiO_2) are widely used for CO oxidation due to their stability and ability to enhance particle dispersion. However, they exhibit low oxygen mobility, limiting their effectiveness in redox reactions. While Al_2O_3 and SiO_2 are known to exhibit high thermal stability and surface area, their inherent low oxygen mobility limits the redox activity and therefore applicability as CO-PROX catalyst support.[20]

Inert supports like silicon carbide (SiC) are particularly advantageous in case of harsh PEM fuel cell operating conditions. By stabilizing the metallic phase, the inert nature minimizes the formation of irreducible mixed oxides, thereby preserving the activity of the supported metal catalysts. This avoids unwanted side reactions.[21]

With respect to integrating CO-PROX catalysts into the fuel cell, porous carbon supports offer a variety of advantages including high surface area and tuneable porosity to promote uniform catalyst dispersion, excellent electrical conductivity (efficient electron transfer within the catalyst layer) as well as chemical stability. One key advantage of using carbon supports is their potentially straightforward integration into the fuel cell catalyst layer. As conventional fuel cell catalysts use carbon-based support, established fabrication protocols could be easily adopted for CO-PROX layer manufacturing, as is described in later sections of this text.

3.3.3 Stability and durability

The stability and durability of CO-PROX catalysts remain critical challenges with respect to PEM fuel cell integration. Long-term stability is essential to prevent catalyst deactivation, structural degradation, and loss of selectivity over time.

Gold-based catalysts, such as Au/CeO_2, are highly active at low temperatures. However, their performance declines due to sintering, loss of active surface oxygen, and changes in the oxidation states of Au species during extended operation. During long-term CO-PROX reactions, Au/CeO_2 experience reduction of Au^{3+} and Au^+ species to metallic Au^0, lowering their ability to activate oxygen which is required for maintaining catalytic efficiency.[17]

The ceria support itself can also undergo redox reactions, with an increase in the Ce^+/Ce^{4+} ratio being linked to oxygen depletion from the ceria lattice. This hinders the oxygen supply necessary for CO oxidation and contributes to catalyst deactivation over time. Moreover, sintering of the gold nanoparticles can further contribute to this decline by reducing the active surface area available for CO adsorption and oxidation.[17]

Bimetallic systems, such as AuCu catalysts, have been explored to enhance both, the stability and selectivity of CO-PROX catalysts. Such systems benefit from electron transfer between the two metals to strengthen CO sorption while weakening H_2 dissociation. These synergetic effects minimize the competing H_2 oxidation, thereby extending the temperature window for effective CO removal to maintain stability over prolonged usage.[16]

Platinum-group metal catalysts supported on ceria, such as Pt/CeO_2, offer another robust alternative, as they combine high activity with improved resistance to thermal degradation compared to their alumina-supported counterparts. Solution combustion synthesis methods have been shown to produce highly dispersed metal nanoparticles with strong metal-support interactions which enhance stability. However, at elevated temperatures, challenges such as phase transformations and complex Rh and Ru structural changes persist.[14]

Base metal oxides, like Co_3O_4, present cost-effective options but are prone to undesirable reduction of their metallic state as well as sintering processes under typical operating conditions. These changes result in reduced selectivity and increased H_2 consumption through competing reactions such as methanation. Advanced in situ and in operando characterization techniques have been employed to identify the different degradation mechanisms showing correlations between structural changes and the resulting catalytic performance.[22]

In the case of PEM fuel cell operation, one major disadvantage of Co_3O_4 is cobalt leaching to the cathode site. Co^{2+} leaching can lead to depletion of active metal in the CO-PROX catalyst by migrating into the proton exchange membrane. The cobalt ions can then replace proton sites resulting in a worsening of ionic conductivity.[23]

3.1 Types of CO-PROX catalysts

3.1.1 Noble metal catalysts

Noble metals, such as gold, platinum, palladium, and ruthenium have attracted significant interest as catalysts for CO oxidation due to their excellent catalytic activity, selectivity, and stability. This makes noble metals particularly valuable for removing CO from hydrogen-rich gas streams which is critical for proton exchange membrane fuel cells, where even trace amounts of CO can poison the catalyst on the fuel cell anode.

Among the noble metals, Au-based catalysts are particularly interesting with respect to their outstanding catalytic performance at low temperatures. Bulk Au is inert under ambient conditions, but when being finely dispersed in the form of nanoparticles (NP) with sizes smaller than 5 nm, the catalytic activity of Au with respect to PROX of CO drastically increases. This is mainly attributed to an increase in available Au surface atoms. This phenomenon was first observed by Haruta et al. who demonstrated that Au NPs supported on metal oxides like TiO_2 exhibit outstanding CO oxidation activity at low temperatures. The activity of Au NPs is highly dependent on the particle size and the nature of the support, as reducible metal oxides such as CeO_2, TiO_2, and MnO_2 provide oxygen vacancies and facilitate oxygen activation at the metal-support interface. For instance, gold supported on CeO_2 (Au/CeO_2) shows enhanced catalytic activity since CeO_2 stabilizes cationic Au species (Au^{3+}) and provides lattice oxygen participating in the reaction via the Mars-van Krevelen mechanism. The interaction between Au and CeO_2 creates an active site at the interface, where CO and O_2 can adsorb and react. The redox properties of CeO_2 also stabilize the active sites, preventing Au particle agglomeration during the reaction. Further, Au/FeO_x catalysts were reported to be highly active for CO oxidation, making them interesting for CO-PROX application in PEM fuel cells.[24]

Similarly, TiO_2 and MnO_2 supports improve NP the dispersion and offer increased CO oxidation activity by their reducible nature. For instance, Au/TiO_2 exhibits strong metal-support interaction (MSI) yielding highly dispersed Au species being active even at low temperatures around 50°C.[25, 26] Au/MnO_2, on the other hand, benefits from MnO_2's redox properties and its role in supplying oxygen species to facilitate CO oxidation. In addition to the particle size and support effects, the electronic state of Au also plays a pivotal role in its catalytic performance. Cationic Au species (Au^{3+} or Au^+) are significantly more active for CO oxidation than neutral Au, as they enhance O_2 activation and thus promote CO oxidation. The stabilization of such cationic Au species is strongly influenced by the choice of support material. Here, reducible oxides provide a favorable environment for maintaining the oxidized state of Au. However, despite their exceptional performance, gold-based catalysts are sensitive to H_2O and CO_2 at higher temperatures, leading to catalyst deactivation over time. However, with respect to a PEM fuel cell operating at lower temperature, Au-based catalysts are highly interesting for PEM fuel cell integration.[26]

Pt-based catalysts, on the other hand, are amongst the most extensively studied CO-PROX catalysts since they show superior performance across a range of temperatures, especially below 200 °C. Platinum exhibits high CO oxidation activity but is also prone to CO poisoning (i.e. strongly adsorbed CO molecules block active Pt sites). This limits the catalyst's performance at low

temperatures. To address this, Pt catalysts can be modified by incorporation of hydroxyl groups (OH) and formation of PtO_x species, which improve CO oxidation while suppressing hydrogen oxidation. For example, $PtO(OH)_x$ which is formed during the reaction can act as an active intermediate to facilitate the oxidation of CO to CO_2.[27]

Employing single-atom Pt catalysts has emerged as efficient strategy to maximize Pt utilization while minimizing CO poisoning. Single Pt atoms anchored on alumina or silica supports showed exceptional activity and selectivity for CO-PROX. In these systems, isolated Pt atoms exhibit weaker CO adsorption in comparison to conventional Pt nanoparticles, making the active sites more accessible for the oxygen required for CO oxidation. Another example includes Pt single atoms with high loading being stabilized by hydroxyl species on alumina. Those achieved 99.8 % CO conversion efficiency and 70 % CO selectivity at relatively mild operating temperatures of 110 °C. Such catalysts also showed remarkable stability under prolonged operating times, required for fuel cell applications.[27]

The choice of support in Pt-based (single-atom) catalysts is equally significant. Reducible supports facilitate the formation of active Pt-O species and enhance the oxidation state of Pt, thereby improving CO oxidation activity. For example, Pt/CeO_2 catalysts demonstrate excellent low-temperature CO oxidation performance due to the synergistic interaction between Pt atoms and the oxygen vacancies on the CeO_2 surface. This interaction can stabilize the active Pt species while ensuring facile activation of O_2 molecules at the metal-support interface.[27]

While gold and platinum dominate CO-PROX research, other noble metals such as Pd, Rh, Ir and Ru also demonstrated notable catalytic performance, albeit with some limitations. Palladium exhibits strong CO adsorption characteristics, which can block active sites and reduce overall efficiency. However, alloying Pd with other metals and modification of the support can mitigate this effect and improve performance. Pd catalysts are often studied for their ability to selectively oxidize CO while withstanding deactivation, particularly when supported on reducible oxides like CeO_2.[8]

Rhodium and ruthenium catalysts have shown potential in preferential CO oxidation, particularly in the form of small clusters or alloyed systems. Rhodium catalysts benefit from efficient CO and O_2 activation, however their high cost and lower selectivity compared to Au and Pt limits their use in commercial applications. Ruthenium-based catalysts, particularly Ru clusters, exhibit high activity at low temperatures but suffer from competitive hydrogen oxidation, which leads to decreased CO-PROX selectivity.[5]

3.1.2 Base metal oxide catalysts

Metal oxide catalysts share several characteristics that make them particularly suitable for the CO-PROX reaction. A key feature is their ability to facilitate the redox (Mars-van Krevelen) mechanism in which lattice oxygen participates directly in CO oxidation and is subsequently replenished by gas-phase oxygen. The oxygen mobility, oxygen vacancy formation, and interaction with CO are critical factors determining their activity and selectivity. Metal oxides generally exhibit high stability under reducing and oxidizing conditions, which is advantageous

with respect to their durability during long-term operation. Additionally, their ability to tune oxidation states enables precise control over catalytic performance, particularly for multivalent metals like copper, cerium, manganese and cobalt.

Copper oxides, particularly CuO and its composites, are among the most widely studied materials for CO-PROX due to their excellent activity and selectivity at low temperatures. CuO_x/CeO_2 catalysts exhibit remarkable performance, with strong synergistic interactions between copper and cerium species. In these systems, Cu^+ species at the interface are identified as the active sites for CO oxidation, where cerium plays a critical role in oxygen vacancy generation and lattice oxygen replenishment. Operando studies have shown that oxygen vacancies enhance the reducibility of CuO_x species and facilitate faster CO oxidation compared to H_2 oxidation.[28]

The redox interplay between Cu^+ and Cu^{2+} states being stabilized by the ceria surface allows for CO oxidation at low temperatures while simultaneously suppressing H_2 oxidation. Studies also demonstrated the great impact of the synthetic approach (e.g. surfactant-assisted hydrothermal processes) on the dispersion of CuO_x species and oxygen vacancy density. For instance, CuO-cryptomelane catalysts exhibited high performance by exploiting a similar redox interplay. Here, cryptomelane's Mn^{3+}/Mn^{4+} cycle was hypothesized to play a key role in stabilizing active Cu^+ species and increasing oxygen mobility. However, the thermal stability of CuO-cryptomelane is of concern as spinel Mn_3O_4 formation may occur upon long-term operation. Nonetheless, these catalysts remain promising because of their well-tuneable properties, low material costs, and low dependence of the activity on water and CO_2 concentrations.[29, 30]

MnO_x exhibits promising CO-PROX activities due to its unique redox cycling capability between Mn^{3+} and Mn^{4+} states. Cryptomelane-type manganese oxides demonstrate significant catalytic performance when doped with transition metals like Cu or Co. The cryptomelane structure, characterized by its tunnel framework embedding water, enhances oxygen mobility and features active oxygen species required for CO oxidation.[30]

Interestingly, the incorporation of copper species into MnO_x materials improves their performance by creating additional active sites and enhancing oxygen vacancy formation. The interplay between Cu^+ and Mn^{3+}/Mn^{4+} states further drives CO oxidation, even at low temperatures.[30] DFT-based models have confirmed MnO_x catalysts to selectively oxidize CO at Mn(IV) sites, while significantly suppressing hydrogen oxidation.[31]

However, MnO_x systems exhibit lower intrinsic oxygen mobility compared to ceria-based catalysts. To address this, studies researched the presence of water vapor and concluded that the vapor can stabilize the cryptomelane structure and act as an auxiliary oxygen source improving both activity and stability.[30]

Cobalt-based oxides, such as Co_3O_4, have been explored as effective catalysts for CO-PROX as well, particularly due to their ability to provide oxygen vacancies and activate lattice oxygen. Mixed metal oxides like $CuCoMnO_x$ have gained recent attention because of their superior performance being attributed to the strong synergistic interactions amongst copper, cobalt, and manganese. These ternary systems benefit from enhanced oxygen mobility, active site generation, and increased CO adsorption capabilities due to the formed Cu^+ species. Photothermal studies on $CuCoMnO_x$ spinel oxides have revealed their ability to achieve high CO conversion under solar

irradiation, further enhancing their sustainability and practical application potential. Advanced in-situ characterization techniques, such as DRIFTS and XAFS, could show that Cu^+ species and oxygen vacancies at the catalyst surface are the primary active sites for CO oxidation.[25, 29]

However, one challenge with respect to CO-PROX integration into the MEA of a PEM fuel cell is the stability under the common operation conditions. Leaching of the metal, as well as support degradation must be considered under realistic operating conditions, i.e. acidic environment, varying potentials, and switching between H_2 and air in long shutdowns.

3.1.3 Bimetallic catalysts

Bimetallic catalysts play an important role in the preferential oxidation of carbon monoxide. These catalysts, which combine two different metals, often outperform monometallic systems by benefiting from unique synergistic interactions that improve their catalytic activity, selectivity, and durability. Their superior performance is a result of a combination of electronic and structural properties, which can be tailored to the specific needs of the system, including core–shell particles, exploiting various alloys, or heteroatom doping.[32]

AuAg catalysts supported on ceria have shown superior low-temperature activity compared to their monometallic counterparts. This is due to the beneficial interaction between gold and silver, which improves the reducibility of ceria supports resulting in eased oxygen activation. This contributes to enhanced CO oxidation selectivity while minimizing hydrogen oxidation.[32]

PtFe systems show exceptional performance at low temperatures as well. The addition of iron alters the electronic properties of platinum, weakening the CO adsorption strength and enhancing oxygen activation. Additionally, oxygen spillover from iron to platinum sites promotes CO oxidation, making these systems highly effective with respect to the purification of hydrogen.[33]

The incorporation of Co into Pt modifies both, the electronic and geometric properties of the catalyst, leading to improved CO oxidation activity. This is achieved through a dual-site mechanism, where Pt and Co act as separate adsorption sites for CO and O_2, reducing the competition between CO and H_2 for catalytic sites. Additionally, PtCo catalysts, when supported on materials such as zeolites, maintain high CO conversion rates over a wide temperature range, typically from 50 °C to 130 °C, showcasing superior performance relative to Pt only.[34]

The bifunctional mechanism in PtRu systems is a key contributor to their enhanced CO tolerance. Platinum weakens the CO adsorption strength, while ruthenium facilitates the dissociation of O_2, promoting CO oxidation without significant oxidation of hydrogen fuel. This enables PtRu catalysts to perform CO-PROX at lower temperatures compared to Pt only. The donation of electrons from Ru to Pt reduces the binding energy of CO on platinum, thereby mitigating CO poisoning. This interaction enables PtRu catalysts to operate efficiently under hydrogen-rich conditions.[35, 36]

PtCu catalysts benefit from a dual-site mechanism where CO and oxygen adsorb onto distinct active sites. The electronic interaction between copper and platinum modifies the redox

properties, yielding high CO oxidation selectivity even in the presence of water or carbon dioxide. These systems also show impressive stability and resistance to deactivation.[19]

Combinations of Au and Cu have a wide operational temperature window for the conversion of CO to CO_2. Electron transfer from gold to copper increases CO adsorption strength while suppressing hydrogen dissociation, thereby improving the overall selectivity and efficiency. This synergetic effect makes gold-copper catalysts particularly valuable for practical applications.[16]

3.1.4 Trimetallic systems

Trimetallic systems, such as those combining iron, copper, and platinum combine the advantages of the different metal components. The trimetallic catalysts excel under realistic operating conditions, yielding remarkable catalytic activity and stability. Adding iron and copper promotes oxygen activation while simultaneously reducing platinum's CO binding affinity. This can further increase the overall efficiency of trimetallic catalysts.[37]

3.2 CO-PROX catalyst integration via flow-field, MEA, and CCM design concepts

3.2.1 Flow-field integration

A fuel cell is composed of multiple layers, each serving a specific function. *Figure 1* shows a simplified scheme of a typical PEM fuel cell. At the core is the proton exchange membrane (PEM), an electrically insulating but proton-conducting electrolyte layer. It allows protons to travel through the membrane while preventing the crossover of reactant gases. The PEM is sandwiched between the anode and cathode catalyst layers (CL), where the key electrochemical reactions take place: hydrogen is split into protons and electrons at the anode, while oxygen is reduced at the cathode. The PEM together with the two CLs is also commonly termed catalyst-coated membrane (CCM). Surrounding the CCM are the gas diffusion layers (GDL) to ensure uniform gas distribution to the catalyst layers and to provide mechanical stability. Finally, flow fields, located on the outermost sides, direct the reactant gases (i.e. hydrogen and oxygen) to the GDLs, facilitate the removal of byproducts like water, and provide mechanical stability.
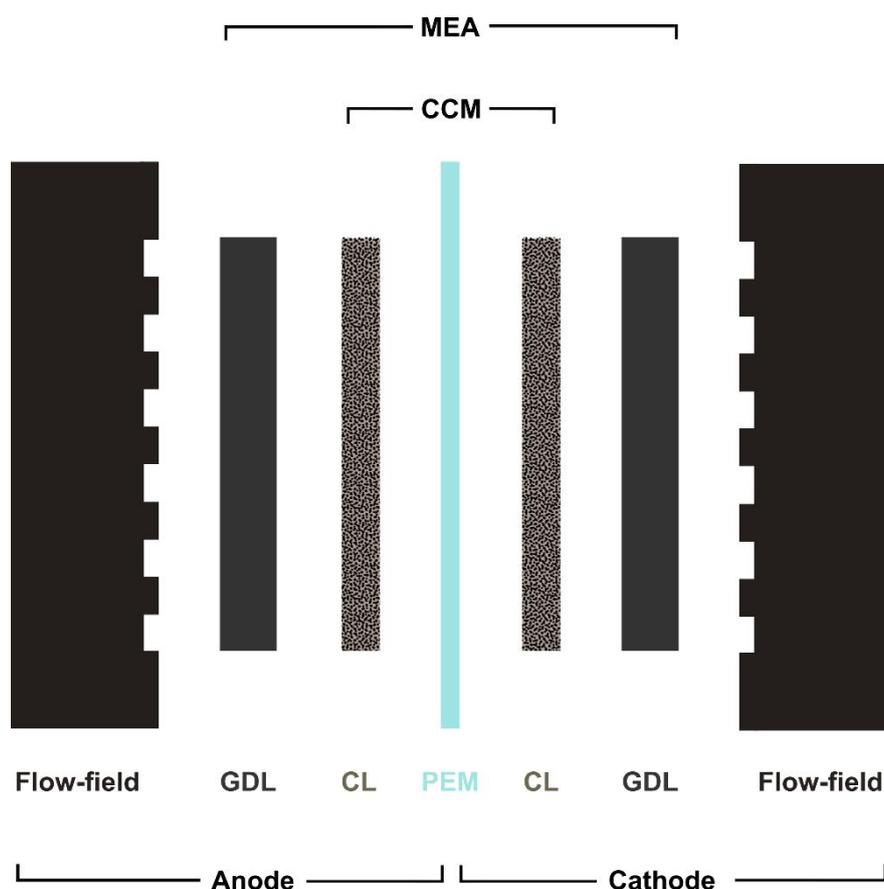
Figure 1 Simplified scheme of a PEM fuel cell consisting of a proton exchange membrane (PEM) sandwiched between an anode and cathode catalyst layer (CL). This so-called catalyst-coated membrane (CCM), together with two gas diffusion layers (GDL), yields the 5-layer membrane electrode assembly (MEA). The fuel cell is complemented by two flow-fields adjacent to the MEA.

A CO-PROX catalyst can be implemented into the PEM fuel cell following three approaches. The first option is to locate the CO-PROX catalyst directly on top of the anode flow-field. Here, the CO-PROX catalyst is placed upstream of the anode catalyst such that CO removal takes place before the contaminants can reach the anode catalyst layer. Secondly, it is possible to introduce the CO-PROX catalyst as a separate layer right next to the anode CL, either in-between the CL and PEM or on top of the anode CL/PEM configuration. Another option is to embed the CO-PROX catalyst within the catalyst-coated membrane (CCM), essentially as part of the anode CL.

The first option of flow-field integration of a CO-PROX catalyst is depicted in *Figure 2*. In this approach, the CO-PROX catalyst is placed upstream of the anode catalyst, within a separate catalyst bed or wash-coated onto a monolithic support structure. This configuration allows the CO-PROX catalyst to interact with potentially contaminated hydrogen feed before reaching the anode catalyst, thereby effectively removing CO through selective oxidation. By converting CO into CO_2, the catalyst prevents CO from adsorbing onto the anode catalyst. This prevents blocking

of the anode catalyst's active sites and would thereby allow for prolonged fuel cell operation and enhanced PEMFC efficiency.
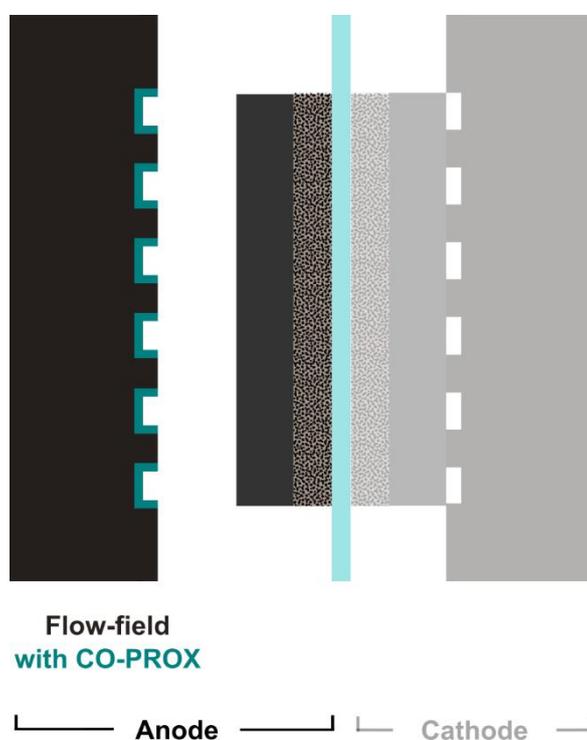

Figure 2 One option to integrate a CO-PROX functionality into the PEM fuel cell is by directly placing the CO-PROX catalyst onto the anode flow-field. As a result, CO within the hydrogen fuel is removed prior to reaching the anode catalyst layer.

The design of the CO-PROX catalyst for flow-field integration must meet the following criteria. First and foremost, the CO-PROX catalyst must exhibit high activity for CO oxidation while operating within a temperature regime around 80 – 120 °C, typical for PEMFC operation. This is crucial due to the exothermic nature of CO oxidation; catalysts must perform efficiently at these temperatures to optimize CO removal while maintaining high fuel cell performance. Additionally, the CO-PROX catalyst must be highly selective for the oxidation of CO over H_2 to minimize any losses of the hydrogen fuel.

The choice of support material is essential for flow-field integration method as well. The support material must provide structural stability for the catalyst while also enabling efficient heat transfer and distribution during CO oxidation. Silicon carbide (SiC), graphitized carbon and cordierite can be used as support materials due to their high thermal conductivity, which helps to prevent the formation of local hot spots potentially damaging the catalyst and reducing its activity.
This however might not pose a challenge as the bipolar plates typically exhibit sufficient heat conductivity and allow for proper heat dissipation. The support material must also stabilize the catalyst such that it remains stable during fuel cell operation, preventing mechanical breakdown,

e.g. by excessive thermal expansion. The catalyst further must withstand sintering processes where catalyst particles coalesce at high temperatures, reducing the surface area and catalytic activity.

Catalyst stability is of high importance as well, particularly because the catalyst is typically exposed to fluctuating gas compositions during fuel cell operation or longer shutdowns, e.g. H_2 - air - H_2. For example, CO concentrations in the hydrogen feed can vary, and the catalyst must be able to adapt to these changes without degrading and any losses in activity. Further, CO_2 and H_2O are common components of the hydrogen-rich reformate gas, and the catalyst must be resistant to deactivation by these substances.

3.2.2   Separate PROX layer adjacent to anode CL

The second concept to embed the CO-PROX catalyst into the PEM fuel cell is its integration as a separate layer directly next to the anode CL. This might be achieved by placement between the anode catalyst layer and PEM or on top of the anode CL/PEM configuration. Both concepts are outlined in *Figure 3.*

While placement on top of the anode CL seems like the more intuitive choice (i.e. CO is oxidized prior to reaching the anode catalyst), the other strategy of CO-PROX placement in-between the anode CL and PEM is particularly of interest with regards to internal air bleeding. Since the internal air bleed exploits oxygen molecules diffusing through the membrane from the cathode to the anode side, the concentration of diffused O_2 molecules is expected to be highest at the anode CL/PEM interface.

As for the case of flow-field integration, the general requirements for successful integration of CO-PROX catalysts as a layer next to the anode CL include long-term material stability under the system's typical operating conditions, high electrical conductivity, as well as good processability of the layers. However, with both routes presenting promising ways to integrate the CO-PROX into the MEA of the PEM fuel cell, more research will be needed to confirm the applicability in real fuel cell applications.

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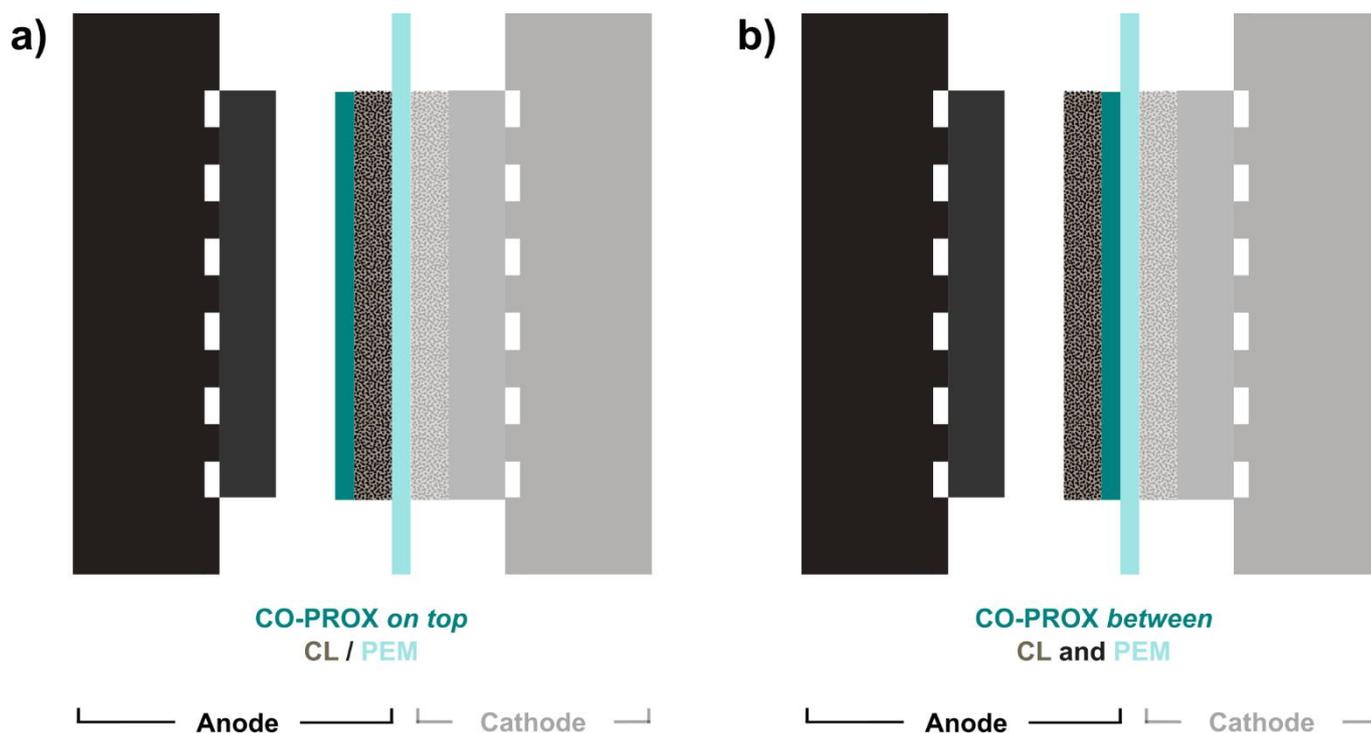Clean Hydrogen
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Figure 3 Concept of CO-PROX catalyst integration as a separate layer sitting either on top of the anode CL, i.e. on top of the anode side of the CCM (a), or in-between the anode CL and PEM (b).

3.2.3 CCM integration approach

The third approach of implementing a CO-PROX functionality into the PEM fuel cell is to locate the CO-PROX catalyst directly within the catalyst-coated membrane (CCM) as part of the anode catalyst layer. This design approach of placing the CO-PROX catalyst directly within the CCM offers several advantages, with the most prominent being the system's simplicity and compactness, compared to using external CO-PROX components.[38]

Figure 4 (A) shows an exemplary anode catalyst layer, however without added CO-PROX functionality, yet. This catalyst layer consists of many primary catalyst particles as well as an ionomer binder. In this context, it is important to distinguish between the actual catalyst, primary catalyst particles, and secondary catalyst particles. The term **primary catalyst particle** refers to a carbon particle being loaded with multiple Pt or Pt alloy nanoparticles (i.e. the catalytically active component) and is typically around 20 to 50 nm in size. The respective catalyst nanoparticles (2 - 4 nm) ease the electrochemical hydrogen oxidation reaction, while the catalyst support (e.g. highly porous carbon) provides high surface area and stability for the catalyst nanoparticles. The ionomer (e.g. Nafion) is proton-conducting and enables proton transfer to and from the proton exchange membrane. Larger aggregates of several primary catalyst particles are commonly referred to as **secondary catalyst particles** which are commonly in the order of 100 – 300 nm.

CO-PROX implementation into the CCM, i.e. as part of the anode CL, can either be accomplished by loading both, the anode catalyst and the CO-PROX catalyst, onto the same carbon support

particle. This yields primary catalyst particles, where the anode catalyst and the CO-PROX catalyst are located within the same primary particle as seen in *Figure 4 (B).*

The second option of embedding the CO-PROX catalyst within the CL is to have to distinct types of primary catalyst particles, one being primary anode catalyst particles and the other being the primary CO-PROX catalyst particles as outlined in *Figure 4 (C).*

While the former design benefits from unique catalytic properties due to the intrinsic nature of the catalyst containing both, anode catalyst and CO-PROX catalyst activities within the same primary particle as well as good processability, a shortfall are more sophisticated fabrication routes toward this type of catalyst.

In contrast, the latter option enables simpler synthesis routes toward the distinct primary anode catalyst particles and primary CO-PROX catalyst particles, respectively, while possible disadvantages include less efficient performance and potential processability hurdles because of distinct primary particle sizes.

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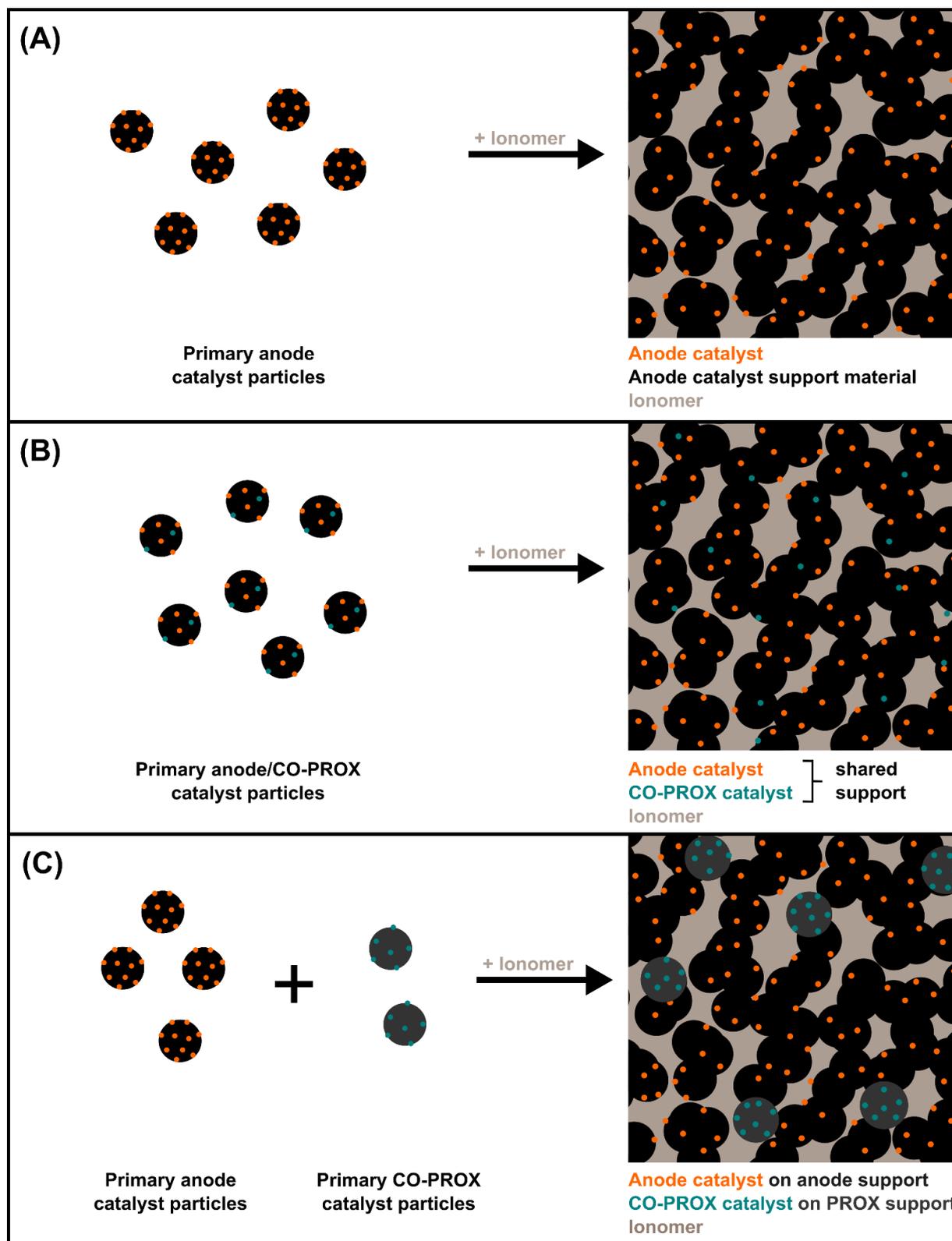Clean Hydrogen
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Figure 4 Integration of CO-PROX catalyst into the CCM of a PEM fuel cell. (A) shows a typical anode catalyst layer (CL) consisting of primary anode catalyst particles (i.e. active anode catalyst on a support material) and ionomer without any CO-PROX material. The CL in (B) shows the integration of a CO-PROX functionality through primary particles employing the anode catalyst and CO-PROX catalyst on a shared catalyst support material (i.e. chemical mixture). In (C), the CL consists of both, primary anode catalyst particles and primary CO-PROX catalyst particles, that are physically mixed.

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Regardless of the chosen method (same or distinct primary CO-PROX catalyst and/ or primary anode catalyst particles), both approaches require careful fine-tuning of the primary anode and/or CO-PROX catalyst particles to maintain high catalytic performances (for both, anode hydrogen oxidation reaction and CO-PROX reaction) and to ensure good processability and long-term stability. The following subsection provides the general material requirements that are needed for CO-PROX integration into the CCM.

3.2.4 General material requirements

In addition to exhibiting high CO oxidation activity and good selectivity toward the competing hydrogen oxidation reaction at low temperatures (80 – 120 °C), following parameters are crucial for a successful incorporation of CO-PROX catalysts into the CCM of the PEM fuel cell.

Regardless of the CCM integration method chosen, one key parameter is the size and morphology of both, the active catalyst and the primary catalyst particles. The active catalyst material should be in the range of around 2 – 4 nm to ensure a good balance between a high number of available active sites while maintaining sufficient stability. While smaller particles in general have more active sites available for the CO-PROX reaction, the nanoparticle size cannot be reduced indefinitely, as excessively small particles present challenges such as agglomeration, reduced stability, and catalyst deactivation, all of which can impair performance. These particles are prone to sintering or coalescence under the harsh operating conditions of the fuel cell, leading to a loss of active sites over time and further diminishing stability.[38, 39]

Nanoparticles in the stated size range perform particularly well at low temperatures where reaction rates are slower in general as they can benefit from increased CO interaction and thus enhanced CO-PROX activity.[39] Relevant fabrication methods include sol-gel processing, wet-impregnation, or ALD, all potentially providing control over size, shape, and particle dispersion. The latter point of nanoparticle distribution over the support material is critical as well: the active catalyst must be well dispersed over support for maximum catalytic performance.

Additionally, the primary catalyst particles. i.e. catalyst nanoparticles on support material, should be in the appropriate size to meet established CL processing protocols. Here, targets for typical primary particle sizes would be 100 – 250 nm, depending on the used catalyst layer fabrication method.[38]

Important in this regard is the requirement of similar size of the primary particles for the case that different supports are chosen for the anode catalyst and the CO-PROX catalyst, i.e. distinct anode and CO-PROX primary catalyst particles (see also section 3.2.3). Here, both distinct primary particles should be similar in size to ensure good mixing and thus processability during catalyst layer fabrication. Methods like spray coating or decal transfer, rely on uniform dispersions of the primary catalyst particles (i.e. homogeneous catalyst ink dispersions) and significant discrepancies in the primary particle size will undermine the layer fabrication. A mismatch in particle size could eventually introduce issues, e.g. layer cracking or poor particle dispersion, resulting in an overall worse performance or even lead to a complete failure of the CL.[38]

Another key consideration for successful incorporation of CO-PROX catalysts into the CCM is the requirement of an electrically conductive catalyst layer, i.e. the support material must be electrically conductive, since good electron transport to and from the catalytically active sites is detrimental for the performance. A non-conductive support would hinder the overall reaction by limiting electron flow, thus reducing the cell's performance. In practice, support materials are typically carbon-based, e.g. carbon black or graphitized carbon derivates in case higher stabilities are required. These materials exhibit both conductivity and stability under the harsh operating conditions of a fuel cell.[38]

One exception to this is when using two distinct support materials for anode and CO-PROX catalysts. The support employed for the primary anode catalyst particles would still require high electrical conductivity. However, with respect to the relatively small amount of CO-PROX catalyst needed for CO oxidation, the support used in the primary CO-PROX catalyst particle could be non-conductive as well. However, the concentration of primary CO-PROX particles with non-conductive support had to be chosen to never underpin the percolation limit of the anode catalyst and extreme care must be taken with respect to narrow powder particle size as well as the concentration of CO-PROX catalyst within the CL.

Critical for selecting suitable CO-PROX catalysts is also their stability under realistic PEM fuel cell operating conditions. Specifically, the catalyst must remain stable in acidic media and under the potential encountered during fuel cell operation. This stability can be assessed using the electrochemical series and Pourbaix diagrams, which provide insights based on the specific operating conditions. Additionally, system specific operating conditions, e.g. high-potential recovery strategies, should be considered as well.

Further, the stability of the employed catalyst (nanoparticles and primary particles) should withstand the thermal fluctuations and humidification cycles that are common for PEMFC operation as well as varying reactant gas concentrations. In any case, catalyst sintering or leaching should be minimized to allow for long-term PEM fuel cell performance.[5, 40]

3.3 Commercial CO-PROX catalysts

The integration of CO-PROX catalysts into the anode catalyst layer of the PEM fuel cell as discussed in previous sections, is of particular interest for improving catalyst tolerance against CO poisoning originating from impurities in the hydrogen feed.

While commercial CO-PROX solutions often use Au or Pt supported on Al_2O_3 due to their outstanding activity and selectivity, these catalysts typically lack high conductivity and suitable particle sizes on the nanoscale such that integration into the CCM becomes challenging.[41]

A viable alternative present CO-PROX catalysts employing carbon-based supports. Although at the expense of a potentially lowered CO oxidation activity, carbon supports like carbon black or graphene offer high electrical conductivity and can be modified toward high stability under the respective operating conditions of the PEM fuel cell. This is an acceptable trade-off with respect to the requirement of long-term durability of the PEMFC system.[42]

The following commercially available CO-PROX catalysts were selected as promising materials (see *Table 1*). The selection of the potential CO-PROX materials to be integrated into the catalyst layer to exploit internal air bleeding is discussed in detail:

Table 1: Selection of commercial PROX catalysts

Product / Manufacturer	Composition	Particle sizes	Available Data
CPCO5001 / ACS Materials	PtCo/C (50 wt.% Pt, 15 wt.% Co)	Catalyst: 4.5 nm Support: ~30-40 nm	https://www.acsmaterial.com/50-platinum-cobalt-on-carbon-catalyst-50-ptco-c.html
738565-1G / Sigma Aldrich	Pt_3Co/HDC (27 wt.% Pt, 3 wt.% Co)	Catalyst: < 5 nm Support: inquiry	https://www.sigmaaldrich.com/DE/de/product/aldrich/738565
CPCU4001 / ACS Materials	PtCu/C (40 wt.% Pt, 13 wt.% Cu)	Catalyst: 4 nm Support: nm range	https://www.acsmaterial.com/platinum-copper-on-carbon-catalyst-ptcu-c.html
(PRICAT MFC 100A)	Au/C (n.a.)	n.a.	https://minamataconvention.org/sites/default/files/inline-files/Ready%201031B-NRDC.pdf

3.3.1 PtCo/C

PtCo bimetallic catalysts offer significant potential for improving the performance of PEM fuel cells by enabling the CO-PROX reaction in hydrogen-rich environments. PtCo catalysts, in their bimetallic form, show several advantages over monometallic Pt catalysts, including improvements in catalytic activity, stability, selectivity, as well as an expanded operating temperature window.

- **CO oxidation activity:** PtCo bimetallic catalysts exhibit enhanced CO oxidation activity compared to their monometallic Pt counterparts. The addition of cobalt introduces a synergistic effect that lowers the binding strength of CO to platinum, thereby facilitating CO oxidation at lower temperatures. The Pt-Co interaction is key to enhancing CO oxidation while minimizing the competing hydrogen oxidation reaction. This dual-site mechanism ensures high selectivity for CO oxidation in hydrogen-rich environments.[34, 43]

- **Stability and resistance to deactivation:** Stability is a critical factor for catalyst longevity in PEMFCs, especially under fluctuating operation temperatures and under the presence of CO and CO_2. While PtCo catalysts, due to their bimetallic structure, are more stable against sintering and deactivation compared to Pt alone. Possible leaching of cobalt at typical PEM fuel cell potentials to the cathode side might even enhance the performance of the cell.[44, 45]

- **Working temperature range:** PtCo bimetallic catalysts are particularly effective in a temperature range of 60 to 100 °C. This aligns well with the target operating temperatures of a PEMFC stack and is of particular interest as the CO oxidation becomes more challenging at lower temperatures (i.e. strong adsorption of CO onto Pt). The presence of cobalt in PtCo alloys facilitates CO oxidation by modulating the electronic structure of Pt and promoting the formation of active sites for oxygen adsorption.[34, 43, 46]

- **Metal particle size:** The particle size of PtCo catalysts also significantly impacts the catalytic performance. Small particle sizes (typically in the range of 2 – 4 nm) provide a high surface area, maximizing the number of active sites that are potentially available for the CO oxidation reaction. Smaller particle sizes would however pose stability issues. Moreover, PtCo particles should be finely dispersed over the support structure to allow for efficient interaction with the reactants. This prevents sintering and allows for long-term stability of the PEMFC stack.[45, 47]

3.3.2 PtCu/C

PtCu bimetallic catalysts are particularly useful for CO preferential oxidation in low-temperature proton exchange membrane fuel cells, as they improve the purification of hydrogen by removing CO impurities. These catalysts exhibit several key properties that enhance CO oxidation efficiency.[48]

- **Synergistic Effects**: PtCu bimetallic catalysts combine the unique properties of Pt and Cu to enhance catalytic performance. The Pt atoms facilitate CO oxidation, while Cu modifies

the electronic structure of Pt, improving oxygen activation, which is critical for CO oxidation at low temperatures. This synergy also helps mitigate CO poisoning by weakening the CO binding energy on Pt and promoting its oxidation via Cu-activated oxygen.[49, 50]

- **Geometric and Electronic Effects**: The interaction between Pt and Cu atoms in PtCu alloys modifies the electronic structure of Pt, promoting CO oxidation while minimizing the competing hydrogen oxidation reaction. The structure of the catalyst can be fine-tuned by optimizing the Pt/Cu ratio.[51]

- **Enhanced CO Selectivity and Stability**: One of the main advantages of PtCu over pure Pt is its improved selectivity for CO oxidation. The copper in PtCu catalysts promotes the dissociation of oxygen, necessary for efficient CO oxidation, without oxidizing significant amounts of the hydrogen fuel.[51]

- **Low-Temperature Performance**: PtCu catalysts are highly active at low temperatures, below 100 °C, aligning well with the operating conditions of PEMFCs. This makes them suitable for in-situ integration into the MEA, where such catalyst can effectively remove CO without compromising the fuel cell performance.[48]

3.3.3 Au/C

Gold-based catalysts (Au/C) might present a suitable alternative for CO-PROX reactions in hydrogen-rich environments, particularly at low temperatures. Compared to platinum-based catalysts, Au/C offers distinct advantages in selectivity and stability, making it a viable candidate for PEM fuel cell integration. Au nanoparticles supported on carbon demonstrate excellent CO oxidation activity, particularly at lower temperatures (≤80 °C). Unlike Pt-based catalysts, which suffer from hydrogen oxidation side reactions, Au/C catalysts exhibit high selectivity for CO oxidation while minimizing hydrogen consumption. This is attributed to the unique electronic properties of gold, which favor CO activation in the presence of O_2 while limiting H_2 oxidation. Gold catalysts are known for their resistance to deactivation, especially under PEMFC operating conditions. The inert nature of gold prevents metal leaching or dissolution, although further studies are required to state long-term stability under actual PEM fuel cell operating conditions. Au/C catalysts perform well in the 50 – 80 °C range, aligning well with PEM fuel cell operating temperatures.[52–56]

This makes gold an interesting choice as catalyst support material. However, to the best of our knowledge, particle sizes of commercially available Au/C material need to be optimized toward smaller primary particle size to allow for anode catalyst layer integration of such CO-PROX functionality. Typical Au/C materials are well above the typical primary catalyst particle size required to work with standard CL fabrication protocols. One straightforward method to yield a suitable Au/C primary particle size could be mild milling of the material which is why a commercially available Au/C catalyst was added in the selection albeit needing further – however straightforward – pre-processing by grinding, e.g. ball-milling under wet conditions.[57]

3.4 Alternative CO-PROX catalyst design

A possible alternative for low temperature CO-PROX catalysts suitable for MEA integration involves the deposition of Pt nanoparticles on commercial reducible oxide nanoparticles, followed by further deposition onto graphitized carbon supports.

One approach could be a wet impregnation route, where a solution containing a platinum precursor is introduced onto an oxide support, followed by drying and calcination to form Pt nanoparticles on the surface of the oxide. After impregnation of Pt, the catalyst is transferred onto graphitized carbon support. The graphitized carbon provides a conductive matrix ensuring efficient electron transfer, stabilizing the catalyst nanoparticles, and providing high surface area for Pt/MO_x nanoparticle dispersions.

The working temperature of Pt/CeO_2 catalysts for CO-PROX typically ranges from 60 – 150 °C. In this temperature range, Pt/CeO_2 catalysts exhibit high CO conversion rates and good CO_2 selectivity. The exact temperature at which the maximum CO conversion and selectivity are observed vary depending on the preparation method and Pt loading on the CeO_2 support. Due to its excellent oxygen storage and release capacity, ceria is a widely studied support material. The presence of oxygen vacancies in CeO_2 enables the activation of oxygen molecules, which is crucial for the following CO oxidation step. These vacancies can participate in the Mars-van Krevelen mechanism, where oxygen from the oxide support is transferred to the CO molecules, facilitating the oxidation reaction. In addition to ceria, SnO_2 and TiO_2 have been explored as supports for CO-PROX reactions as well. However, unlike CeO_2, their catalytic performance in CO oxidation is often lower due to their less pronounced oxygen storage capacity. This makes these materials interesting supports for catalyst development targeting CO-PROX integration into the anode CL of PEM fuel cells.

Selection of commercial support materials

Product / Supplier	Composition	Particle size	Available Data
580800PD005 / Halbleiter Materials	CeO_2	15 – 30 nm	https://vimaterial.de/en/product/cerium-oxide-2/?gad_source=1&gclid=Cj0KCQiAkJO8BhCGARIsAMkswyjn9u4i3Ldys9fPmrB_yXa-KOfXXhucL9eEfupYGhv-gMo4-Nn0GrkaArRLEALw_wcB#form-popup
NG04SO3504 / Nanografi	TiO_2	20 – 30 nm	https://nanografi.com/nanoparticles/titanium-dioxide-tio2-nanopowder-nanoparticles-anatase-purity-99-5-size-20-30-nm?value=1
NG04SO3302 / Nanografi	SnO_2	18 nm	https://nanografi.com/nanoparticles/tin-oxide-sno2-nanopowder-nanoparticles-high-purity-99-99-size-18-nm?value=1
Vulcan XC72 / Nanografi	Carbon	250 nm	https://nanografi.com/vulcan-xc72-conductive-carbon-black/
Vulcan XC 72 / Fuel Cell Store	Carbon	30-60 nm	https://www.fuelcellstore.com/vulcan-xc72?search=Vulcan

4. CONCLUSION

The development and integration of CO preferential oxidation (CO-PROX) catalysts into proton exchange membrane fuel cells (PEMFCs) presents a promising concept in hydrogen purification strategies with the aim to allow long-term PEMFC system operation on industrial hydrogen. This approach addresses one of the key challenges encountered in long-term PEMFC operation: the presence of carbon monoxide in industrial hydrogen fuel, which can poison the fuel cell catalyst by blocking the catalyst's active sites with CO. Incorporating a CO-PROX catalyst directly into the PEMFC system, either by placement on top of the anode flow-field or via direct location within the catalyst-coated membrane (CCM), as part of the anode catalyst layer, could potentially lead to various system advancements, including:

- Enhanced overall fuel cell efficiency by minimizing performance losses linked to the detrimental effects of CO contaminants on the anode fuel cell catalyst.
- Improved durability and longevity of the PEM fuel cell system.
- Reduced system cost because for long-term operation less amount of expensive catalyst could be used with active sites on the anode catalyst remaining free from CO impurities.
- Reduced system cost, complexity, and size due to external CO-PROX components becoming redundant.

This concept, if successfully developed and implemented, will contribute to more compact, efficient, and cost-effective PEMFC systems. It presents a promising direction for future research and development in the field of fuel cell technologies, advancing the widespread use of PEM fuel cells in various sectors.

The report presents key advancements in the design and implementation of CO-PROX catalysts, thoroughly evaluating their potential to meet stringent hydrogen purity standards. Given the limited documentation on the direct integration of a CO-PROX catalyst into the MEA, the report starts by introducing the reader to fundamental concepts of CO-PROX mechanisms. A detailed analysis of catalytic mechanisms, including Langmuir-Hinshelwood, Mars-van Krevelen, Eley-Rideal, and Termolecular Eley-Rideal pathways, serves as basis for the general understanding of PROX catalysts.

Further, this report explores the key performance parameters of CO-PROX catalysts, discussing activity and selectivity with respect to the operating temperature, the role of the support material, and overall material stability. These factors are examined in detail to provide a comprehensive understanding of the challenges and opportunities in optimizing CO-PROX catalysts for practical applications.

One critical aspect hereby is the role of catalyst support materials and its metal-support interaction (MSI) to achieve increased performance. Reducible oxides such as ceria have been identified to present effective supports due to their high oxygen storage capacity (OSC) which eases oxygen activation. Secondly, carbon-based supports provide good electrical conductivity and stability, ensuring compatibility with the harsh operating conditions of PEM fuel cells.

Optimum particle sizes for the active catalyst component are within a size between 2 to 4 nm, balancing the need for high surface area and long-term stability. This prevents issues such as agglomeration and sintering while yielding maximum performance.

Notable advancements in single-atom catalysts (SACs), bimetallic systems, and base-metal oxides are also highlighted within the discussion of different CO-PROX catalyst types, showcasing improvements in catalytic activity, selectivity, and stability. Special emphasis lies on the synergistic interactions between metal and support materials, such as platinum-ceria systems, which are beneficial in selective CO oxidation and enhanced catalyst durability under typical PEM fuel cell operating conditions.

The integration of CO-PROX catalysts into the MEA of a PEM fuel cell has been discussed following various design strategies: (1) placement of the CO-PROX catalyst onto the anode flow-field, (2) as separate catalyst layer (CL) adjacent to the anode CL, or (3) embedded within the catalyst-coated membrane (CCM) as part of the anode CL. The latter approach, direct integration of a CO-PROX functionality within the anode CL, could potentially benefit from:

- In case of shared support which yields same primary catalyst particles: Unique catalytic CO oxidation properties, straightforward processability, but sophisticated catalyst synthesis.
- In case of CO-PROX and anode primary catalyst particles featuring distinct support: Simplified catalyst synthesis, but performance trade-offs and possible processability hurdles. Careful selection of CO-PROX catalyst regarding applicability with the used anode catalyst could however avoid these challenges.

Commercially available CO-PROX catalysts, including bimetallic systems like PtCo, have shown significant potential for integration into PEMFCs due to their high CO oxidation activity, selectivity, and stability, making them suitable for hydrogen purification. However, PtRu-based systems are less favourable for long-term application due to stability issues. Ruthenium tends to leach from the catalyst, migrate through the membrane, and deposit on the cathode's platinum surface, severely impairing the oxygen reduction reaction (ORR) performance. In contrast, PtCo systems not only avoid these issues but may even enhance cathode performance by activating the ORR rather than suppressing it. Further investigation is needed to understand the behaviour of other elements, such as copper, at the cathode completely to optimize Co-based PROX catalysts for CCM integration. For this case, the focus should be on developing catalysts that ensure electronic conductivity, nanoscale particle size, long-term durability, and minimal impact on the cathode performance. This highlights the need for CO-PROX catalysts that meet the harsh operation requirements of PEM fuel cell operation.

After providing and discussing commercially available catalytic CO-PROX solutions, the report extends by presenting a selection of promising CO-PROX catalysts for CL integration, as well as commercially available support materials to be used for CL integration and discusses the most important performance factors of each listed option.

In conclusion, the advancements in PROX catalyst design and integration provide a clear pathway toward overcoming the current challenges of hydrogen purification for PEMFCs. Future research should continue to explore novel material combinations and innovative synthesis techniques to enhance CO oxidation efficiency to ensure compatibility with fuel cell technologies. By addressing these critical challenges, CO-PROX catalysts will play a critical role in enabling a sustainable energy future, by advancing hydrogen purification strategies for PEM fuel cells to comply with the stringent requirements for the purity of industrial hydrogen used in PEM fuel cell systems.

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CLEANER
Clean Heat and Power from Hydrogen

Grant agreement no.: 101137799

Clean Hydrogen
Partnership

Co-funded by
the European Union

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