# Palladium-Based Nanostructured Electrocatalysts for Fuel Cells: Design, Activity and Durability

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**Abstract.** The development of fuel cell technology based on low temperature has been accelerated by the discovery of Pd as a cheap and abundant alternative to Pt; with good catalytic activity for the alcohol oxidation reaction and acceptable properties for oxygen reduction reaction (ORR) in alkaline conditions; further enhanced by its unique resistance to carbon monoxide poisoning and ability to quickly produce hydroxyl species on its surface. However, despite all this progress there remains significant knowledge gaps. Many reports about the activity of Pd based electrocatalysts overestimate the activity of the material due to the fact that they used very low metal loadings and expressed the normalized current density per mass of the metal. Furthermore, many of the methods employed to increase the activity of the material when tested as a half-cell failed to be translated into real world application when tested as membrane-electrode assemblies. In this review article we evaluate the status of the field of Pd electrocatalysis for both alkaline fuel cells and alcohol oxidation reactions. We provide an evaluation of the areas in which Pd excels, and in which it falls short of Pt. We also evaluate the various approaches that are being taken to create Pd based electrocatalysts that can be applied to practical devices. This review should provide direction for researchers working towards developing Pd electrocatalysts that can be demonstrated to work effectively under conditions representative of real-world fuel cell applications, and that will ultimately help to advance the conversion of chemical energy to electrical energy in a sustainable manner.

## 1. Introduction

Decarbonisation of energy demands efficient and scalable conversion technologies. Fuel cells convert chemical energy directly into electricity without combustion. Proton-exchange membrane fuel cells (PEMFCs) dominate today's automotive and stationary applications. [1,2] They rely on acidic electrolytes and high loadings of platinum. The high cost and

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scarcity of platinum limit broad adoption. In response, alkaline anion-exchange membrane fuel cells (AEMFCs) have emerged. They operate in alkaline media, allowing the use of non-precious metal catalysts for the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR). Alkaline conditions also reduce corrosion of some support materials and enable simpler water management. Among the candidate catalysts for AEMFCs, palladium stands out. [3]

Palladium is a group ten metal with an electronic configuration that favors adsorption of both hydrogen and oxygen species. In alkaline environments, palladium surfaces readily form adsorbed hydroxyl groups. These species assist the oxidation of organic molecules and poison intermediates. Palladium shows high activity for the electro-oxidation of methanol, ethanol, ethylene glycol and glycerol. [4] It can also reduce oxygen at reasonable rates in alkaline media, although its activity is lower than that of platinum. The cost of palladium is lower than platinum because of larger reserves and recycling. These features make palladium attractive for the anode in direct alcohol fuel cells and for co-alloying with platinum in the cathode. Although palladium has advantages as an electrocatalyst, it has significant disadvantages. For instance, in acidic solution, palladium has the potential to dissolve at high potentials and to produce less stable oxides; in addition, palladium's ORR activity is poor in proton exchange membranes; and some palladium alloys are subject to degradation through dealloying due to leaching of base metals. Therefore, the palladium electrocatalyst must be carefully evaluated based on all of the above factors. [5] As illustrated in Figure 1, palladium serves as a versatile electrocatalyst capable of efficiently catalyzing both anodic fuel oxidation reactions (EOR and FAOR) and cathodic reactions (HOR/HER and ORR), underscoring its broad relevance in fuel cell technologies.

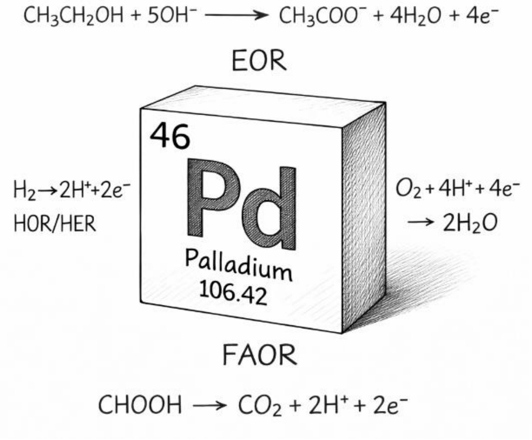

**Fig. 1.** Schematic illustration of palladium (Pd) as a multifunctional electrocatalyst, highlighting its activity toward the hydrogen oxidation/evolution reactions (HOR/HER), oxygen reduction reaction (ORR), ethanol oxidation reaction (EOR), and formic acid oxidation reaction (FAOR). The diagram summarizes the key electrochemical pathways enabled by Pd in fuel cell and electrolysis systems.

Palladium's fundamental electronic structure is quite different than most transition metals. The d-band center of palladium lies closer to the Fermi level than that of platinum, which leads to a weaker interaction between the surface and oxygen-containing species. [6] This means that palladium's surfaces can recover from oxidation much faster than platinum or many other transition metal surfaces, and therefore, they can operate in fast electrochemical cycles in alkaline media. On the other hand, the weak interaction between the surface and oxygen-containing species will lead to decreased stability at high potentials, especially under acidic conditions. Palladium also has the property of forming hydrides, which affect the operation of the electrocatalyst. Hydrogen can diffuse into the bulk of palladium nanoparticles (and can spill over onto support materials) and form hydrides in the palladium. Hydrogen spillover, hydrogen diffusion, and hydride formation can create stress in the lattice and change the electronic structure of the material. Also, during electrocatalysis, the reversible absorption/desorption of hydrogen can help mitigate poisoning and act as a reservoir for reactive intermediates. Understanding the fundamental properties of palladium is essential for designing palladium-based electrocatalysts rationally. [7,8] As shown in Figure X, Pd exhibits both surface and subsurface hydrogen chemistry, enabling multiple HER pathways (Volmer–Tafel and Volmer–Heyrovsky) that proceed through equilibria between $H^+$, H_ads, and H_sub.

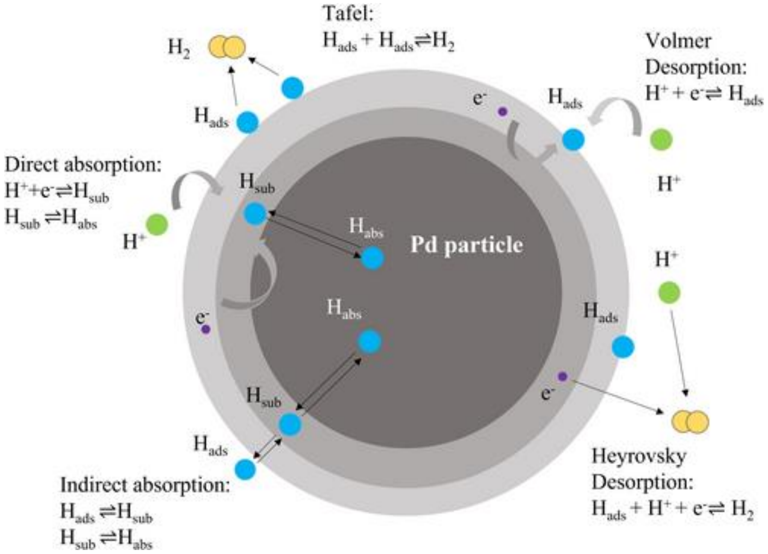

**Fig. 2.** Schematic representation of hydrogen evolution on a palladium (Pd) particle illustrating direct and indirect hydrogen adsorption, formation of surface-adsorbed (H_ads) and subsurface hydrogen (H_sub), and $H_2$ generation via Volmer, Tafel, and Heyrovsky mechanisms. The interconversion between H_ads and H_sub highlights Pd's ability to store and transport hydrogen, which critically influences HER activity and kinetics.

This paper reviews the state-of-the-art for the use of palladium-based electrocatalysts for low temperature fuel cell applications. The paper is organized into a few sections. First, we describe where palladium is actually competitive in fuel cell applications, and where it is not. Second, we criticize the misuse of performance metrics (such as mass activity and ECSA normalization). Third, we analyze the reaction mechanisms for the oxidation of alcohols, emphasizing that breaking carbon-carbon bonds continues to be a major barrier. Finally, we review how the electronic structure of palladium can be modified by alloying with other transition metals, and by forming intermetallic compounds. High-entropy and multi-component systems are considered. We assess the effects of supports, ionomers and electrode architecture on catalyst performance. Degradation mechanisms, including dissolution, poisoning and carbonate formation, are scrutinised. Finally, we propose guidelines for future research. Throughout, we draw on recent literature and foundational studies to provide a balanced and critical perspective.

## 2. Electrocatalytic Properties of Palladium in Alkaline Fuel Cells

Palladium has long been used as a hydrogen storage and purification material. Its hydride-forming behaviour arises from the ability of hydrogen to occupy interstitial sites in the face-centred cubic lattice. In electrocatalysis, this property translates into rapid hydrogen absorption and desorption. Palladium catalysts on carbon supports deliver high current densities for the hydrogen oxidation reaction in alkaline media. In combination with anion-exchange membranes, palladium has demonstrated near-ambient operating voltage with low overpotential. For example, carbon-supported palladium dispersed on oxygen-deficient supports can reach peak power densities comparable to platinum in alkaline direct ethanol fuel cells [9]. Palladium also exhibits strong tolerance to carbon monoxide. This is crucial because reformate gases or incomplete oxidation of organic fuels produce CO, which poisons platinum catalysts by blocking active sites. Palladium surfaces are able to oxidise CO via adsorbed OH species, freeing sites for further reaction [10].

Palladium is effective in a wide range of applications including direct alcohol fuel cell systems; and has been shown to have advantages over platinum in the oxidation of methanol, ethanol and glycerol in alkaline media. Palladium achieves these benefits by binding reactants much less tightly than does platinum and by forming and removing surface adsorbates quickly. Higher peak current density and longer term durability of palladium compared to platinum was reported in studies comparing the performance of Pd/C and Pt/C anodes for the oxidation of ethanol [11] and in direct ethanol fuel cells, palladium-based anodes show better performance in combination with ceria or tin oxides as they also provide additional oxygen species. Operating in alkaline conditions at low temperature reduces the need for expensive platinum on both sides of the electrochemical reaction, thereby allowing AEMFCs to be cost-competitive alternatives to PEMFCs.

The formation of a hydride by Palladium is another benefit that arises from Palladium's capability to store hydrogen within its crystal structure during use. The Palladium lattice stores hydrogen internally which is then released to the surface where it reacts. Storing hydrogen within the Palladium lattice reduces the fluctuation in the availability of reactants. Also, hydrogen diffusing through the Palladium lattice promotes spillover onto the support (e.g., metal oxide) reducing oxides present on the support; modifying surface chemistry; and creating new sites with catalytic activity. Spillover has been demonstrated to be enhanced when Palladium particles are present on reducible metal oxides and facilitate an enhancement of the oxygen reduction reaction rate.

Despite these advantages, palladium is not universally superior. For the oxygen reduction reaction in acidic conditions, palladium is significantly less active than platinum. The intrinsic ORR activity of palladium is about an order of magnitude lower than that of platinum on a per-site basis. In addition, palladium dissolves at high positive potentials and forms unstable surface oxides, leading to rapid performance loss in acidic PEMFC cathodes. Alloying palladium with cobalt or nickel enhances activity somewhat, but platinum still provides the benchmark. Studies of palladium-based cathodes in PEMFCs show lower power densities and faster degradation than platinum alloys. Therefore, palladium is competitive primarily in alkaline environments and as an anode catalyst for alcohol oxidation. It can act as a co-catalyst in platinum alloys to lower cost and improve CO tolerance, but it cannot replace platinum entirely for proton-exchange membrane fuel cells. [12]

## 3. Reaction-pathway limits in alkaline alcohol oxidation

Direct alcohol fuel cells oxidise organic molecules such as methanol and ethanol to produce electricity. Ideally, the fuel is fully oxidised to carbon dioxide, releasing the maximum number of electrons. In practice, oxidation often stops at intermediate products such as acetaldehyde or acetic acid. Palladium catalysts in alkaline media are effective at removing adsorbed CO species. Hydroxyl groups on palladium surfaces attack CO, forming $CO_2$ and restoring active sites. This process yields high current densities and reduces poisoning. However, the ability to oxidise CO does not mean that palladium breaks the carbon–carbon bond of ethanol or glycerol. Bifunctional catalysts that combine palladium with tin oxide or ceria promote CO removal but still produce mostly $C_2$ products. The majority of the current results from dehydrogenation and partial oxidation. Gas chromatography and in situ Fourier-transform infrared spectroscopy show that palladium-based anodes often yield acetaldehyde and acetate rather than $CO_2$ [13]. Figure X presents time-resolved ATR-SEIRA spectra recorded on a Pd electrode during ethanol oxidation in alkaline media, revealing the rapid formation and evolution of surface-bound reaction intermediates. Isotopic substitution ($CH_3CH_2OH$ vs. $CH_3CD_2OH$) enables clear assignment of C–H and C–D related vibrational modes, providing mechanistic insight into C–C bond retention and partial oxidation pathways. [14]

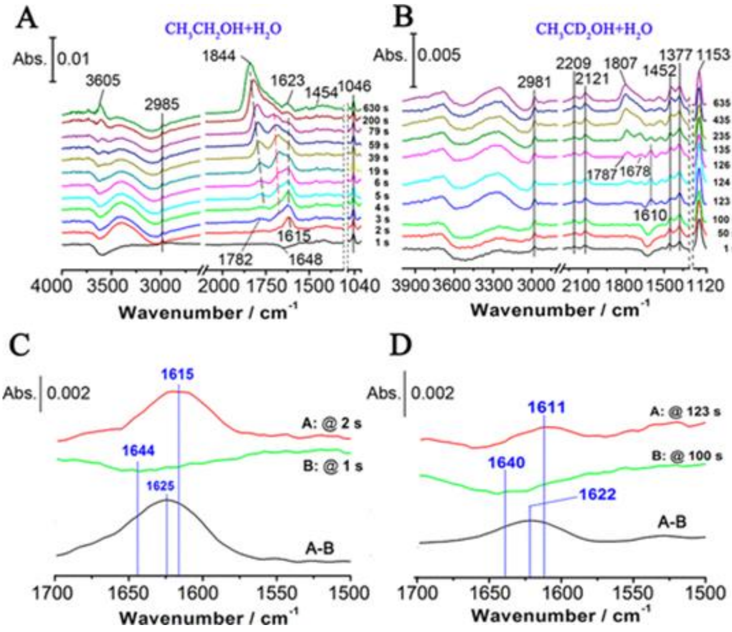

**Fig. 3.** Time-dependent ATR-SEIRA spectra obtained on a palladium electrode during ethanol electro-oxidation in alkaline solution using protonated ($CH_3CH_2OH$) and deuterated ($CH_3CD_2OH$) ethanol. Panels (A) and (B) show sequential spectra highlighting the development of characteristic vibrational bands associated with adsorbed intermediates. Panels (C) and (D) present magnified spectral regions at selected reaction times along with difference spectra, illustrating isotopic shifts and temporal changes in surface species. A background spectrum recorded in NaOH/$H_2O$ electrolyte was employed as the reference. [14]

Breaking the C–C bond in ethanol requires adsorbed oxygen species that can attack the carbon–carbon bond. Platinum–ruthenium and palladium–oxides can provide such species, but the reaction pathway competes with easier dehydrogenation steps. Ceria-supported palladium shows some evidence of deeper oxidation. Ceria supplies lattice oxygen that participates in oxidation and regenerates via redox cycling. Palladium–ceria composites produce more $CO_2$ than palladium alone and deliver higher power densities in direct ethanol fuel cells. Nonetheless, even in these systems, the faradaic efficiency to $CO_2$ rarely exceeds 10 %. The challenge of C–C bond cleavage remains unsolved for palladium catalysts.

The misconception that CO tolerance equates to complete oxidation stems from the use of chronoamperometry without product analysis. A high and stable current can result from continuous formation of acetaldehyde and acetate. To evaluate catalysts, researchers must perform product analysis and calculate faradaic efficiencies. Only then can claims about breaking the C–C bond be substantiated. Without such analysis, statements that palladium catalysts fully oxidise ethanol or glycerol are misleading.

Different alcohols exhibit different oxidation pathways on palladium. Methanol oxidation on palladium in alkaline media proceeds via adsorption of methoxide, dehydrogenation to formaldehyde and formate, and eventual formation of carbonate. The C–H bonds in methanol are relatively strong, and formation of CO is limited on palladium. This leads to moderate current densities but relatively low energy conversion. Ethylene glycol, with two carbon atoms, undergoes complex oxidation. The molecule can be oxidised to glycolate, oxalate and carbonate. Breaking the C–C bond yields formate and carbonate. Palladium catalysts promote dehydrogenation of the hydroxyl groups but struggle to cleave the central C–C bond. Glycerol, which has 3 carbon atoms, has an even larger range of potential products (glycerate, tartronate, and mesoxalate) than ethylene glycol; however, achieving complete oxidation of glycerol on palladium still remains a challenge. [15]

Interaction between reaction intermediates and alloys or supports can stabilize or destabilize them. For instance, palladium-silver catalysts show a different selectivity in ethylene glycol oxidation than does palladium alone. The silver weakens the adsorption of glycolate and promotes its desorption. As such, this limits further oxidation. [16] On the other hand, palladium-nickel catalysts favor additional oxidation to oxalate. This illustrates how the composition of a catalyst can influence the selectivity of a reaction and understanding these pathways is essential in developing catalysts that will maximize electron extraction from alcohols. Real time spectroscopy and density functional theory (DFT) calculations can provide useful information for studying these types of mechanisms.

## 4. Electronic-structure tuning: alloys and intermetallics versus superficial surface modifications

One method of adjusting the electronic configuration of palladium is through alloying of palladium with other metals. Tin (Sn) has been a popular choice as an alloying element to modify the electronic properties of palladium and therefore enhance its ability to catalyze alcohol oxidation reactions. Pd-Sn alloys exhibit increased activity for alcohol oxidation compared to pure palladium. Computational studies employing density functional theory (DFT) demonstrate that Sn lowers the activation energy required for ethanol dehydrogenation and decreases the binding energy of intermediate carbon-based species [17]. Additionally, experimental studies demonstrate that Pd-Sn/C displays increased peak current densities and lower onset potentials compared to pure Pd/C. The electron-to-electron interaction between Pd and Sn results in a shift of the d-band center facilitating the adsorption of OH species that will facilitate the oxidative removal of adsorbed CO species. Similar to Pd-Sn alloys, Pd-Ni and Pd-Co alloys have demonstrated enhanced activity for ethanol and glycerol oxidation in alkaline solution. In these systems, Ni or Co is capable of generating additional O-containing species as well as modifying the surface electronic structure of the alloy. However, the leaching of base metals into electrolytes may cause dealloying and structural degradation of the alloy surface during electrochemical operation. Formation of intermetallic compounds (where atoms are fixed within defined lattice sites) may help mitigate leaching by stabilizing the crystal structure. Several intermetallic Pd-Ga and Pd-Zn phases have been evaluated for their potential application in formic acid oxidation; both phases displayed enhanced stability relative to their non-intermetallic counterparts.

Alloys consisting of three or four components may be formed by combining palladium with another transition metal (e.g., Pt) along with a third metal (e.g., Co). In this manner, the unique attributes of each metal can be leveraged to produce alloys with enhanced activity while minimizing the amount of expensive Pt needed. As examples, Pt-Pd-Co alloys have shown that it is possible to reduce the amount of Pt required to achieve high activity levels while maintaining high activity. The addition of a third metal adds to the entropic contribution to the free energy of the system, which helps to homogenize the alloy, thereby reducing phase segregation [186]. The multi-component alloys often exist as single-phase structures upon heat treatment and exhibit enhanced corrosion resistance compared to their binary counterparts. However, the synthesis of these materials requires a high degree of precision regarding both the overall composition and the thermal history of the material. Furthermore, the complexity of the materials makes it difficult to determine whether the enhanced activity is due to a particular metal-metal interaction, the high-entropy effect, or a combination of factors.

Surface-level modifications include the deposition of ultra-thin layers of oxides onto the surface of palladium particles and/or decorating palladium nanoparticles with heteroatoms. Examples include depositing MnOx layers onto palladium surfaces to generate additional O-containing species or adding nitrogen-doped carbon shells around palladium nanoparticles. Both types of modifications have the potential to significantly improve performance. However, the thin layers that are deposited on palladium surfaces may degrade over time via dissolution or restructuring of the surface. Also, during operation, the underlying palladium surface may undergo oxidation or form hydrides, which could result in a degradation of the interfacial structure between the palladium surface and the modification layer. If there is not sufficient chemical bonding between the modification layer and palladium, then the durability of the modification layer will be compromised. Therefore, although surface decoration is a viable tool for conducting exploratory research, surface decorations may not lead to durable performance improvements. Instead, robust electronic tuning using alloying or intermetallic compound formation offers a potentially more durable pathway.

In addition to the previously discussed binary and ternary systems, researchers have investigated the use of several additional metals including Au, Cu, In, and rare-earth metals as part of palladium alloys. Pd-Au alloys exhibit enhanced resistance to corrosion and stability in acidic environments due to Au's ability to electronically tune the electronic structure of Pd and reduce its oxophilicity, which in turn leads to a reduction in the rate of formation of surface oxides. Pd-Cu alloys are of interest since Cu is less expensive than some other transition metals and can add empty d-states to Pd that alter the adsorption characteristics. However, the ease with which Cu leaches out of alloys in alkaline environments limits the usefulness of these alloys in certain applications. Pd-In and Pd-Bi alloys have been investigated as catalysts for formic acid oxidation and have exhibited excellent activity and stability. Rare-earth metals (e.g., La, Ce) can form intermetallic compounds with Pd that provide lattice oxygen and stabilize the structure. Although these systems are still relatively unexplored, they may represent new opportunities for electronic tuning.

Electronic structure can also be tuned by strain. Lattice strain modifies the energy levels of d-orbitals, influencing adsorption energies. Core–shell structures, where a palladium shell is deposited on a core of a different metal, induce compressive or tensile strain in the shell. For example, palladium shells on platinum cores experience compressive strain that weakens adsorbate binding. This can enhance ORR activity. Conversely, palladium shells on nickel cores experience tensile strain, strengthening adsorbate binding. Controlling the thickness of the shell and the lattice mismatch allows fine-tuning of strain and, consequently, catalytic properties.

## 5. High-entropy and multicomponent Pd catalysts

High-entropy alloys (HEAs) are defined by having five or more elements in near-equimolar ratios. The high configurational entropy of mixing is proposed to stabilise single-phase structures and prevent segregation. In catalysis, HEAs may offer a large number of unique active sites, lattice distortion and synergetic interactions. Palladium-containing HEAs, such as PtPdCoNiCu, have been synthesised by thermal shock, wet chemical reduction and mechanical alloying. Some reports show HEA nanoparticles with electrochemically active surface areas of around 60 $m^2$ per gram of precious metal and specific activities for ORR approaching those of state-of-the-art platinum catalysts. These values are promising, and HEAs could reduce reliance on platinum by distributing catalytic functions among many elements. However, the concept faces challenges. First, verifying true high-entropy behaviour requires rigorous structural characterisation. Many claimed HEAs are, in fact, core–shell or phase-separated particles. Transmission electron microscopy combined with energy-dispersive X-ray spectroscopy often reveals clustering of certain elements. Without uniform mixing, the entropy benefit is lost. Second, HEA synthesis can be energy-intensive. Achieving homogeneous mixing of five elements typically requires high temperatures or rapid quenching. These conditions are difficult to scale to kilogram or tonne quantities.

Thirdly, metals like nickel, cobalt and copper are likely to be dissolved out in alkaline environment and consequently undergo leaching when the material is used, leading to a loss of the initial chemical composition (palladium + platinum) and resulting in a loss of performance which will be attributed to a binary or ternary alloy rather than the HEA itself. Fourthly, determining the mechanistic basis for activity is made difficult by the very large number of potential active sites on the surface of the alloy. Therefore, without further mechanistic information it is unlikely that there would be sufficient rationale to guide the design of the material.

In order to go beyond the current level of excitement generated by HEAs and demonstrate their potential as practical materials for catalysis, the areas of concern listed above need to be addressed. To do so, studies using a combination of atomic resolution microscopy and spectroscopy (for example X-ray absorption spectroscopy), need to be performed in order to determine whether the different components of the HEA are uniformly distributed at the atomic level. The electrochemistry tests, likewise, need to assess the long-term stability of the HEA under the same conditions as those of real-world fuel cells. As such, if the HEA has rapid dissolution or segregation, then the high-entropy aspect of the HEA cannot be said to have contributed to the observed practical catalytic behaviour.

Further, researchers need to consider simpler multi-elemental alloys that produce the same performance characteristics with fewer elements. Ternary and quaternary alloys are examples of such systems that might offer the same degree of advantage as HEAs but with significantly easier synthesis and characterization.

Potential advantages of HEAs include the ability to adjust the binding energies over a broad range. In addition, because of the many different elements involved in the surface of an HEA, the surface can present a spectrum of adsorption sites, each one having a preference for either activating a reactant or facilitating the desorption of a product. Such a diversity of adsorption sites could potentially facilitate the catalysis of complex reactions such as glycerol oxidation which involves many different bond breaking and forming events. Also, HEAs may exhibit improved sintering resistance due to lattice distortion and slow diffusion. Such sintering resistance could improve the longevity of the catalyst. However, achieving these potential benefits depends on careful design and fundamental understanding. Data driven approaches including machine learning and high-throughput experimentation may potentially speed up the discovery of optimal HEA compositions.

Another concept related to high-entropy alloys is entropy stabilized oxides. These are materials which contain multiple oxides in a single phase solid solution. An entropy stabilized oxide composed of multiple oxides including palladium could function as both a support and/or as a catalyst in its own right. The variety of cationic species and oxygen vacancies present in the material could lead to a unique set of redox properties. For example, an entropy stabilized oxide composed of palladium, cerium, zirconium, yttrium and gadolinium could possess the oxygen storage capability of ceria along with the catalytic activity of palladium. While this area of research is still in its infancy, it presents an attractive design space.

## 6. Support, ionomer, and electrode architecture effects

While catalysts are an important part of fuel cell electrodes, other components including support materials, ionomer binders and the overall electrode design influence performance. Palladium nanoparticles are often supported by carbon black; these supports provide both a large surface area and good electrical conductivity. However, carbon can be corrosive under fuel cell operating conditions. High potentials and reactive oxygen species present at the cathode make it particularly susceptible to corrosion. Corrosion of carbon results in a loss of support material, aggregation of the catalytic nanoparticles and reduction of the available surface area. While carbon may be somewhat resistant to oxidation in alkaline environments than in acidic ones, it will eventually degrade. Additionally, the formation of a palladium hydride can create mechanical stresses that dislodge particles from their support. More advanced supports such as nitrogen doped carbon, graphene, carbon nanotubes and mesoporous carbon possess higher levels of stability and conductivity than traditional carbon black supports. Also, metal oxide supports such as ceria, titania and zirconia have been employed in addition to providing good surface areas and anchoring sites for the palladium. These oxides can supply oxygen species to the palladium to improve its activity, they can assist in the attachment of the palladium to the support, and they can aid in improving the resistance of the palladium to poisoning. For example, Pd-CeO2 anchored to onion-like carbon exhibits greater stability and reactivity towards ethanol oxidation when compared to Pd-carbon black.

The ionomer is the binder that holds catalyst particles together and provides ionic conductivity. In AEMFCs, the ionomer must conduct hydroxide ions and remain stable in alkaline environments. Different ionomers vary in ionic conductivity, water uptake and compatibility with catalysts. A comparative study of several anion-exchange membranes and ionomers found that the X37-50RT membrane paired with the XB-7 ionomer delivered significantly higher power densities than other combinations. The choice of ionomer influenced the morphology of the catalyst layer, the distribution of reactants and the resistance to flooding. Ionomer–catalyst interactions affect the formation of the triple-phase boundary where electrons, ions and molecules meet. Poor compatibility can block active sites or cause delamination.

Electrode architecture encompasses factors such as catalyst layer thickness, porosity, hydrophobicity and gas diffusion properties. Many half-cell studies use thin films of catalyst drop-cast on glassy carbon electrodes. Such films do not replicate the complex porous structure of real gas-diffusion electrodes. In fuel cells, the catalyst layer must be thick enough to provide sufficient active sites but porous enough to allow gases and liquids to permeate. PTFE is a hydrophobic additive which aids in managing water, and gradient porous structures (i.e., where the pores are larger at the gas diffusion layer and smaller toward the membrane), increase mass-transport. Optimizing electrode design will have an equally significant effect upon improving performance as creating new catalysts.

If the importance of optimizing electrode design is overlooked, catalyst performance may be misunderstood. Electronically, supports can modify the electronic properties of metals via metal-support interactions. Metal-support interactions (MSI) occur when the support alters the electronic structure of the metal. When Pd is deposited on reduced $CeO_2$, electrons are transferred from the support to the Pd; this causes a shift in the d-band, thus changing adsorption energies. MSI can enhance catalytic activity/selectivity and/or create encapsulation of metal within the support due to structural changes (e.g., corrosion protection and/or blocking of active sites). Therefore, understanding MSI is critical to the design of Pd-based catalysts. Modifying the redox state, vacancy concentration, and electrical conductivity of the oxide support can control MSI. The synergistic interaction between Pd species and $CeO_2$ supports facilitates methane activation through oxygen vacancies and interfacial Pd–O–Ce sites, enabling efficient lean $CH_4$ oxidation pathways. [19]

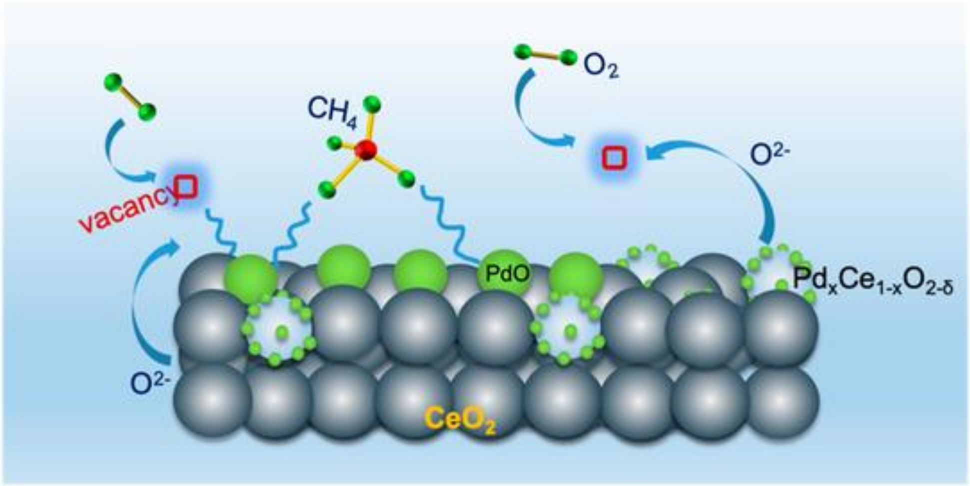

**Fig. 4.** Schematic illustration of methane oxidation over $Pd/CeO_2$ catalysts, highlighting the role of dispersed PdO and $Pd_xCe_{1-x}O_{2-\delta}$ interfacial species, oxygen vacancies, and active lattice oxygen in $CH_4$ activation and conversion. [19]

Another emerging approach to supports involves the use of metal-organic frameworks (MOFs) and MOF-derived carbons. MOFs provide highly ordered pore structures along with tunable chemical compositions. Pd NPs can be incorporated within the pores of a MOF, or they can be formed by pyrolyzing the MOF. The resultant material can contain high surface areas along with strong anchoring of metal NPs. Certain MOF-derived carbon materials contain hierarchal pore structures that can enhance mass-transport in electrodes. Therefore, integration of Pd into such architectures has potential for enhancing performance for alcohol oxidation and ORR. However, long-term stability of MOFs during operation of fuel cells, along with scaling up of MOF syntheses, represent major challenges.

## 7. Future directions and emerging opportunities

The field of palladium electrocatalysts continues to evolve. One emerging direction is the design of single-atom and dual-atom catalysts. In these materials, isolated palladium atoms are anchored on supports such as nitrogen-doped carbon. The atomic dispersion maximises metal utilisation and provides unique electronic structures. Early studies show promising activity for the ORR in alkaline media and for hydrogen evolution. However, stability of single-atom palladium under fuel cell conditions is uncertain. Coordinating atoms to heteroatoms in the support may enhance stability, but further research is needed.

Another opportunity lies in bio-inspired and enzymatic systems. Nature employs palladium-containing enzymes for specific biochemical transformations. Mimicking active sites or catalytic cycles from biological systems could inspire new catalyst designs. For instance, complex ligands or polypeptides could be used to stabilise palladium in unusual oxidation states. Adding palladium with enzymes or cofactors will increase the range of potential fuels to be oxidized using electrochemical reactions. There are many challenges to integrating enzyme inspired catalysts into fuel cells (cost and stability) but this area provides interesting conceptual ideas.

Hybridizing palladium catalysts into hybrid devices is a second major opportunity for development. A hybrid system combines a battery, supercapacitor, and/or a fuel cell to handle short-term load fluctuations and increase overall efficiency. By pairing palladium catalysts that have high power densities and fast reaction rates with the appropriate storage device to provide a dynamic response, it is possible to develop more efficient hybrid systems. To inform the design of these hybrid systems, understanding how the palladium catalyst will perform under different loads and how the palladium degrades in hybrid configurations will be essential.

In addition, there will be an increasing importance of machine learning and computational screening. The compositional space of palladium alloys, HEAs, and intermetallics is very large. Machine learning can use data to determine the best composition based on descriptors (e.g., d-band center, atom size mismatch, and cohesive energy). High-throughput experimentation combined with machine learning should enable the discovery of new catalysts faster than through experimental discovery alone. In addition, computational studies will be able to elucidate the mechanisms of the reactions and identify descriptors that relate to both the activity and the stability of the catalysts.

## 8. Conclusion

The particular characteristics of Palladium are what have made Palladium a prime candidate for use in low temperature fuel cells-especially when used in an alkaline medium. Palladium’s capability to create hydrides, its resistance to carbon monoxide poisoning and ability to perform at relatively modest temperatures (relative to platinum) have created a vast amount of research into using Palladium as a catalyst. Catalysts based upon Palladium far exceed platinum's ability to oxidize alcohols in alkaline environments and appear to have great potential for anion exchange membrane fuel cell applications. Additionally, Palladium is unable to replace platinum in acidic environments or at high current densities for Oxygen Reduction Reaction (ORR). Misuse of Mass Activity and Electrochemical Surface Area (ECSA) normalization has allowed researchers to overestimate their results. A catalyst's ability to resist carbon monoxide poisoning does not imply that all of the products will be completely oxidized - product analysis is required. Mixing Palladium with other metals such as Tin, Nickel etc., can increase the activity of the catalyst, however, there is still an issue with dealloying. High Entropy Alloys present new opportunities for improving the activity of catalysts; however, they have several barriers including synthesizing these alloys, characterization of the alloy and ensuring the long term stability of the alloy. The support material, the ionomer selected and the electrode architecture each play significant roles in the overall performance of the catalyst and therefore must be optimized in conjunction with the optimization of the catalyst. Mechanisms of degradation such as dissolution, dealloying, poisoning and the formation of carbonate require full cell durability testing in order to accurately assess the longevity of the catalyst. Researchers in the future should adhere to a set of evidence-based guidelines, consider the intrinsic activity of the catalyst and also integrate the catalyst into real-world membranes and electrodes. If this approach is taken, Palladium based electro-catalysts will become viable alternatives in sustainable energy conversion.

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