

The Role of Platinum in Proton Exchange Membrane Fuel Cells

Evaluation of platinum's unique properties for use in both the anode and cathode of a proton exchange membrane fuel cell

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Proton exchange membrane fuel cells (PEMFCs) dominate the transportation fuel cell market and platinum (Pt) is the catalyst material used for both anode and cathode. This review sets out the fundamentals of activity, selectivity, stability and poisoning resistance which make Pt or its alloys the best available materials to use in this application. It is clear that Pt is the only element which can meet the requirements for performance while avoiding slow reaction kinetics, proton exchange membrane (PEM) system degradation due to hydrogen peroxide (H₂O₂) formation and catalyst degradation due to metal leaching. Some of the means by which the performance of Pt can be enhanced are also discussed.

Introduction

A PEMFC is a device that electrochemically reacts hydrogen (H₂) with oxygen (O₂) to produce electricity with water as the only by-product. Fuel cells offer the capability to provide clean energy transportation with zero tailpipe carbon dioxide (CO₂) emissions. Even where their fuel must be sourced from fossil fuels, the high efficiency of fuel cells relative to internal combustion engines still offers the potential for reduced well to wheel CO₂ emissions (1).

PEMFCs have dominated the transportation fuel cell market and will do so for the foreseeable future (2) for several reasons. They have a unique set of advantages for use in vehicles: a sufficiently low working temperature (80°C) that they can be started up quickly; a good energy density *versus* other fuel cell types; robust and relatively simple mechanics; the ability to run on pure hydrogen, therefore emitting no CO₂; and the ability to use ambient air as the oxidant.

PEMFCs currently use Pt as the catalyst both at the cathode and at the anode, for reasons which will be described in this paper. The most recent US Department of Energy analysis (3) indicates that Pt would be around 17% of the total cost of an 80 kW PEMFC system using 2012 technology at

mass production scale. Naturally there is interest in developing substitute catalysts based on cheaper metals, although any other catalyst developed would need to exceed Pt in terms of performance against total system cost.

This review focuses on the fundamentals that are required for an idealised PEMFC electrode material and evaluates the performance of pure Pt compared to other pure metals. It finishes with a discussion of alternatives to pure Pt.

The Role of the Catalyst in a Proton Exchange Membrane Fuel Cell

Figure 1 shows how a PEMFC works. Hydrogen gas is fed to the anode where it adsorbs onto the catalyst surface. The adsorbed hydrogen atoms each lose an electron (e^-) and are released from the metal surface as protons (H^+). The electrons flow to the cathode as current through an external circuit and the protons flow across the PEM towards the cathode. Air is fed to the cathode and oxygen is adsorbed onto the catalyst surface. This bound oxygen is subsequently protonated by incoming H^+ and reduced by incoming electrons to produce water which is then released from the catalyst surface. This water is forced to exit the fuel cell by the hydrophobic nature of the surrounding media.

Pt is used as the catalyst for both the hydrogen oxidation reaction (HOR) occurring at the anode and the oxygen reduction reaction (ORR) at the cathode. Usually, the Pt catalyst takes the form of small particles

on the surface of somewhat larger carbon particles that act as a support.

Anode Processes

Hydrogen flows into the fuel cell and reaches the Pt anode where the HOR takes place. Here the hydrogen adsorbs onto the surface of the Pt electrode, breaking the hydrogen–hydrogen bond to give adsorbed atomic hydrogen (H^*) (4), Equation (i):



(where * denotes a surface site).

Subsequent loss of an electron from each adsorbed hydrogen leads to hydrogen leaving the surface as protons (H^+), Equation (ii):



In a PEMFC, the kinetics of the HOR on a Pt electrode are very fast. Voltage losses are vanishingly small even for very low Pt loadings (less than 5 mV loss at Pt anode loadings of 0.05 mg cm^{-2}) (5). As the HOR is fast, the main focus of catalyst improvement has always been on the cathode process.

Cathode Processes

The ORR that occurs at the cathode has a more complicated mechanism and it is well known for its sluggish kinetics (6, 7). The ORR is the major challenge for PEMFCs because the catalyst material must be stable under the extremely corrosive

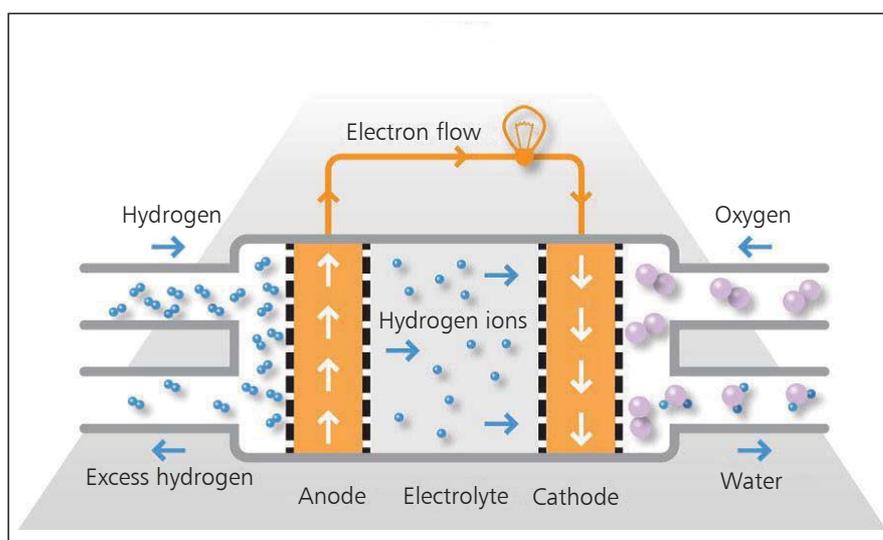


Fig. 1. A schematic of a proton exchange membrane fuel cell (Copyright Johnson Matthey)

conditions at a fuel cell cathode yet chemically active enough to be able to activate O₂. In addition it must be noble enough for facile release of product water from the catalyst surface in order to free up catalytic sites once the reaction is complete. Due to the difficulties of the ORR, the cathode requires a higher Pt loading, typically more than several times that of the anode (8). The ORR at the cathode is the source of more than half of the voltage loss for a PEMFC system (9).

There are two pathways by which ORR can occur in acidic media (4). The first mechanism is the preferred dissociative pathway and follows a concerted 'four electron' transfer process leading to direct formation of water. First O₂ adsorbs to the metal surface and the oxygen-oxygen bond breaks to give adsorbed oxygen atoms (O*), Equation (iii):



These single oxygen atoms are then protonated by the incoming flow of H⁺ across the PEM and reduced by incoming flow of electrons to give surface bound hydroxyl (OH*) (10) groups, Equation (iv):



The surface bound OH* is then further reduced and protonated to give water which then leaves the metal surface, Equation (v):



The alternative pathway is an associative mechanism where the O=O bond does not break upon O₂ adsorption onto the metal surface (Equations (vi) to (vii)) (11):



This alternative 'two electron' route is observed to produce H₂O₂. The details of the mechanism are unclear, but the reaction may proceed as follows (11) (Equation (viii)):



The H₂O₂ may react further or desorb (Equation (ix)):



Figure 2 shows a simplified representation of possible associative and dissociative mechanisms (4).

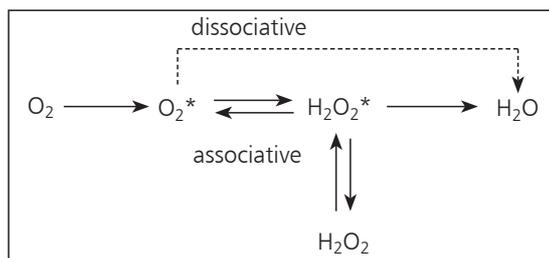


Fig. 2. Generation of hydrogen peroxide through associative oxygen reduction reaction (4)

Generation of H₂O₂ in a PEMFC is highly undesirable as it diffuses into the PEM and results in radical oxidative degradation of the membrane (12). Poor ORR catalysts produce significant amounts of H₂O₂ through associative ORR (13) whereas a good catalyst should produce little or no H₂O₂.

Although the kinetics of HOR and ORR are different, the overall trend in reaction rates on different metal electrodes is similar for both.

Required Characteristics of an Effective Proton Exchange Membrane Fuel Cell Catalyst

There are four main characteristics that are essential for an effective PEMFC catalyst:

- Activity – to be able to adsorb the reactant strongly enough to facilitate a reaction but not so strongly that the catalyst becomes blocked by the reactant or products.
- Selectivity – to make the desired product and minimise the production of undesirable intermediates and side products.
- Stability – to withstand the operating environment in a fuel cell, including strong oxidants, reactive radicals, an acidic environment and high and rapidly fluctuating temperatures, all whilst under an applied voltage.
- Poisoning resistance – to be resistant to poisoning by impurities likely to be found in the fuel cell itself and in the feed gases.

The following sections will discuss the performance of pure Pt compared to other pure metals with respect to these characteristics.

Activity

For heterogeneous catalysis on a metal surface, the catalyst must adsorb species with sufficient strength

to allow chemical bonds to break but weakly enough to release the product when the reaction has occurred. If the binding interaction is too weak, the substrate will fail to adsorb well on the catalyst and the reaction will be slow or not take place; if the binding interaction is too strong, the catalytic surface will quickly become blocked by bound substrate, intermediate or product and the reaction will stop. The Sabatier principle (14) describes the ideal interaction between substrate and catalyst as a balance between these two extremes. This principle is best illustrated by Balandin's volcano diagrams (15, 16), which plot the catalyst activity against adsorption energy for a given reaction. As described, too weak or too strong a catalyst-substrate interaction leads to a low catalytic activity. Therefore the diagrams show a clear activity peak at which there is optimal binding.

Balandin volcano plots (Figure 3 (17)) for metal hydrogen bonding energy show that Pt has the highest activity of all bulk metals. The HOR is extremely quick and already requires much lower Pt loadings than the ORR. That said, Pt is currently used for the anode catalyst for the HOR and hence is a target for fuel cell cost reduction. This effort is primarily focused on

reducing the Pt loadings still further and progress on metal thrifing is still being made.

More interesting is the effort to improve the cathode where the ORR takes place. With ORR as the slowest step, the vast majority of research effort has focused on improving the ORR activity. Figure 4 shows the Balandin plot for binding between single O atoms and various metals (11). It is observed that Pt again is the pure metal that is closest to the theoretical activity peak, although it binds oxygen too strongly by about 0.2 eV (18). The preferred ORR mechanism is actually a two-step process requiring the catalyst first to bind O (Equation (iii)) and then OH (Equation (iv)) and Figure 5 shows the activity against both O and OH binding energies (11). Pt is closest to the optimal binding energy for both reactions and has the highest activity.

Metals such as copper (Cu) and nickel (Ni) bind oxygen too strongly. For metals that bind oxygen too strongly the activity is limited by the removal of adsorbed O and OH species; that is, the surface quickly becomes oxidised and thus unreactive. For metals such as silver (Ag) and gold (Au), the opposite is true and it is difficult to bind oxygen onto

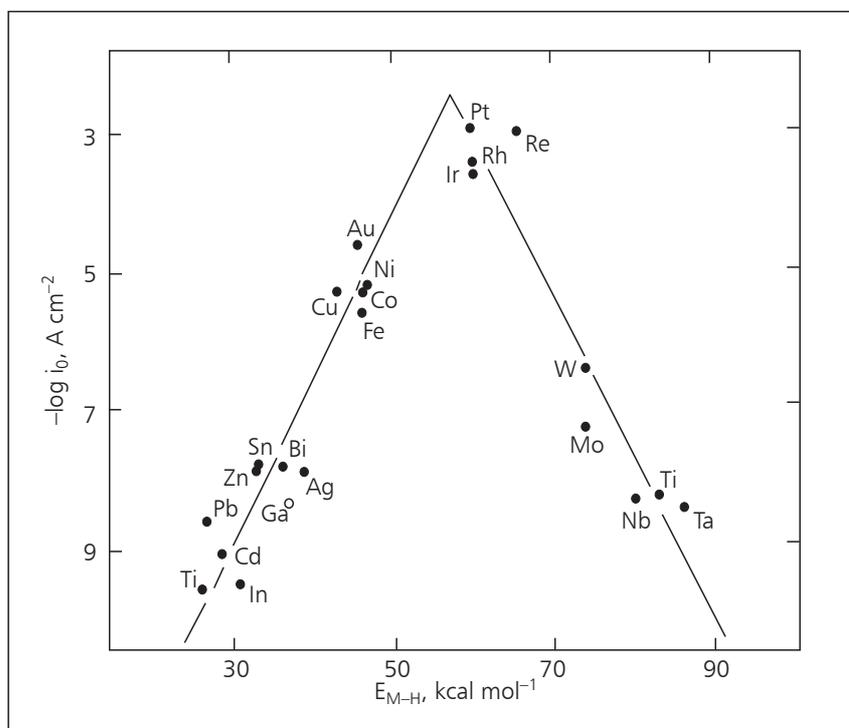


Fig. 3. The logarithm of exchange current densities ($\log i_0$) for cathodic hydrogen evolution vs. the bonding adsorption strength of intermediate metal-hydrogen bond formed during the reaction itself (17)

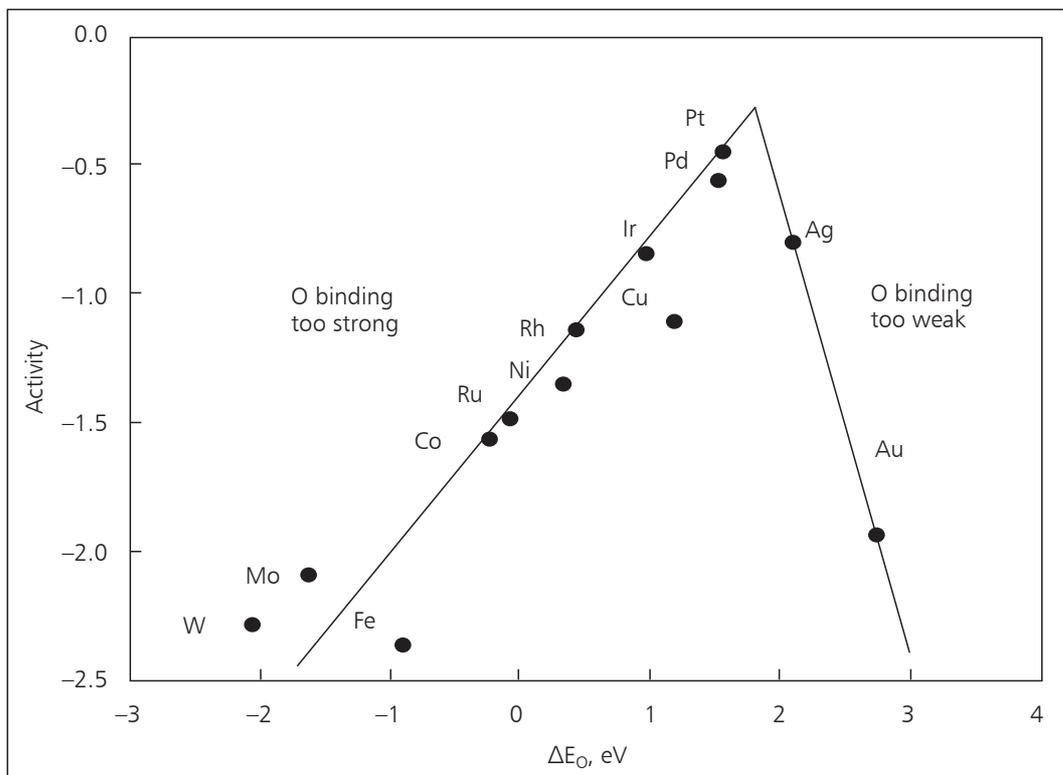


Fig. 4. Trends in oxygen reduction activity plotted as a function of the oxygen binding energy (Reprinted with permission from (11). Copyright 2004 American Chemical Society)

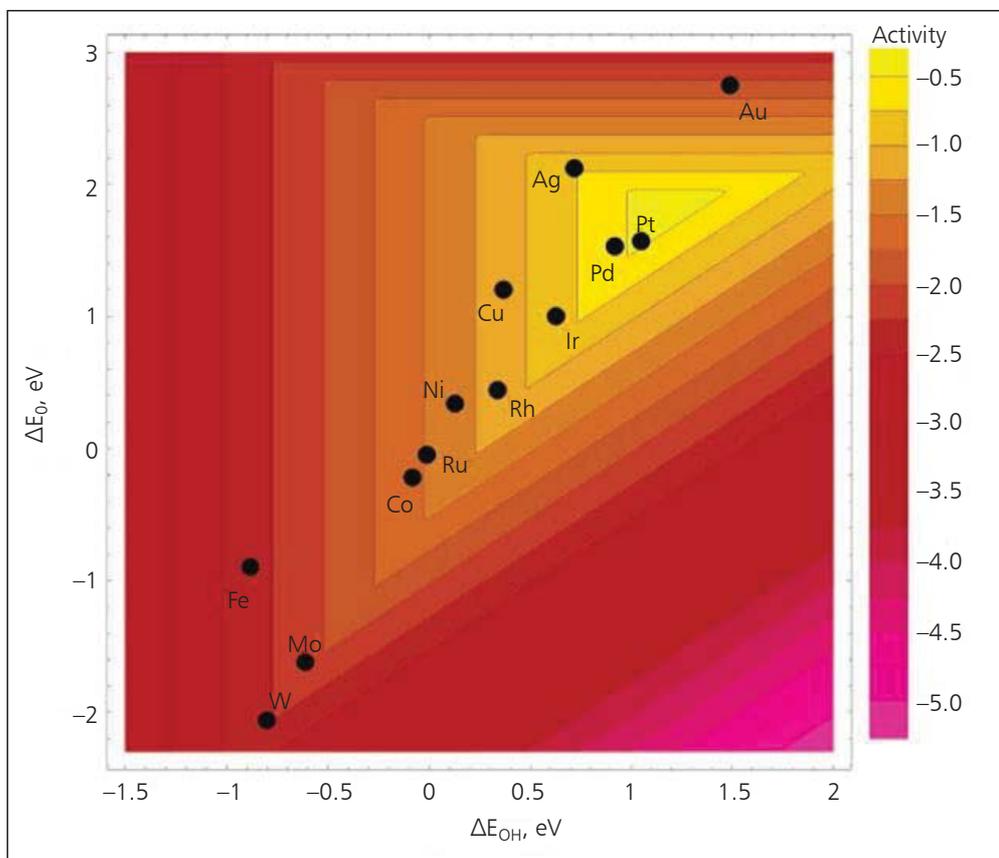


Fig. 5. Trends in oxygen reduction activity plotted as a function of both the oxygen and the hydroxyl group binding energy (Reprinted with permission from (11). Copyright 2004 American Chemical Society)

the metal surface. For these metals the rate is limited by the dissociation of O₂ or the transfer of electrons and protons to adsorbed oxygen species (12).

Selectivity

The second requirement is selectivity. The catalyst must progress the reaction to make the desired product whilst minimising the production of undesirable intermediates and side products. The HOR has only one mechanism and can produce only H⁺ and e⁻. As such, selectivity is not an issue in the context of the HOR.

At the cathode, the ORR reaction can follow one of two pathways and the pathway is determined by the selectivity of the catalyst in the first step (adsorption of O₂). The discussion of activity above has focused on the desired, dissociative four electron ORR mechanism to produce water (Equations (iii) to (v)). However, it

is important to discuss the alternative two electron reaction associative mechanism which produces H₂O₂. Catalyst materials must be chosen to minimise the undesired associative mechanism as the presence of free H₂O₂ within the cell environment is highly damaging (12).

The associative mechanism which leads to H₂O₂ starts when O₂ is adsorbed on a metal surface without the O=O bond being broken. On a Pt surface however, the O=O bond is usually broken upon adsorption. The reaction therefore proceeds almost exclusively according to the desired dissociative mechanism. Since there is no adsorbed O₂ on the Pt surface, H₂O₂ cannot be formed (4).

The amount of H₂O₂ produced on various metal catalyst surfaces has been investigated using scanning electrochemical microscopy and calculation of the total number of electrons transferred (*n*) (Figure 6

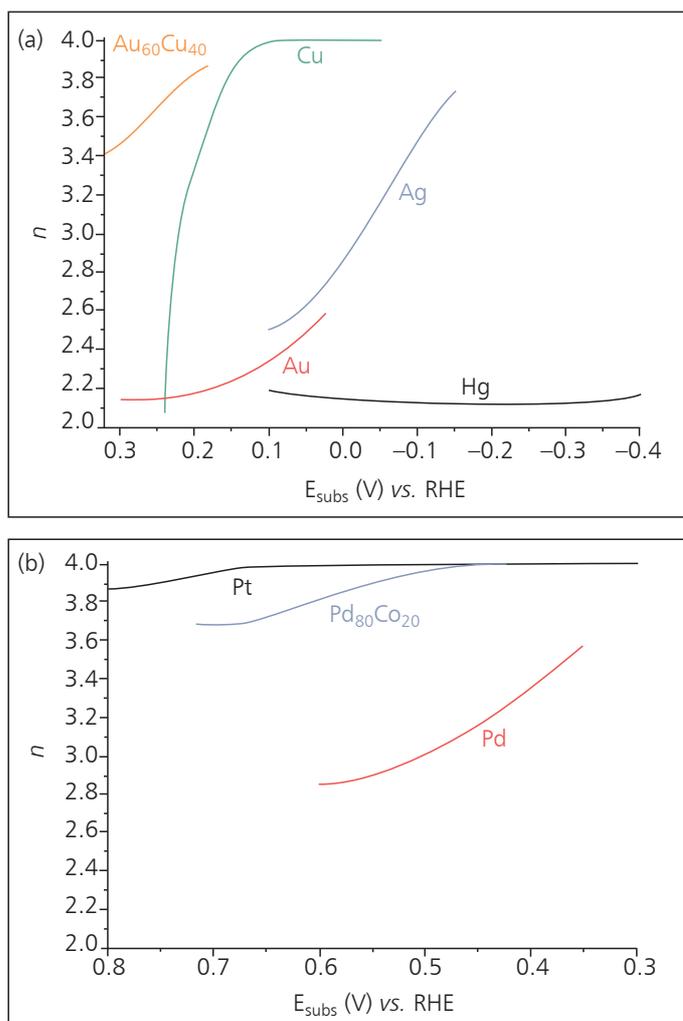


Fig. 6. Number of electrons transferred (*n*) during oxygen reduction reaction at: (a) mercury, gold, silver, copper and Au₆₀Cu₄₀; and (b) platinum, palladium and Pd₈₀Co₂₀ as a function of applied potential in an oxygen saturated 0.5 M sulfuric acid solution (Reprinted with permission from (19). Copyright 2009 American Chemical Society)

(19)). A result of $n = 2$ signifies only H_2O_2 production, with $n = 4$ showing no H_2O_2 (only H_2O) formation. From the study, mercury (Hg) shows the lowest value of n at close to 2, whereas Pt and $\text{Pd}_{80}\text{Co}_{20}$ show the highest values n at almost 4. The other materials tested show intermediate n values which vary as a function of potential.

Thus it may be concluded that Pt is the most selective metal towards the desired ORR at the cathode as it is nearly 100% selective for the dissociative mechanism over a broad potential range.

Stability

For any metal to be suitable as a fuel cell electrocatalyst, it must not only have suitable catalytic activity and selectivity, but it must also be able to withstand the harsh chemical environment within a fuel cell. The presence of strong oxidants, reactive radicals, low pH, high temperatures and rapid potential fluctuations, especially on the cathode, rules out the use of most transition metals in their pure forms. The main problem is that very few metals are sufficiently noble to avoid dissolution at the low pHs and high electrode potentials experienced at the fuel cell cathode. Those that are stable tend to be covered with oxide films that inhibit dissolution, but also the ORR. Lack of short term stability is most immediately obvious as a loss in kinetic activity, but long term stability of the catalyst is key to overall system durability.

Pourbaix diagrams (20) show the thermodynamic stability of different metals under different applied voltages and pH conditions. These diagrams map out the most thermodynamically stable species in each domain on a plot of pH *versus* applied voltage for a particular element. When conditions stray into areas of the diagram that represent a change of the most stable elemental metallic form to an oxide or different oxidation state, then corrosion or passivation – formation of a ‘protective’ layer on the surface of the given metal – can then occur. As an example, the Pourbaix diagram for cobalt (Co) is **Figure 7** (21,22). It can be seen that the low pH conditions in a fuel cell will corrode Co; the immunity domain for Co (in plain white) only exists below around -0.5 V in acidic conditions. This has been observed experimentally; pure Co reacts in acidic media to form soluble products and Co has been shown to rapidly leach out of Co-based electrode materials (23,24).

Figure 8 shows Pourbaix diagrams for different metals listed in order of nobility (unreactivity) (21,22). It can be seen that noble metals such as Au, iridium

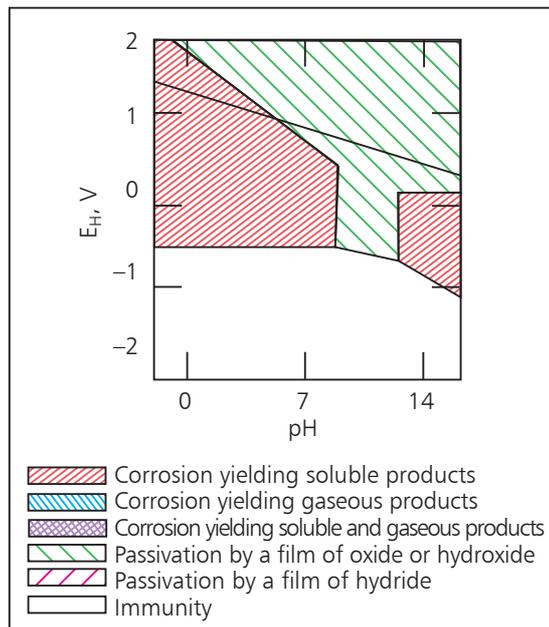


Fig. 7. The Pourbaix diagram for cobalt (With kind permission from Springer Science+Business Media (21, 22))

(Ir) and Pt are quite stable in the fuel cell environment (high cell potential, low pH), whereas metals such as Ni, Co and iron (Fe) are predicted to dissolve. This is indeed what is experimentally observed; these transition metals are electrochemically soluble at a potential range between 0.3 V and 1 V in low pH conditions (25).

The handful of other acid-stable metals have lower activities and selectivities compared to Pt. Therefore the acid/base stability of Pt under typical PEMFC operating conditions, in combination with its activity and selectivity, renders it the only suitable pure metal to be used in the PEMFC application (26).

Poisoning Resistance

A good catalyst must be resistant to poisoning by impurities likely to be found in the fuel cell itself and in the feed gases. Impurities in both the hydrogen and the air streams may have a negative impact upon the workings of a PEMFC. All catalysts are susceptible to poisoning but there are so many different poisons and poisoning mechanisms that it is very difficult to make any meaningful absolute ranking (27).

Most problematic for Pt in PEMFC applications are sulfur species (28) and carbon monoxide (CO) (29). Pt is neither the least nor the most sensitive metal to these or other poisons. In fuel cell applications, as

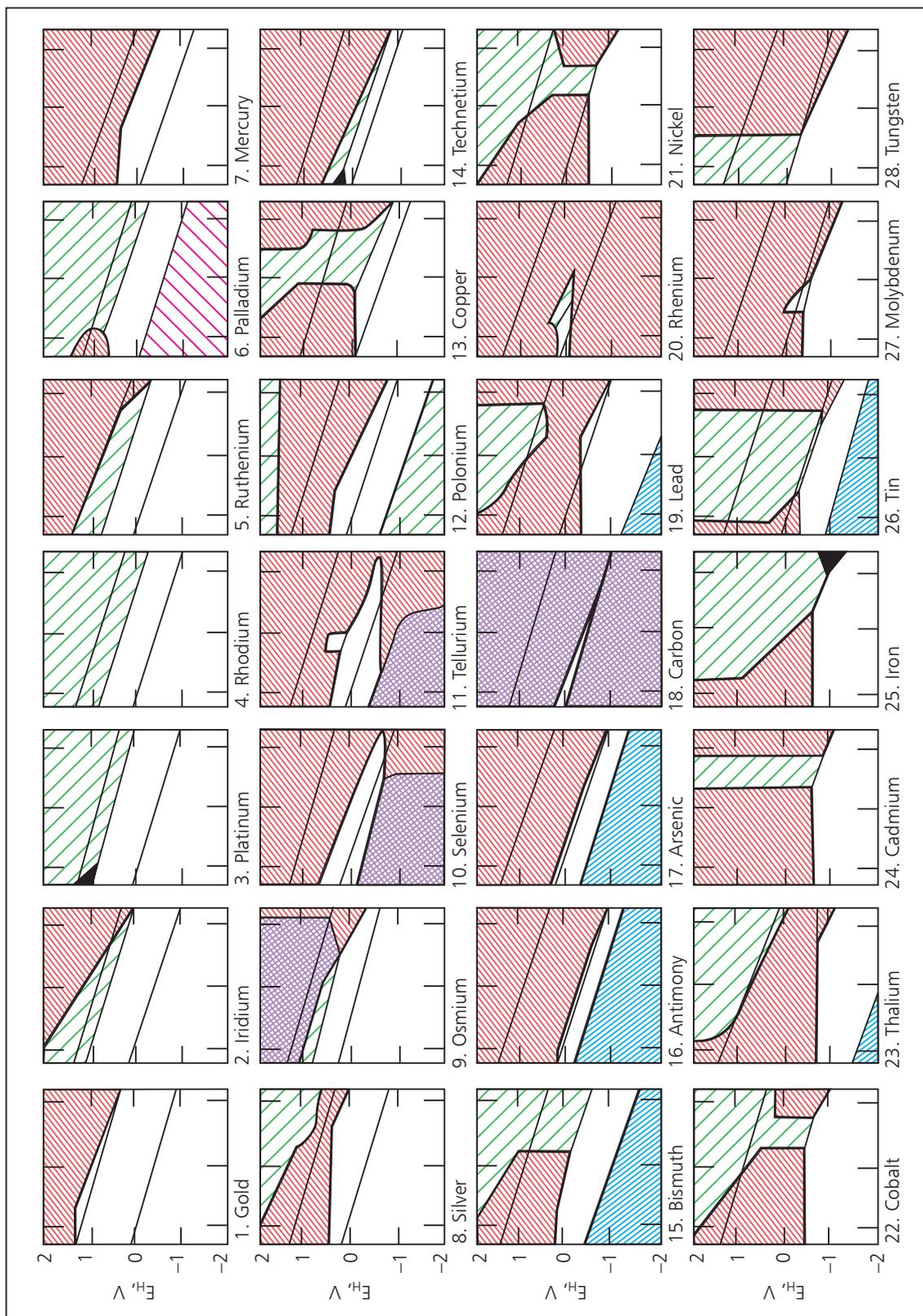


Fig. 8. The Pourbaix diagrams for different elements listed in order of nobility (With kind permission from Springer Science+Business Media (21, 22)). For key to this figure see **Figure 7**

in other catalytic applications for Pt, there are two methods of protection: keeping the poisons out of the system and alloying the Pt with other metals to reduce susceptibility to poisoning. The nature of impurities in the hydrogen fuel stream depends on the source of the hydrogen (29). Strict quality specifications have been agreed for hydrogen intended for use in fuel cell vehicles (30). However improved tolerance to poisons will still be advantageous to avoid any sub-standard batches of hydrogen causing irreversible damage to PEMFCs.

For complicated systems such as alloys, there is no simple way to predict in advance the precise susceptibility to sulfur poisoning (31). Many fundamental studies on the interaction of sulfur species with elemental catalysts have been undertaken (32–41). Unsupported or supported Pt-based alloy catalysts have been demonstrated to exhibit high tolerance to CO poisoning. These include binary, ternary and quaternary Pt alloys, Pt-based metal oxide catalysts (42–44), Pt-based composites and organic metal complexes (45, 46). More information on the development of high-performance and cost-effective CO-tolerant anode electrocatalysts for PEMFCs can be found in several comprehensive review articles (47–52).

Alternatives to Pure Platinum

There is a limited amount of interest in improving the HOR (53); as this review has discussed the major focus has always been on improving the ORR. While Pt is the best pure metal in terms of activity, selectivity and stability for both anode and cathode in a PEMFC, it does not sit at the peak of the Balandin volcano plot for the ORR. The perfect catalyst according to the Sabatier principle would have slightly different electronic properties. Therefore a lot of research focuses on fine tuning the electronic properties of Pt in order to optimise the resulting catalyst material.

Approaches currently used to improve Pt activity are:

- (a) Alloying with one or more other metals;
- (b) Layering Pt on or just below the surface of another metal;
- (c) A core-shell approach where a core of cheaper metal is coated with Pt;
- (d) Alloying Pt followed by dealloying such that the finished Pt lattice structure retains some of the original structural strain associated with alloying.

The objective of all of these approaches is to modify the electronic properties of Pt to bring the adsorption

energy for the O and OH reduction reactions closer to the Sabatier ideal. The improved activity of these modified Pt structures has been attributed to many factors including changes in the number of nearest Pt neighbours, average Pt–Pt distance and Pt 5d band vacancy (54,55).

In addition, various ‘novel technologies’ have been used to support and fine tune the electronic structure of potential catalysts such as supporting metals on graphene or using metal ions held in chelating organic frameworks.

Alloying

Pt-based binary alloys (Pt-X) have shown enhanced activity towards the ORR (56). In the last few years results have shown that many alloys with the general formula Pt₃X (where X is a 3d transition metal) give high activity (**Figure 9**) (18, 57). Pt₃Ni(111) has been presented as the most active surface yet observed with a mass activity 10 times that of Pt(111) and up to 90 times higher than polycrystalline Pt (58). This result has not yet been reproduced in polycrystalline PtNi alloys. However it should be noted that care must be taken when assessing any comparison of activity between Pt systems and alternatives as the mass activity of Pt systems themselves can differ by a large factor.

Whilst these Pt₃X alloys have proven to be highly active towards the ORR, stability as well as activity is crucial for any viable PEMFC catalyst. Hence it must be ascertained whether or not base metal leaches from these systems. Both theoretical predictions (59) and experimental observations (55) indicate that strong leaching takes place.

In the acidic fuel cell environment, dissolution of the base metal in the oxidised form will occur. Base transition metals are electrochemically soluble in low pH media (25). Observed leaching may have several main causes:

- (a) Excess of deposited base metal;
- (b) Incomplete alloying of the base metal due to a low alloying temperature applied during formation;
- (c) Thermodynamic instability of the base metal in the alloy.

Ni, Co and Fe have all been found to migrate easily from the surface of Pt alloys (55) although the bulk of the alloy remained unchanged, indicating it was mainly leaching from the top few monolayers of the alloy surface. Ni has also been found to leach out of the Pt₃Ni system at a high initial rate before a steady state is reached (60).

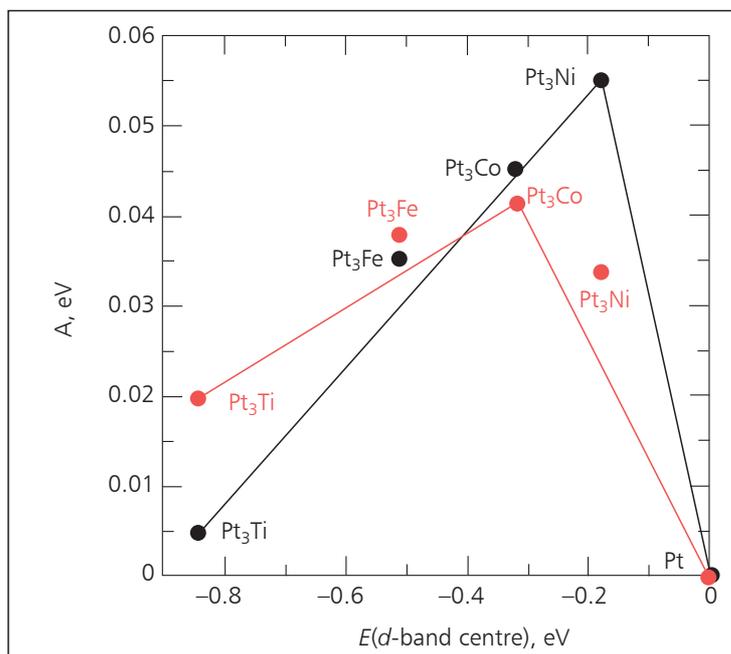


Fig. 9. Activity versus the experimentally measured d-band centre relative to platinum. The activity predicted from DFT simulations is shown in black, and the measured activity is shown in red (Reprinted with permission from (18). Copyright 2006 John Wiley and Sons)

Transition metal ions provide sites for radical formation from any peroxide that is present as a result of the associative ORR mechanism (12), or that is formed on the anode by the reaction between crossed-over oxygen and hydrogen. H_2O_2 will degrade the PEM and other parts of the fuel cell, especially in the presence of any transition metal ions that have migrated there. For example, Fe is widely recognised to catalyse radical formation from peroxide (61). Thus any Fe-containing catalyst could leach Fe into the membrane and cause damage through the associated Fenton chemistry (62). Amongst other transition metal ions, Cu ions are also known to poison the HOR activity of the anode if they migrate through the PEM (63).

Layering

The use of overlayer or underlayer structures is also an area of substantial research interest (64) in order to create a surface that binds O a little more weakly than Pt. Again, in practice it is likely that overlayer/underlayer structures will suffer from metal leaching, reducing the catalyst stability and shortening PEMFC lifespan.

Core–Shell Approaches

The core–shell approach was first used by Adzic and co-workers in order to address both catalytic activity

and Pt thrifting in fuel cells. This approach uses a core of a cheaper metal, such as palladium (Pd), Co or Ni, coated with a monolayer of Pt. Results have been extremely successful in terms of initial activity but stability remains an issue (65). As the catalyst is cycled, the core transition metal atoms tend to diffuse to the surface of the nanoparticles and leach out into the ionomer and membrane (12). If there are any gaps in the Pt monolayer, the same will happen even more quickly.

Dealloying Approaches

The base metal content from the exterior layers of nanoparticles can be leached from Pt_yX_z catalysts by voltammetric surface dealloying. Strasser and co-workers have demonstrated that the residual compressive Pt strain in the dealloyed surface layers is key to the observed activity (66). Experimental control of the Pt shell thickness and the composition of the alloy core controls lattice strain and hence ORR activity because the decrease in Pt–Pt lattice parameter reduces the oxygen binding strength. From this perspective, the initial alloy composition and thickness of the dealloyed layer are important factors that determine catalytic activity (67).

Similar effects were reported by Gottesfeld for electrochemically leached $\text{Pt}_{65}\text{Cr}_{35}$ and $\text{Pt}_{20}\text{Cr}_{80}$

catalysts (68). This work suggested that the selective electrochemical dissolution (dealloying) of non-noble components from noble metal bimetallics could serve as a general strategy towards tuning surface electrocatalytic properties. This approach can be considered as a more sophisticated improvement to core-shell catalysts. Expanding these ideas, some groups are already working towards controlled shape nanoparticles grown with faces composed of the most preferential orientation for the ORR (53,69). Dealloyed Pt electrode materials would be less likely to leach base metal into the electrolyte solution, depending on the exact near-surface composition, offering the possibility for cheaper catalyst materials without an associated increase in fuel cell degradation.

Novel Technologies

Numerous novel alternatives to Pt have been investigated such as doped graphenes (70), macrocyclic transition metal complexes (71–76), transition metal carbides and nitrides, chalcogenides (23, 77, 78) and carbonaceous electrodes (79–81), although none are likely to represent viable options in the near or mid term. Novel base metal containing technologies still suffer from the same lack of stability in the harsh conditions of a PEMFC and none has yet been able to exhibit the activity of Pt.

Conclusions

The great value of platinum as a catalyst in PEMFC applications is that it outperforms all other catalysts in each of three key areas: its activity, its selectivity and its stability. Any potential alternative catalyst must demonstrate not only improved performance in one of these areas, but at least equivalence in the other two. Of all transition metals, Pt is the closest to an ideal catalyst for both the HOR and ORR in the PEMFC system. Bulk Pt is commonly chosen as the benchmark for non-Pt systems, particularly with reference to activity, but it can still be improved by an order of magnitude or more if its electronic properties are fine-tuned by alloying with other metals. It is the performance of these modified Pt systems that represents the true benchmark.

The relative cost of a gram of Pt makes the promise of systems using cheaper metals seductive. However, alternative systems containing base metals have fundamental limitations such as a lack of activity, poor selectivity leading to H₂O₂ formation, or catalyst degradation caused by a lack of stability under the fuel cell operating conditions which all must be addressed. As academia and industry continue to develop both

Pt and non-Pt systems, the question for the future is whether the great lead that the Pt systems have in both utility and economics will reduce or, as seems more likely, increase.

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