Facile synthesis of palladium phosphide electrocatalysts and their activity for the hydrogen oxidation, hydrogen evolutions, oxygen reduction and formic acid oxidation reactions

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Abstract

We demonstrate a new approach for producing highly dispersed supported metal phosphide powders with small particle size, improved stability and increased electrocatalytic activity towards some useful reactions. The approach involves a one-step conversion of metal supported on high surface area carbon to the metal phosphide utilising a very simple and scalable synthetic process. We use this approach to produce PdP2 and Pd5P2 particles dispersed on carbon with a particle size of 4.5-5.5 nm by converting a commercially available Pd/C powder. The metal phosphide catalysts were tested for the oxygen reduction, hydrogen oxidation and reduction, and formic acid oxidation reactions. Compared to the unconverted Pd/C material, we find that alloying the P at different levels shifts oxide formation on the Pd to higher potentials, leading to greater stability during cycling studies (20% more ECSA retained, 5k cycles) and in thermal treatment under air. Hydrogen absorption within the PdP2 and Pd5P2 particles is enhanced. The phosphides compare favourably to the most active catalysts reported to date for formic acid oxidation, especially PdP2, and there is a significant decrease in poisoning of the surface compared to Pd alone. The mechanistic changes in the reactions studied are rationalised in terms of increased water activation on the surface phosphorus atoms of the catalyst. One of the catalysts, PdP2/C is tested in a fuel cell as anode and cathode catalyst and shows good performance.

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1. Introduction
The activity and durability of electrocatalysts for low temperature fuel cells is a subject of steadily increasing interest and importance. The availability and shortcomings of Pt catalysts contribute to the limited commercial availability and high cost of fuel cells. Other Pt-group transition metals, such as Pd, Ru, Rh and others have been touted as possible replacements for Pt in fuel cells, particularly for the oxidation of formic acid[1] and methanol[2]. While these transition metals can have high intrinsic activity towards fuel cell reactions, long term stability in acidic media still remains an issue, even for Pt-group metals. The alloying of different transition metals or the use of metal-chalcogenides, carbides, nitrides and phosphides have been the most promising approaches to replace Pt[3-6]. On a worldwide basis palladium reserves are greater than those of platinum[7] and also the cost of palladium is about 45% that of platinum (metal price averaged over the five years before 2015 based on data from [8]). Palladium has been considered as a catalyst in its own right and alloyed with other transition metals for a range of fuel cell relevant reactions such as oxygen reduction, hydrogen evolution and oxidation, and oxidation of organic compounds such as alcohols and organic acids[9]. Indeed, Pd-Pt alloys are more active than Pt towards the oxygen reduction reaction (orr)[10], and Pd or Pd-metal alloys are exceptionally active towards formic acid oxidation[1, 11]. However, attempts to use palladium as a fuel cell catalyst are typically stymied by the lower stability of this material and its propensity to form oxides and to undergo dissolution or corrosion processes at potentials lower than for the comparable processes on platinum.

Alloying a transition metal with phosphorus to produce a transition metal phosphide affords an interesting opportunity to improve the corrosion resistance of the underlying transition metal. The resulting materials are typically metallic conductors or low-bandgap semiconductors and show low electrical resistivities[12]. Furthermore, the materials can be produced through a range of chemical routes and the resulting materials show excellent stability in acidic & basic media compared to that of the unalloyed metal[13-15]. A range of different M-P phases are possible, allowing some degree of tailoring of relevant properties. Although many transition metals are unstable in even weak acids, metal phosphides, especially those with high phosphorus content are exceptionally resistant. For instance, MP phosphides are only dissolved in hot aqua regia (e.g., CrP, VP, TiP, TaP)[16]. Protective
Electroless coatings utilising metal-phosphorus alloys (typically less than 10 at% P), are used in a wide variety of objects due to their high corrosion resistance. They have been investigated previously as corrosion resistant coatings by electroplating from phosphite baths[17, 18]. These coatings have proved to be effective and durable in a wide range of corrosive environments and it has been shown that the durability of metal phosphides in acidic media increases with increasing P content[19], although such baths only allow up to 10-15 at.% P to be incorporated into the metal matrix. Corrosion of these metal phosphides may be thermodynamically less favoured when alloyed with phosphorus due to high enthalpy of alloying of the materials. Furthermore, metal phosphides often form amorphous films which are immune to attack at grain boundaries. Finally, the phosphorus may be oxidised to phosphate, which can then combine with the liberated metal ions to produce an insoluble metal phosphate. As well as materials for anti-corrosion coatings, transition metal phosphides have been considered as insertion anodes for lithium ion batteries[20], and heterogeneous catalysis for hydrogenation of alkenes and hydrodesulfurisation reactions[13, 21].

The electrocatalytic properties of transition metal phosphides have been investigated particularly for the hydrogen evolution reaction (HER) and various metals-phosphide compounds have been used for this purpose including those in which the metals are Ni[19, 22-24], Co[25], Mo[26] and W[27]. There are a limited number of other studies where these materials have been examined for the hydrogen oxidation reaction (HOR)[28] and the oxygen reduction reaction[29].

Although there have been previous attempts to incorporate phosphorus in palladium electrocatalysts, these have typically involved utilisation of a phosphite based plating bath. This approach typically produces non-phase pure material with low levels of P (typically < 10 at%)[30]. More recently, newer methods of phosphiding via solvothermal synthesis have been used to create transition metal phosphide nanoparticles with yields of up to 100%[15, 28]. In these approaches, phase pure materials can be produced. However, the typical process involves in situ generation of metal particles followed by conversion into the appropriate metal phosphide in the same reaction mixture by using trioctylphosphine. Because of the non-aqueous nature of the synthesis process, the precious metal starting material must typically be a somewhat expensive organometallic precursor. Furthermore, it
can be difficult to prevent agglomeration of the metal particles as they are produced, and so surfactants are often added to limit particle growth and aggregation. Clean-up of the catalyst after synthesis may thus require significant washing steps to remove all of the surfactants, as these have a detrimental effect on catalytic activity. Because of the cost of the precursors and the clean-up steps, scale-up of the above approach is difficult.

In our new approach, which is easily scalable, we pre-synthesise (or purchase off the shelf) metal nanoparticles dispersed on carbon as our metal precursor. We then apply the phosphiding methods utilising trioctylphosphine to convert the metal nanoparticles to their phosphide counterparts, Figure 1. In this paper Pd/C is used to create PdP₂/C and Pd₅P₂/C electrocatalysts. These materials are then tested for a number of appropriate reactions: hydrogen oxidation, hydrogen evolution, oxygen reduction and formic acid oxidation reactions along with tests of the durability of the phosphides in acidic media and at high temperatures under air. These results are compared to the Pd/C precursor as well as an optimised commercially available Pt/C electrocatalyst.

2. Materials and Methods
Pd₅P₂/C and PdP₂/C nanoparticles were prepared from carbon-supported Pd nanoparticles (Alfa-Aesar, 20 wt.% Pd). The Pd/C particles were dispersed in trioctylphosphine (TOP, Sigma-Aldrich, 97%) using ultrasonication and subsequently heated to 300°C under an Ar atmosphere for 1 h. The reaction was quenched using ethanol and the Pd₅P₂/C and PdP₂/C were separated using a centrifuge and washed with ethanol and hexane then dried under Ar.

The powders were characterised using TEM, EDS and XRD. X-ray diffraction measurements were performed on a PANalytical diffractometer with a Cu anode (Kα=1.54 Å) at 40 kV and 120 mA. TEM was performed using a JEOL 2010 coupled with energy dispersive spectrometry (EDS).

The thermal stability of the electrocatalyst powders in air was determined by thermogravimetric analysis (TGA) (Q500 Thermogravimetric Analyser; TA Instruments) in an oxygen atmosphere from a temperature range of 100 to 800 °C, at a heating rate of 10 °C min⁻¹. The samples were initially heated from room temperature to 100 °C under a nitrogen atmosphere.
Electrocatalyst inks were prepared from the dried Pd₅P₂/C and PdP₂/C nanoparticulate powders. Pd/C and Pt/C (Alfa-Aesar HiSPEC 9100) inks were also prepared using the same methods for comparison purposes. The inks were prepared by dispersing the electrocatalyst powders in a mixture of 2-propanol (Sigma Aldrich, anhydrous 99.95%) and ultrapure water (Millipore MilliQ, 18.2 MΩ cm). Nafion (Sigma Aldrich, 5 wt. %) was used as a binding agent and to promote electrolyte conductivity to the metal nanoparticles.

For electrochemical testing, ink was deposited on a glassy carbon rotating disc electrode (RDE) tip, which has been previously polished using a 0.05 µm alumina slurry for 30 s. The geometric area of the RDE tip was 0.196 cm² and amount of ink was adjusted to give a loading of 20 μgₚd cm⁻² in each case. The inks were dried by rotating the RDE at 700 rpm under N₂ (BIP Plus, 99.99998%, Air Products).

Electrochemical tests were performed using the rotating disc electrode in a glass cell which had been thoroughly cleaned by immersion in acidified potassium permanganate, followed by acidified hydrogen peroxide and rinsing in copious amount of ultrapure water. The counter electrode was Pt wire (Advent, 99.998%) and the reference electrode a Gaskatel Hydroflex. The cell was controlled by an Autolab PGSTAT302N potentiostat.

PdP₂/C fuel cell electrodes were prepared by brushing an ink of PdP₂/C dispersed in 2-propanol onto a 5 cm² Toray carbon paper electrode (Alfa Aesar TGP-H-60). The loading of the electrode was 0.71 mgₚdP₂/cm² (equivalent 0.45 mgₚd/cm²). A commercially available Pt/C electrode (Alfa Aesar 45372, 0.4 mgₚt/cm²) was used as the other electrode. A pretreated Nafion membrane (50.8 μm thickness) was sandwiched between these two electrodes and hot pressed at 160 °C for 180 s to form a membrane electrode assembly (MEA). The MEA was tested with the PdP₂/C as a hydrogen anode and as an oxygen cathode in a fuel cell (FC-01-02; Electrochem Inc., USA). The cell was galvanostatically broken in for 8 hours before each test at 0.3 A/cm², with pure hydrogen on the anode and pure oxygen on the cathode. The cell was operated at 80 °C with humidified gases and
backpressure of 70 kPa. A fuel cell load (KFM2030; Kikusui, Japan) was used for cell polarisation and response measurements.

The electrolyte was 0.1 M perchloric acid (Merck Suprapur, 70%) for the electrochemical characterisation including the HOR, HER, ORR and durability tests. Formic acid oxidation was tested in a solution of 0.5 M sulphuric acid and 0.5 M formic acid. All gases used were ultrapure grade (BIP Plus, 99.99998%, Air Products), and all solutions were made using ultrapure water (18.2 MΩ cm, Millipore, Milli-Q).

3. Results and Discussion

1.1. Characterisation of materials

XRD of the synthesised palladium phosphides in Figure 2(a) shows that the synthesis conditions produced monoclinic Pd₅P₂/C (PDF 00-019-0887) and monoclinic PdP₂/C (PDF 00-077-1421) where the particle size of the phosphides was very similar to that of the Pd/C precursor, indicating only a limited amount of ripening of the precursor during the synthesis. Some small amount of PdP₂ is seen to exist in the Pd₅P₂ sample, but none of the Pd precursor. This is confirmed by image analysis of the TEM images (Figure 2(b)) which show individual nanoparticles of Pd₅P₂ and PdP₂ with diameters of 4.5 – 5.5 nm (inset in the TEM images). Within the accuracy of the image analysis the particle size remains the same as for the Pd/C precursor.

Voltammetry of the Pd₅P₂/C and PdP₂/C and Pd/C precursor (for comparison) in 0.1 mol dm⁻³ HClO₄ under nitrogen are shown in Figure 3(a). There are a number of interesting features of the voltammetry. For both the Pd₅P₂/C and PdP₂/C there is a slight decrease in the double layer capacitance. This probably results from a small loss of oxygenated groups on the carbon during the formation of the metal phosphides at elevated temperature and under the presence of the TOP chemical reductant. Three peaks are seen in the hydrogen region, during the anodic scan (A1-A3) and during the cathodic scan (C1-C3). Palladium is well known for its ability to absorb hydrogen. and the peaks in the hydrogen region can be due to either hydrogen absorption or hydrogen adsorption. For bulk palladium, the absorption process masks any surface processes as the amount of hydrogen absorbed may
be considerably more than that adsorbed to the surface. Hence, it is only in nanoparticles, 
that the absorption and adsorption processes can be easily convoluted, with the lower 
potential peaks associate with the absorption process[31, 32]. For both of the phosphorus 
containing catalysts there is a sharpening of the hydrogen adsorption/absorption region, 
with the upper limit of the hydrogen region shifting to a lower potential. Furthermore, there 
is indication that the hydrogen absorption process is more facile on the Pd₅P₂/C and PdP₂/C 
catalysts then on the Pd/C precursor. Bi-Gaussian fitting[33] of the positive going scan of 
the voltammogram, highlighted as the dotted box in Figure 3(a), is used to deconvolute 
each of the peaks in the hydrogen region, Figure 3(b). This function is used in preference to 
the Gaussian function as it is more able to accommodate the asymmetry of peaks A1 and 
A2. As has been previously noted for palladium nanoparticles, the peak at higher potential is 
due to hydrogen adsorption whereas those at lower potentials are due to hydrogen 
absorption[31, 32]. The C1/A1 sets of peaks correspond to the θ-phase region of the Pd-H 
phase diagram whereas C2/A2 corresponds to the α-phase region[32]. We thus assign peaks 
C1/A1, and C2/A2 to hydrogen absorption/desorption from the lattice and C3/A3 due to the 
surface adsorption process. The fitting results provide asymmetric peaks for A1 and A2 (C1 
and C2) and a symmetric peak for A3(C3). This also strengthens the assignment of A1(C1) 
and A2(C2) to the absorption process, and A3(C3) to the adsorption process. Figure 3(c) 
provides the integrated peak charges for each of the components of the voltammogram. It 
is interesting to see that the charge associated with A1 and A2 increases when phosphorus 
is alloyed with the palladium suggesting that the equilibrium hydrogen concentration is 
increased when phosphorus is alloyed with palladium. For all catalysts the adsorbed 
hydrogen charge associated with A3 remains constant within error, supporting the 
conclusion that there is no increase of particle size after the treatment to produce the Pd-P 
compounds.

In Table 1 we compare the surface areas of the catalysts determined from both TEM image 
analysis and from the integrated charge of peak A3. We use a conversion factor of 213 μC 
cm² for the charge associated with a monolayer of hydrogen on Pd. This value is calculated 
from the surface density of palladium atoms and assumes that hydrogen forms a maximum 
coverage of 0.8 on the surface (the same value as observed for platinum). In both cases we 
find that there is no significant change in dispersion of the catalyst following formation of
the phosphide compound. However, there is some disagreement in the absolute surface area. This may be due to an overestimation of the surface charge due to some inclusion of hydrogen absorption charge. Henceforth we use the hydrogen adsorption charge as a measure of surface area, and correct our results to these surface areas. At anodic potentials, there is evidence of a shift in peak A4 associated with the initial formation of oxide on the palladium by ca. 100 mV more anodic on the phosphorus containing catalysts. This is significant and could be important in maintaining stability of the catalyst under oxidising conditions as well as enhancing the oxygen reduction reaction at higher potentials. At higher potentials, the current associated with the oxidation of the palladium to palladium oxide is enhanced over that seen for the Pd/C sample. This is confirmed during the oxide reduction phase in which peak C4 is sharper and somewhat larger than that seen on Pd/C. It would appear that oxide growth is shifted to higher potential but becomes somewhat more facile at higher potentials.

There are two aspects of stability of catalysts to long term degradation. The first involves the stability of the catalyst itself, the second involves the stability of the catalyst support and more specifically whether the catalyst interacts with the substrate in a deleterious way. For instance, as most precious metals are catalysts for oxidation of organic molecules, they act as catalysts for the degradation of the carbon support on which they are attached. Hence, we used two different methods to study the stability of the both the catalysts and the catalyst-support interaction: under electrochemical cycling and by thermogravimetric analysis (TGA) under oxygen.

Electrochemical degradation of the catalysts is shown in Figure 4(a). Cycling of catalysts to high potentials is a common method of assessing catalyst degradation through dissolution and Ostwald ripening processes. In the electrochemical studies we have cycled the potential from 0.6 to 1.0 V (RHE). In this potential range it is know that precious metals are especially sensitive due to repeated oxidation and reduction of the catalyst surface. For the palladium phosphide catalysts it is seen that the phosphorus rich PdP₂ material shows significant stability improvements compared to the Pd/C catalyst, although that stability is still not as good as a commercial Pt/C catalyst (HiSPEC 9100). The palladium rich Pd₅P₂/C catalyst shows similar surface area loss to the Pd/C catalyst. It seems that for this latter catalyst, the amount of phosphorus included in the material is insufficient to impart significant extra
stability whereas for the P-rich material, there are some beneficial effects associated with the higher phosphorus content.

TGA provides a somewhat indirect method to test the activity of the catalysts towards chemical oxidation of the carbon support – an important mechanism for the loss of electrocatalysts under fuel cell conditions. However, as the TGA results occur in a water free environment, the result must be taken with some caution, as catalyst catalysed oxidation of the support may be more facile through a reaction pathway involving water. In comparison, the electrochemical cycling study tests the likelihood of catalyst dissolution and subsequent loss of active materials. Both mechanisms are important in fuel cell degradation. TGA traces for the two catalysts and Pd/C, shown in Figure 4(b), and they demonstrate a significant shift in the region of predominant mass loss. The temperature at which rapid weight loss occurs shifts from ~450 °C for Pd/C, to ~580 °C for Pd₅P₂/C and 600 °C for PdP₂/C. The proportion of retained material is also higher in the case of the phosphides and is in proportion to the amount of phosphorous in the metal phosphate compounds if it is assumed that the final product is PdO and Pd₃(PO₄)₂. Dashed lines in Figure 4(b) provide estimates of the final weight of the sample assuming that the Pd loading is 20wt% and all of the carbon is burnt off. There is good agreement between the predicted final weight of the sample and the results from the TGA measurements. For the phosphorus rich compound, PdP₂, there is too much phosphorus to form the stoichiometric Pd₃(PO₄)₂ compound, and so excess P₂O₅ is also likely to form. As P₂O₅ has a boiling point of 360°C the excess phosphorus will be lost, and so the dashed in Figure 4(b) represents the remaining Pd₃(PO₄)₂ after vaporisation of the excess P₂O₅. The enhancement in stability of carbon to oxidative attack could be due to two possibilities. In the first, the phosphide treatment leads to improvement in the stability of the carbon support. This could be due to a reduction in the content of surface oxygen on the carbon due to reduction by the TOP, removal of some amorphous carbon, or maybe chemical change in the carbon. This process leads to a slight diminution of the double layer capacitance. The second possibility is that the improved thermal stability is associated with reduced activity of the catalyst towards carbon oxidation. This would be associated with reduced formation of PdO during oxidative treatment. Instead of PdO, Pd₃(PO₄)₂ is produced, and the reaction of carbon with this
material is very slow as phosphate is only reduced by carbon at very high temperatures, and indeed is used to improve the stability of graphite towards high temperature oxidation.[34]

1.2. Hydrogen oxidation and hydrogen evolution reaction
Comparison of the Pd-phosphide catalysts to the Pd/C precursor material for the hor and her reactions is provided in Figure 5. All catalysts show a similar curve for the hor although there is slight reduction in the limiting current of the PdP₂/C catalyst. The likely explanation is a non-uniform coating of the catalyst across the RDE surface leading to sub-optimal reactant distribution across the electrode surface. Both phosphide containing catalysts show a slight peak before they attain a limiting current. This peak is likely associated with oxidation of hydrogen absorbed in the lattice of the phosphide particles, and suggests that hydrogen diffusion in the particles may be greater than in precursor Pd/C. This is also suggested in the voltammetry shown in Figure 3 in which the low lying oxidation peak due to oxidation of absorbed hydrogen is enhanced in both phosphorus containing particles. These peaks seem well correlated with the voltammetric peaks in the absence of hydrogen, Figure 3. By plotting the current density divided by the limiting current for the hor, it can be seen that both phosphide containing catalysts show faster onset for the hor than the Pd/C precursor catalyst, especially the phosphorus rich catalyst, Figure 5(a) inset. As has been noted in a number of previous papers[35, 36], attempting to extract exchange current densities for the hydrogen reaction from RDE data may lead to anomalously low values (e.g. see table 1 in [36] and Table 4 in [35]). Therefore it is necessary to use methods with much higher mass transport regimes to determine these values such as microelectrodes[37], scanning electrochemical microscopy[38], floating electrodes[35], or fuel cell studies[39]. Hence we have not attempted to extract an exchange current from these data. It is also interesting to note that the point at which the hor current starts to decay at high potentials is shifted more anodically on the phosphide containing catalysts by about 30-50 mV. As the decay at high potentials is associated with surface oxide blocking the hor, this process is easily rationalised in terms of the shift in oxide formation on the Pd-phosphide catalysts as seen in Figure 3.

The her reaction was examined using a low loading of the electrocatalyst (20 μgₚd cm⁻²) RDE electrodes under continuous rotation in 0.1 mol dm⁻³ HClO₄ under long term polarisation (three hours) at a range of different potentials. For the her reaction, both phosphide
containing catalysts do not perform as well as the Pd/C precursor over a range of different cathodic potentials, Figure 5(b). The PdP₂ phosphide rich catalyst is approximately 10-fold worse than the Pd/C catalyst whereas the Pd-rich Pd₅P₂/C catalyst performs about 30% worse than the Pd/C catalyst. The decreased performance of the phosphorus containing materials suggest that the recombination reaction is hindered in the presence of the phosphide, especially considering the improved performance of the PdP₂ material for the hor reaction. Long term potentiostatic polarisation of the catalysts (3 hours per potential) shows relatively stable performance for both the Pd/C and Pd-rich Pd₅P₂/C, whereas the PdP₂ shows some degradation over time except at the most cathodic potential[1, 40-42]. A Tafel plot of the pseudo steady-state performance (after three hours) of the different catalysts is shown inset in Figure 5(b). It is seen that the Tafel plots are not linear but exhibit significant curvature. This is probably due to significant mass transport polarisation occurring at the larger overpotentials. Although we used continuous RDE rotation to aid efficient detachment and removal of the evolved hydrogen, it would seem that at large current densities bubble formation enhances shielding of the electrode increasing resistive effects and impeding transport of protons to the electrode surface. There also might be a continuous change of the slow step of the her reaction mechanism with potential[43].

The PdP₂/C catalyst was tested as anode catalyst in a H₂/air fuel cell utilising a commercial 0.4 mgPt cm⁻² electrode as the cathode, Figure 7. The performance of the fuel cell is moderately good, although the system suffers from a somewhat low open circuit potential of 0.85V. The difference between the use of PdP₂/C as anode and cathode catalyst shows, rather unsurprisingly that the catalyst performs better as an anode catalyst than a cathode catalyst.

1.3. Oxygen reduction reaction
The oxygen reduction reaction was performed on carbon ring-disk electrodes utilising the catalysts and comparing to an industry standard Pt/C catalyst (Johnson Matthey HiSPEC 9100), Figure 6. At the same as the experiments were performed the formation of hydrogen peroxide was assessed by monitoring the ring current. The Pd/C catalyst performs somewhat poorer than the Pt/C catalyst, in agreement with single crystal work which shows that Pd(111) is less active than Pt(111)[44]. Both of the phosphorus containing catalysts perform less well than the Pd/C catalyst. In contrast, Cheng et al saw an increase in
performance of an electrodeposited PdP catalyst compared to a similar Pd/C catalyst[30]. However, their PdP/C catalyst showed an XRD pattern very similar to their Pd/C suggesting specific palladium phosphide compounds had not been formed as in our case. Compared to their Pd/C sample, the PdP/C catalyst they produced showed significantly smaller particle size with larger hydrogen peaks in voltammograms. Thus it would seem that the increased performance they saw in their oxygen reduction was, at least in part, due to increased dispersion of their PdP/C catalyst compared to their Pd/C catalyst. Plotted inset into Figure 6 is the mass transport corrected kinetic current corrected for the specific surface area. We used the surface areas calculated from the hydrogen adsorption charges in Table 1 to determine the active surface area. Within the Tafel region it can be seen that all the Pd/C catalysts perform about one order of magnitude poorer than the Pt catalyst. The phosphorus containing palladium catalysts perform slightly poorer than the Pd/C catalyst alone. This may well be due to the larger amount of oxide which appears to form on the surface, Figure 3(a).

In our results we see increased production of hydrogen peroxide for the phosphorus containing catalysts. It is found that the Pd₅P₂/C catalyst shows a lower onset potential and also a greater amount of peroxide than the PdP₂/C catalyst. The increased peroxide yield might be associated with interaction of the surface phosphorus with the oxygen binding sites. For instance, it is known that palladium is more strongly affected by anions than Pt for the \( \text{o}rr \) – for instance the \( \text{o}rr \) on Pd in moving from perchloric to sulphuric acid is much more strongly suppressed on Pd than Pt[45]. Furthermore, chloride, even at a concentration of 1 \( \mu \text{mol dm}^{-3} \) significantly inhibits the \( \text{o}rr \) reaction on Pd deposited on top of Pt(111)[46]. Hence the presence of the surface phosphorus atoms, especially if they are partially oxidised to contain oxygen groups due to the oxophilic nature of phosphorus

\[
PdP + \text{H}_2\text{O} \rightarrow \text{PdP-OH} + \text{H}^+ + e^- \quad \text{Eq 1}
\]

may lead to destabilisation of the intermediates formed during oxygen reduction and hence an enhanced peroxide yield.

As the PdP₂/C performed showed the highest onset potential and lowest peroxide yield during the RRDE experiments this material was tested as cathode catalyst in a H₂/air fuel cell utilising a commercial 0.4 mgPt cm⁻² electrode as the cathode, Figure 7. The performance of the fuel cell is moderately good, although the system suffers from a somewhat low open
circuit potential of 0.75V, as might be expected from the relatively low onset potential of
the catalyst in the RRDE experiments, Figure 6. It would seem that the presence of the
anionic sulphonate acid groups have a rather negative affect on the performance of the
cathode, supressing the \( \text{orr} \) and leading to rather poor performance.

1.4. Formic acid oxidation

Formic acid oxidation on Pd/C, Pd\(_5\)P\(_2\)/C and PdP\(_2\)/C (20 \( \mu \)g\(_{\text{Pd}} \) cm\(^{-2}\)) in 0.5 mol dm\(^{-3}\) \( \text{H}_2\text{SO}_4 \) +
0.5 M HCOOH at 298K is shown in Figure 8(a). For the Pd\(_5\)P\(_2\)/C and PdP\(_2\)/C catalysts, formic
acid oxidation commences at a potential 10-20mV lower than that seen on the Pd/C
catalyst. The activity of the Pd-phosphides to formic acid oxidation is remarkably high with
a peak oxidation current density over 60 % higher than that of Pd/C alone. This is one of the
highest reported current densities for formic acid oxidation and suggests that alloying with
phosphorus has a significant and beneficial effect on formic acid oxidation
[41, 42, 47-49]. The best performance is achieved with the highest phosphorus content
(PdP\(_2\)/C), which shows formic acid oxidation mass specific currents 3-4 times greater than
that of refs. [42] and [49]. Correction for the specific surface areas (Figure 8(a), inset) shows
that the ordering is retained. Indeed, the PdP\(_2\) catalyst improves significantly on the Pd/C
catalyst showing over twice the activity over most of the potential range studied. The
improved performance for formic acid oxidation may be associated with the increased
hydrogen absorption ability of the catalyst as displayed in figure 3.

Chronoamperometric transients for the oxidation of formic acid at a potential of 0.4 V(RHE)
is displayed in Figure 8(b). The PdP\(_2\)/C performs the best, although all of the catalysts show a
degradation of performance over time. The Pd/C catalyst shows a faster degradation in
performance than either of the phosphorus containing catalysts, both of which show similar
degradation rates which suggests that the oxidation mechanism is modified on the
phosphide containing catalysts[50]. The presence of the phosphorus may be important in
activating oxygen at low potentials and improving the resilience of the catalyst towards
poisoning. The general HCOOH electrooxidation mechanism on noble metals has been
proposed by both Capon and Parsons[51], and Wieckowski and Sobkowsk[52] with the first
step involving a one-electron transfer.

\[
\text{HCOOH} \rightarrow (\text{COOH})_{\text{ads}} + \text{H}^+ + e \quad \text{Eq 2}
\]
This is followed by the decomposition of the unstable intermediate COOH to CO$_2$ or CO, via two different reaction pathways, and the ratio of these two pathways is potential dependent. At potentials within the broad double layer region, the weakly bound $(\text{COOH})_{\text{ads}}$ then contributes to the main oxidation pathway

$$(\text{COOH})_{\text{ads}} \xrightarrow{\text{fast}} \text{CO}_2 + \text{H}^+ + e^- \quad \text{Eq 3}$$

Parallel to this reaction, bulk HCOOH may interact with COOH to produce a poisoning intermediate.

$$\text{HCOOH} + (\text{COOH})_{\text{ads}} \rightarrow (\text{COH})_{\text{ads}} + \text{H}_2\text{O} + \text{CO}_2 \quad \text{Eq 4}$$

Competition between Eq 3 and Eq 4 causes the rate of intermediate formation to be an inverse function of the rate of the oxidation reaction. In contrast, in the region where hydrogen atoms adsorb, the poison forms by the sequence

$$(\text{COOH})_{\text{ads}} + 2\text{H}_{\text{ad}} \rightarrow (\text{COH})_{\text{ad}} + \text{H}_2\text{O} \quad \text{Eq 5}$$

$$(\text{COH})_{\text{ad}} \rightarrow \text{CO}_{\text{ad}} + \text{H}^+ + e^- \quad \text{Eq 6}$$

Interaction of these species with the oxygen containing species formed on the phosphorus surface via Eq 1 may act to free the surface of the poison in a similar way to the bifunctional mechanism associated with the activity of platinum-ruthenium towards methanol or carbon monoxide.

$$\text{PdP-OH} + \text{CO}_{\text{ad}} \rightarrow \text{CO}_2 + \text{H}^+ + e^- \quad \text{Eq 7}$$

$$\text{PdP-OH} + (\text{COH})_{\text{ad}} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \quad \text{Eq 8}$$

1.5. Conclusions

A simple conversion process amenable to high volume catalyst production is used to convert previously obtained Pd/C catalyst to either Pd$_2$P$_2$/C or Pd$_3$P$_2$/C catalysts by introduction of phosphorus via the use of trioctylphosphine. The modified catalysts show an improvement in stability over the precursor Pd/C due to incorporation of the phosphorus in both electrochemical cycling and thermal stability within a pure oxygen environment. The improved stability offsets one of the problems associated with the use of palladium as an electrocatalyst. There is a shift in the formation of surface oxides on the phosphorus containing materials to higher potential, although this process does not lead to a concomitant shift to the onset of oxygen reduction. Indeed, the catalysts perform slightly poorer towards oxygen reduction with enhanced yields of peroxide. Similarly, hydrogen evolution is less active on the phosphorus containing materials with the catalyst activity
towards the her negatively correlated to the phosphorus content. In contrast, both the hydrogen oxidation reaction and formic acid oxidation reactions are significantly enhanced on the catalysts, with a positive correlation of activity to phosphorus content. The peak catalytic activity towards formic acid oxidation is around 2.5 A mg\textsubscript{Pd}^{-1} at 0.4 V (RHE), which is one of the best mass-specific activities currently reported. The performance of these catalysts is rationalised in terms of the oxophilic nature of surface phosphorus atoms and their ability to activate water.

1.6. Acknowledgements
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References


Table 1. Comparison of surface areas determined for the catalyst from TEM image analysis and integrated hydrogen adsorption using the data for peak A3 in Figure 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TEM image analysis</th>
<th>Hydrogen adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>46± 2</td>
<td>83 ± 16</td>
</tr>
<tr>
<td>Pd₅P₂/C</td>
<td>42± 3</td>
<td>90 ± 1</td>
</tr>
<tr>
<td>PdP₂/C</td>
<td>46± 4</td>
<td>70 ± 30</td>
</tr>
</tbody>
</table>
Figure 1: Representative diagram of the formation of palladium phosphide nanoparticles from the interaction of trioctylphosphine (TOP) with a palladium particle.
Figure 2: (a) X-ray diffraction patterns and (b) transmission electron micrographs of as received of Pd/C, and the synthesized PdP₂/C and Pd₅P₂/C. Inset in the TEM images are the results of particle size analysis. Dotted lines in the XRD patterns represent peaks associated with the carbon support and the Pd(111) diffraction line.
Figure 3 (a) Electrochemistry of Pd/C, Pd$_5$P$_2$/C and PdP$_2$/C (all 20 $\mu$g$_{Pd}$ cm$^{-2}$) catalysts in N$_2$ saturated 0.1 M perchloric acid at a temperature of 298K; (b) deconvolution of positive going voltammetric scans into three separate components for each of the samples using the data from (a) in the region highlighted by the dotted box. The dash line represents the sum of all three components; (c) Integrated charge for each of the peaks in (b). $\frac{dV}{dt}$=20 mV s$^{-1}$
Figure 4 Stability of Pd/C, Pt/C, Pd$_5$P$_2$/C and PdP$_2$/C catalysts towards (a) electrochemical cycling, and (b) thermal oxidation in pure oxygen. Electrochemical durability was performed 0.1 M perchloric acid under a N$_2$ atmosphere at a temperature of 298 K. Each cycle involved a scan from 0.6→1.0→0.6 V(RHE) with $\frac{d\nu}{dt} = 50$ mV s$^{-1}$. The relative surface areas were obtained by measuring the hydrogen underpotential deposition charge. TGA was carried out under oxygen at a heating rate of 10 °C min$^{-1}$.
Figure 5: Hydrogen oxidation and reduction reaction on Pd/C, Pd₅P₂/C and PdP₂/C (20 μgₚd cm⁻²) in 0.1 mol dm⁻³ HClO₄ at 298K: (a) hydrogen oxidation in a H₂ saturated solution, Inset: hor response normalised to limiting hor current density, \( \frac{dv}{dt} = 20 \text{ mV s}^{-1} \). Currents are iR corrected and corrected for double layer capacitance. (b) chronoamperometric transients for hydrogen evolution at different cathodic potentials in a N₂ saturated solution. Rotation rate of 1600 rpm.
Figure 6: Oxygen reduction in an O₂ saturated 0.1 mol dm⁻³ HClO₄ solution for Pd/C, Pt/C, Pd₅P₂/C and PdP₂/C (20 μgpd cm⁻²) at 298K. Also displayed is the amount of H₂O₂ produced as a percentage of oxygen reduced as calculated from the ring current. Displayed inset into the diagram is the mass transport corrected Tafel plots for each of the catalysts. A rotation rate of 1600 rpm on a RRDE with a glassy carbon disk and Pt ring. Currents are iR corrected and corrected for double layer capacitance. \( \frac{dV}{dt} = 50 \text{ mV s}^{-1} \)
Figure 7: Operation of PdP₂/C containing 0.45 mg\textsubscript{Pd} cm\textsuperscript{-2} catalyst in a fuel cell as either anode or cathode catalyst at 80°C under H₂/air operating conditions. Cathode (or anode) opposite the PdP₂/C electrode composed of 0.4 mg\textsubscript{Pt} cm\textsuperscript{-2} fuel cell electrode.
Figure 8: Formic acid oxidation on Pd/C, Pd$_5$P$_2$/C and PdP$_2$/C (20 $\mu$g Pd cm$^{-2}$) in 0.5 mol dm$^{-3}$ H$_2$SO$_4$ + 0.5 M HCOOH at 298K. (a) Cyclic voltammetry at $\frac{dV}{dt} = 20$ mV s$^{-1}$, Inset: Data converted to surface specific activity (b) chronoamperometry at 0.4 V(RHE). Inset: semilogarithmic plot of data in the main figure. Rotation rate of 1600 rpm on a RDE with a glassy carbon disk.

(a) (b)