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 PdP_2 and Pd_5P_2 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 evolution, 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 PdP_2 and Pd_5P_2 particles is enhanced. The phosphides compare favourably to the most active catalysts reported to date for formic acid oxidation, especially PdP_2, 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, PdP_2/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 a 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 and basic media compared to that of the unal-loyed 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 dis-solved 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 effec-tive 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 metals 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 bound-aries. 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 hydrodesulphurisation 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 lev-els 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 phos-phide 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 pro-duced, 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, Fig. 1. In this paper, Pd/C is used to create PdP_2/C and Pd_5P_2/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 phos-phides in acidic media and at high temperatures under air. These
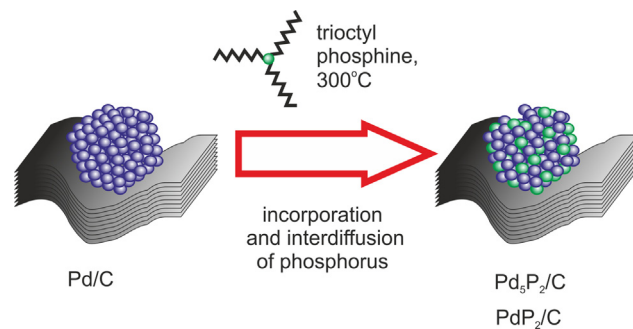

Fig. 1. Representative diagram of the formation of palladium phosphide nanopar-ticles from the interaction of trioctylphosphine (TOP) with a palladium particle.

results are compared to the Pd/C precursor as well as an optimised commercially available Pt/C electrocatalyst.

2. Materials and methods

Pd_5P_2/C and PdP_2/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 Pd_5P_2/C and PdP_2/C were separated using a cen-trifuge 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 diffrac-tometer 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 Thermo-gravimetric 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 temper-ature to 100 °C under a nitrogen atmosphere.

Electrocatalyst inks were prepared from the dried Pd_5P_2/C and PdP_2/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 bind-ing agent and to promote electrolyte conductivity to the metal nanoparticles.

For electrochemical testing, ink was deposited on a glassy car-bon 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 cm^2 and amount of ink was adjusted to give a loading of 20 μg$_{Pd}$ cm^{-2} in each case. The inks were dried by rotating the RDE at 700 rpm under N$_2$ (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 acid-ified 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.

PdP_2/C fuel cell electrodes were prepared by brushing an ink of PdP_2/C dispersed in 2-propanol onto a 5 cm^2 Toray carbon paper electrode (Alfa Aesar TGP-H-60). The loading of the electrode was 0.71 mg$_{PdP_2}$/cm^2 (equivalent 0.45 mg$_{Pd}$/cm^2). A commercially