Cite this: Chem. Commun., 2012, 48, 1063–1065

COMMUNICATION

Atomic layer deposition synthesis of platinum-tungsten carbide core-shell catalysts for the hydrogen evolution reaction[†]

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Received 20th September 2011, Accepted 17th November 2011 DOI: 10.1039/c1cc15812k

Pt was deposited onto tungsten carbide powders using atomic layer deposition to produce core-shell catalysts for the hydrogen evolution reaction (HER). The Pt loading on these catalysts was reduced nearly ten-fold compared to a bulk Pt catalyst while equivalent HER activities were observed.

Despite the promise of fuel cells, photoelectrochemical cells, and electrolyzers as clean alternative energy sources, the high loadings of precious metal electrocatalysts drive up the cost of these devices and affect their competitiveness with conventional power sources. Precious metals, notably Pt, are necessary for the operation of fuel cells and photoelectrochemical cells because they facilitate the electrochemical reactions at the electrodes. However, Pt is expensive and scarce. A reduction in its use is essential to ensure that these clean energy devices are economically viable. Therefore, there is a need to develop electrocatalysts with lower Pt loadings that can perform as well as conventional bulk Pt catalysts.

One strategy to lower Pt loadings is to use tungsten monocarbide (WC) as a bulk replacement to support one monolayer (ML) of Pt in a core-shell structure. WC has been found to possess Pt-like catalytic properties and has been identified as a promising support material for Pt in fuel cells since Pt has shown good adhesion on WC.¹⁻⁶ Additionally, WC is much less expensive than Pt. However, for electrochemical applications, the similarities between WC and Pt often deviate at the surface, making it difficult to use WC as a direct replacement for Pt. It has been observed that modifying the WC surface with Pt can produce Pt-like activity while minimizing the amount of Pt used.^{2,7-9} An optimal lower limit to the Pt loading is a single ML that fully covers the WC surface. The ML Pt–WC system has previously been demonstrated with thin films as model catalysts for a few electrochemical reactions, such as the methanol oxidation reaction and the hydrogen evolution reaction (HER). For example, one ML of Pt deposited onto a WC foil substrate by physical vapour deposition (PVD) was previously shown to perform as well as a bulk Pt catalyst for the HER.⁷ These exciting results demonstrate that the Pt loading can be reduced considerably while the surface is still able to produce activities comparable to bulk Pt catalysts. These results, however, were produced on thin films, which are impractical for real world applications that require catalysts to be in powder form.

Synthesis of ML Pt-WC powder catalysts is challenging, and to date no established methods exist. PVD has been shown to successfully produce monolayers on planar substrates, but PVD is a line-of-sight technique, and therefore, not applicable to particle substrates. Previously, Pt-modified WC particle catalysts were made using a wet impregnation method, but were unable to exhibit the same activities for the methanol oxidation reaction that were observed on thin film catalysts produced with PVD.¹⁰ This confirms that wet impregnation methods, which are industrially the most common way to produce catalysts, do not provide sufficient control to produce a complex system such as ML Pt-WC powder catalysts. Core-shell particles have been produced for other systems, but to our knowledge no synthesis method for producing Pt-WC core-shell particles has been reported. For Pt-Ni or Pt-Pd, a method using ion exchange of an underpotentially deposited Cu adlayer has shown some success in producing Pt monolayers.^{11,12} However, this is not applicable to WC because Cu does not form an underpotentially deposited adlayer.^{13,14} Other synthesis methods must then be explored to produce thin Pt layers on WC particles. Atomic layer deposition (ALD) was determined to be one possibility because it can produce ultra-thin films with nanometre-level control on a number of substrates. Furthermore, ALD is not a line-of-sight technique and has been demonstrated on different substrate geometries such as thin films, nanotubes, and microspheres.

The objectives of the current communication are (1) to utilize ALD to produce Pt–WC core–shell catalysts, and (2) to evaluate whether they show promising HER performance as predicted from ML Pt–WC thin films. The WC particles were synthesized using a solid state method detailed previously where WO₃ and carbon black were heated to 1300 $^{\circ}$ C in the presence of KCl and a Ni catalyst to promote WC synthesis.^{15,16}

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[†] Electronic supplementary information (ESI) available: Detailed experimental procedures, powder XRD patterns, and electrochemical characterization. See DOI: 10.1039/c1cc15812k



Fig. 1 TEM images of ALD Pt–WC samples. (a) Low-magnification HAADF-STEM image of ALD Pt–WC. (b) High resolution BF TEM image of the 10 ALD cycle sample. (c) 5 Pt ALD cycles on WC and (d) 30 Pt ALD cycles on WC.

The resulting WC particles are about 1 micron in diameter on average, as seen in the high annular angular dark field (HAADF) STEM image shown in Fig. 1(a). ALD of Pt was achieved in a flow-through type reactor using a design by George *et al.*¹⁷ in a quartz tube furnace fitted with a frit to prevent solids from entering the vacuum foreline. The Pt precursor molecule used for ALD was trimethyl-methyl-cyclopentadienylplatinum (MeCpPtMe₃), which has been studied extensively for Pt ALD on a variety of oxide surfaces and on carbon.^{18–20} Oxygen was used as the co-reactant. Pt ALD has been demonstrated on WC thin films in a previous article,²¹ showing that Pt grows by forming small particles on the WC surface, which eventually coalesce to form a film with increasing number of ALD cycles.²¹

A similar growth mechanism was observed on the WC powders as seen in the TEM images shown in Fig. 1. Pt particles are observed on the WC surface. An example is seen in Fig. 1(b) showing a high magnification image of the ALD Pt-WC after 10 cycles. The particles are cubooctahedral shaped, which is consistent with an fcc metal such as Pt. Lattice fringes observed on the cubooctahedral particles were measured and matched with Pt(111) and Pt(200) d-spacings, identifying these particles as Pt. Fig. 1(c) and (d) show bright field (BF) TEM images of the ALD Pt-WC samples after 5 and 30 ALD cycles, respectively. The BF TEM images show that the Pt particle size increases with increasing Pt ALD cycles. After 5 ALD cycles, the Pt particles are ~ 2 nm in diameter and well dispersed throughout the WC surface. The particles grow to be slightly wider after 10 ALD cycles. Fig. 1(d) shows that the WC surface is essentially covered with Pt after 30 ALD cycles.

The HER is one of the most fundamental and extensively studied electrochemical reactions, and is often used as a probe reaction to evaluate the catalytic activity of Pt and Pt-based



Fig. 2 Tafel plots of WC powder; 5, 10, and 30 ALD Pt–WC catalysts; and 10 wt% Pt/C produced from HER measurements.

electrocatalysts. In the current study, HER measurements for samples of WC powder; 5, 10 and 30 ALD cycles Pt–WC; and 10 wt% Pt supported on high surface area carbon (Pt/C) are compared in the form of Tafel plots shown in Fig. 2. The current is normalized with respect to the geometric surface area of the electrodes. The trend displayed here is in agreement with what has previously been observed on thin films. Based on the previous study, WC is expected to have poor HER activity.⁷ This is reflected in the location of its Tafel plot shown in Fig. 2. On the other hand, Pt is known to have very good HER activity. When Pt is deposited onto the WC powder substrates, the HER activity increases.

As few as 5 Pt ALD cycles on WC increases the HER activity considerably from unmodified WC, as seen in the upward shift in its Tafel plot. Furthermore, after only 10 ALD cycles, the HER activity is nearly equivalent to the Pt/C catalyst, indicated by their nearly overlapping Tafel plots. The 30 ALD cycle Tafel plot also falls on the Pt Tafel plot, showing that the low loading Pt reaches a limiting HER activity which is equivalent to that of Pt/C. Fig. 2 shows how little Pt is needed on WC to achieve the same activity as the Pt/C catalyst.



Fig. 3 Log of exchange current density plotted against (a) the number of Pt ALD cycles and (b) Pt surface area on WC determined from Cu stripping voltammetry.

Table 1 Pt wt% loadings for each catalyst and total Pt mass on electrodes for each HER measurement

Electrode	Pt wt%	Mass of Pt on electrode/mg
5 ALD cycles Pt-WC	0.20	0.00055
10 ALD cycles Pt-WC	0.49	0.0031
30 ALD cycles Pt-WC	0.85	0.0055
Pt/C	10	0.025

The log of the exchange current densities were calculated from the Tafel parameters and are plotted against Pt ALD cycles shown in Fig. 3(a) and Pt surface area as determined by Cu stripping measurements shown in Fig. 3(b). These figures show that a limiting value for HER activity is reached, which corresponds to the Pt/C value. The exchange current densities of the 10 wt% Pt/C catalyst and the WC powders are indicated by dashed lines. As shown in Fig. 3(a) and (b), increasing the Pt deposition brings the Pt/WC exchange current density to the Pt/C value, which is in agreement with the previous study on planar thin film catalysts.⁷

Furthermore, similar to what was observed with ML Pt–WC thin film catalysts, Pt/C HER activity is reached as the Pt coverage on WC increases to an equivalent of 1 ML.

Although an ideal single ML of Pt is not produced on the WC powder using ALD, the presence of a thin Pt layer on the WC substrate is sufficient to bring about activities that are comparable to conventional Pt catalysts. The Pt loadings are also considerably less than what is typically used in electrochemical experiments. The Pt wt% for each of the abovementioned ALD Pt-WC catalysts were determined from atomic absorption spectroscopy (AAS) measurements after digestion of the powder samples in aqua regia, and are displayed in Table 1. By comparison, the literature typically uses Pt loadings of 10-40 wt%. Table 1 also shows the total mass of Pt loaded onto the electrode for each HER measurement. The mass of Pt for each of the ALD Pt-WC electrodes is a fraction of the mass of Pt used for the Pt/C electrode, clearly demonstrating how the ALD Pt-coated WC catalysts utilize Pt more efficiently than the bulk Pt catalyst.

Previous work with ML Pt–WC thin films postulated that the reasons for the similar HER activities are due to the similarities in the electronic properties between bulk Pt and ML Pt on WC. This can be observed when the hydrogen binding energy (HBE) is used as a chemical descriptor for the HER reaction. The HBE of WC is very strong, but when a ML Pt is added on top of it, the HBE value decreases to be very similar to that of Pt.⁷ Although more than the ideal one single ML of Pt is deposited onto WC in this work (Fig. 1), ultra-low loading Pt thin films are achieved. Additional work should be devoted to determine ways to make the Pt nucleation more efficient, which in turn will create smaller particles and thinner Pt layers on the WC powder. WC was shown here to be a good core material for Pt for this particular electrochemical reaction.

In a previous study, the stability of Pt/WC was investigated using a well-characterized WC film with one monolayer Pt.⁷ The Pt/WC thin film was characterized using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) before and after HER measurements, which revealed that Pt/WC remained stable under HER conditions. Similar studies should be performed on the ALD Pt/WC and Pt/C powder catalysts to further understand the electrochemical stability of these catalysts.

In conclusion, Pt–WC core–shell particles were synthesized using ALD to deposit thin Pt layers on WC powder substrates in order to scale up the ML Pt–WC thin film system to a more industrially relevant powder catalyst. In terms of reducing the Pt loading while maintaining bulk-like performance, the Pt–WC core–shell powder catalysts produced HER results that are equivalent to the ML Pt–WC thin films reported previously. To our knowledge, no other method has been demonstrated to produce core–shell Pt–WC catalysts. While improvements to the synthesis of these catalysts can be made in making even thinner Pt films and using smaller WC particles, the positive results observed here are a significant step towards more efficiently utilizing precious metals in powder catalysts in electrochemical devices.

We acknowledge financial support from the Department of Energy (DE-FG02-00ER15104). We thank Ying Liu and Dr William Mustain for synthesizing and providing the WC particles.

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