The beneficial effect of the addition of tungsten carbides to Pt catalysts on the oxygen electroreduction†

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Tungsten carbide nanocrystal modified Pt catalysts have been prepared by an intermittent microwave heating (IMH) method and show an improved activity for oxygen electroreduction in alkaline media.

The electroreduction of oxygen has been a major concern in the electrochemical reaction kinetics due to its importance in energy conversion systems, corrosion and other important electrochemical processes.[1–4] From the catalytic point of view, the reaction mechanism on a Pt catalyst has attracted most attention because Pt and Pt-alloys are still the best catalysts for low-temperature fuel cells.[5,6] In contrast to hydrogen oxidation on Pt, which is a very fast reaction, oxygen reduction on Pt exhibits a slow and complicated kinetic behavior. The standard reversible potential for O_2 reduction is 1.23 V, but kinetic limitations for the oxygen reduction reaction (ORR) lead to cell voltage losses of at least 0.3 to 0.4 V under typical operating conditions, which is about 10 times larger than that for H_2 oxidation at an anode. This large overpotential loss has been attributed generally to the sluggish kinetics of ORR and OH^- (from H_2O) or other anion adsorption. Further improvements in the performance of ORR will require finding a catalyst more active than Pt.

It is well known that alkaline solution has an intrinsic advantage over acidic solution in cathode kinetics. However, only limited results were found from the literature for investigating the effect of physical properties of Pt and other catalysts on the activity of ORR in alkaline solutions.[7–11] Herein we report the results of a study on the electrocatalytic activity of tungsten carbide modified Pt catalysts for the ORR. The intermittent microwave heating (IMH) method[12,13] was used to prepare tungsten carbide nanocrystals on carbon (W_2C/C) (see ESI†). Pure W_2C could be prepared by controlling the ratios of W to C less than 20 wt% with a particle size of <10 nm (see Figs. S1 and S2†). The electrocatalytic properties of the tungsten carbide nanocrystals and the tungsten carbide nanocrystal modified Pt catalysts (Pt-W_2C/C) for ORR were evaluated.

As shown in Fig. 1a the tungsten carbide nanocrystals are active towards oxygen reduction. The ORR on a Pt/C catalyst could reduce the overpotential by 150 mV compared with that on a pure tungsten carbide nanocrystal catalyst. The fact is that the performance of ORR was further improved on a Pt-W_2C/C catalyst at a lower Pt loading (Fig. 1c). According to the results as summarized in Table 1, we can find that the onset potentials for ORR on different electrocatalytic electrodes are different. It is noted that the potential was shifted towards the positive side more than 50 mV on Pt-W_2C/C than that on Pt/C at a reasonable reduction current density. In other words, the current density could be ten times larger on Pt-W_2C/C than that on conventional Pt/C operating at interesting potentials. The effect of the Pt content in the catalysts on the electrode activity was determined. The better performance of the 80 μg W_2C + 40 μg Pt/C composition has been demonstrated (see Fig. S3†). The reduction in the use of Pt in the catalysts is significant in terms of the cost and the resource limitation.

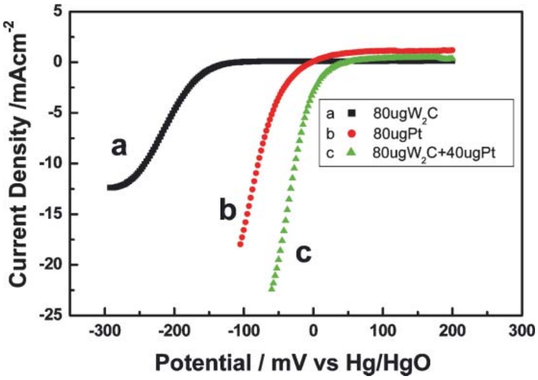

Fig. 1 Linear potential sweep curves of different catalysts for oxygen electroreduction.

The actual mechanism for the improvement of oxygen electroreduction on the present dual functional catalyst is unclear at this stage. There has been considerable interest in the electrocatalytic properties of transition metal carbides and they were found to show exceptionally high activities similar to those of noble metal catalysts in a number of reactions, such as electrooxidation of hydrogen,[14] electrochemical oxidation of aldehydes, formic acid and carbon monoxide.[15] The conventional preparation techniques for metal carbides inherited from the metallurgical industry involve the reaction of metals, metal hydrides, or metal oxides with appropriate amounts of carbon in a protective or reducing atmosphere. Reaction temperatures are generally very high. The resulting materials have a low specific surface area and low purity, and these commercial materials are unsuitable as catalysts. Liang and co-workers prepared nanostructured tungsten carbides on ultrahigh-surface-area carbon material *via* carbothermal hydrogen reduction and metal-promoted carbothermal hydrogen reduction under relatively

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Table 1 Comparison of the kinetic parameters of the catalysts

Catalysts	Onset potential/mV *vs.* Hg/HgO	Potential at 10 mA cm^{-2}	Onset potential with 0.1 mol dm^{-3} methanol/mV	i_0/mA cm^{-2}
W_2C/C	−117	−245	−118	0.079×10^{-5}
Pt/C	37	−80	−48	0.119×10^{-5}
$Pt\text{-}W_2C/C$	52	−25	50	0.180×10^{-4}

mild conditions.[16] The nanostructured tungsten carbides show high catalytic activity for the removal of sulfur in oil. The small-scale effect of the tungsten carbide nanocrystals might play an important role in enhancing catalytic activity.

It is common sense that the direct methanol fuel cells (DMFCs) operate in acid rather than base due to carbonation. We have proposed the concept of an alkaline fuel cell in which an anion (OH^-) exchange membrane (AEM) was used as a solid electrolyte instead of a conventional liquid electrolyte.[17] The use of an AEM would allow for avoiding problems of leakage, carbonation, precipitation of carbonate salts and prevents the gas electrode flooding in a DMFC. This means that in the case of alkaline DMFCs, the use of caustic alkali is not necessary. The presence of CO_2 from the air dissolving in the aqueous solution and/or the membrane to form H_2CO_3 would be a problem. However, the equilibrium concentration of CO_3^{2-}/HCO_3^- is less than 0.07%. Therefore, the influence of the dissolved CO_2 is small. Moreover, the absence of cations (K^+, Na^+) eliminates the formation of a precipitate. The anion exchange membrane fuel cells (AEMFCs) combine the advantages of proton exchange membrane fuel cells (PEMFCs), alkaline fuel cells (AFCs) and DMFCs, whilst also minimizing the disadvantages of each type. However, the application of AEM in fuel cells is limited[18–21] due to the instability of the AEMs available.

Another obstruction for DMFC is that the crossover of methanol from anode to cathode poisons the electrocatalyst. Circulating the solution can minimize this problem but using a catalyst that cannot oxidize the methanol will provide a better solution. The ORR electrocatalyst used in DMFCs needs to be active and resistant to poisoning.[22,23] We compared the electrocatalytic activities of tungsten carbide nanocrystal modified Pt catalysts and traditional Pt based catalysts for oxygen electroreduction in the presence of methanol at different concentrations. The effect of methanol on the performance of ORR on the $Pt\text{-}W_2C/C$ electrode is shown in Fig. 2a. From the linear potential sweep curves we can find that the activity of ORR on the $Pt\text{-}W_2C/C$ electrode was hardly affected by methanol at concentrations of up to 1 mol dm^{-3} at room temperature. However, the oxygen electroreduction on the Pt/C electrode was seriously affected by methanol (Fig. 2b). At higher methanol concentrations, the electrode processes transformed to methanol oxidation instead of oxygen reduction due to the competitive adsorption between methanol and oxygen molecules on the electrode surface.

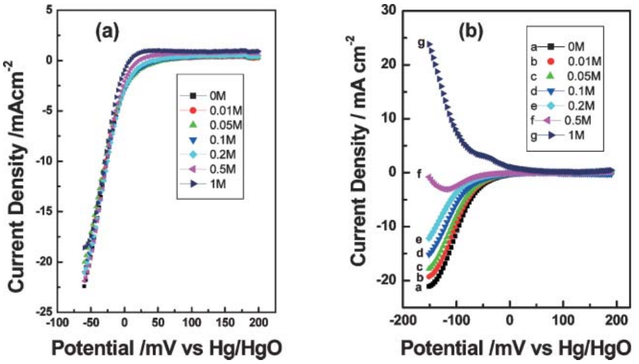

Fig. 2 Influence of methanol at different concentrations on oxygen electroreduction on (a) $Pt\text{-}W_2C/C$ and (b) Pt/C electrodes.

The Tafel plots provided further information on kinetic parameters. The onset potentials of ORR on different catalysts are summarized in Table 1 from the Tafel plots as shown in Fig. 3. The $Pt\text{-}W_2C/C$ catalysts exhibited the more positive onset potential and the higher exchange current density, i_0, than that of the Pt/C catalysts (Table 1), indicating better kinetic properties.

Fig. 3b shows typical Tafel plots of ORR on different electrodes in the presence of 0.1 mol dm^{-3} methanol. The onset potential of ORR on Pt/C moved to the negative side for more than 85 mV. In fact, the electrode reaction transferred to methanol oxidation instead of oxygen reduction at higher methanol concentrations.

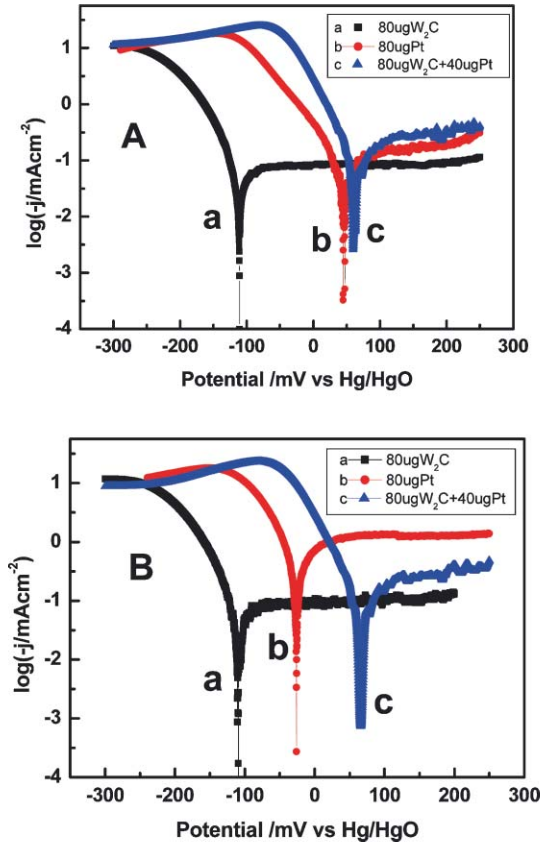

Fig. 3 Tafel plots of different catalysts for oxygen electroreduction in oxygen saturated 1 mol dm^{-3} KOH solution in the absence (A) and the presence (B) of 0.1 mol dm^{-3} methanol at 25 °C. Scan rate: 1mV s^{-1}.

Tungsten carbide nanocrystal and tungsten carbide nanocrystal modified Pt catalysts were prepared by an IMH method and tested for the electroreduction of oxygen for the first time. The results revealed that both of them were active for the electroreduction of oxygen in alkaline media. However, the overpotential was significantly reduced on the tungsten carbide nanocrystal modified Pt catalyst, showing a synergic effect to improve the activity for oxygen reduction. The unique properties of the selectivity and immunity to methanol of the Pt-W_2C/C catalysts favor them for potential applications in anion exchange membrane hydrogen or alcohol fuel cells,[17] alcohol monitors and metal–air batteries.‡

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Notes and references

‡ Electrochemical experiments were performed on an IM6e electrochemical workstation. A standard three-electrode cell was used. A platinum foil (3.0 cm^2) and Hg/HgO (1.0 mol dm^{-3} KOH) were used as counter and reference electrodes, respectively. All experiments were carried out in 1 mol dm^{-3} KOH solution with or without the presence of methanol at 25 °C.

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