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Sol–gel derived WO_x and WO_x/Pt films for direct methanol fuel cell catalyst applications

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Abstract

WO_x was synthesised from $W(OC_2H_5)_6$ by two different methods using the sol–gel (SG) approach, Type 1 using ethanol as the solvent, while Type 2 was water-based. Films and powders made from these sols were subjected to analysis by cyclic voltammetry (CV), powder X-ray diffraction (XRD), and scanning electron microscopy (SEM). Sweep rate experiments revealed that compared to Type 1 films, Type 2 films have a significantly greater number of electroactive WO_x sites, and that a smaller proportion of the total active sites are surface sites, indicative of a higher film porosity (consistent with the SEM results). XRD analysis showed that both Type 1 and Type 2 WO_x were poorly crystallised. However, the patterns for the two WO_x types were distinctly different, with Type 2 WO_x giving a more well-defined pattern. WO_x sols were also successfully combined with a pre-formed Pt sol. Unlike Pt-only catalysts, methanol oxidation currents on Type 2 WO_x/Pt films did not decay rapidly with potential cycling, indicating the occurrence of co-catalytic behaviour, while Type 1 films were not very active, overall. The low resistance exhibited by the WO_x component makes it suitable as an ionically and electronically conducting support for direct methanol fuel cell electrocatalysts.

Keywords: Methanol oxidation; Tungsten oxide; Platinum; Sol–gel; Co-catalyst

1. Introduction

Direct methanol fuel cells (DMFCs) are seeing increased interest as an efficient alternative to fossil fuel combustion as an energy source. In addition to increased fuel efficiency, DMFCs, which operate at ∼70 °C, only exhaust CO_2 and H_2O, without releasing any pollutants such as NO_x, SO_x, and particulate matter [1]. In general, Pt is an excellent electrocatalyst for most fuel cell purposes. Unfortunately, the use of Pt as the anode catalyst in a DMFC has the inherent problem that an intermediate of methanol oxidation, CO, adsorbs onto Pt sites, poisoning the catalyst, and reducing the performance of the fuel cell [2–7]. Several transition metals and their oxides, including RuO_x, SnO_x, VO_x, and MoO_x, have been investigated as possible co-catalysts that are believed to operate via the bifunctional mechanism, as shown in reaction (1), where M refers to Ru, Sn, V, Mo, etc. [2–5].

$$\text{M-OH} + \text{Pt-CO} \rightarrow \text{M} + \text{Pt} + \text{CO}_2 + \text{H}^+ + \text{e}^- \quad (1)$$

WO_x is also becoming of interest in this role, as well as in possibly aiding methanol oxidation by the hydrogen spillover effect (reaction (2)) [8], in which hydrogen is abstracted from methanol, and then transferred via Pt to WO_3.

$$\text{WO}_3 + x\text{Pt-H} \rightarrow \text{H}_x\text{WO}_3 + x\text{Pt} \rightarrow \text{WO}_3 + x\text{Pt} + x\text{e}^- + x\text{H}^+ \quad (2)$$

This mechanism increases the methanol oxidation rate because free Pt sites are regained more quickly than when WO_3 is absent [8].

Current Pt DMFC electrocatalysts are supported on carbon, which is electronically, but not ionically conductive [1]. This necessitates the addition of the fuel cell electrolyte, typically a polymer such as Nafion™, into the Pt/C mixture

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to create a high surface area triple phase boundary where the catalyst, fuel, and electrolyte meet. Any Pt sites that are not in contact with the Nafion^{TM} electrolyte cannot act catalytically and are therefore wasted. By using a support material such as WO_x, which is both ionically and electronically conductive, a significantly greater portion of the Pt catalyst should be utilised. WO_x has been investigated as a co-catalyst, for methanol oxidation, using carbon as the catalyst support [9], and also as the support material without carbon [8,10,11], showing improved results over similar electrodes with no WO_x content.

WO_x/Pt materials have been previously synthesised in several ways, including co-sputtering [10,11], freeze-drying [12,13], co-electrodeposition [8], and the sol–gel (SG) approach [14–16]. There are several benefits to SG syntheses, including ease of preparation and use, and the formation of particles small enough to be suspended in solution (sols), thus offering greater surface area per unit volume. Sol–gel syntheses also facilitate the combination of materials, in this case WO_x and Pt, in the liquid phase, which significantly increases the homogeneity of the product. The SG method has been used to synthesise WO_x in WO_x/Pt films, with Pt added in the form of H_2PtCl_6 or K_2PtCl_4, which was then reduced to Pt(0) under H_2 gas [14,16]. The generation of Pt nanoparticles via a similar approach, i.e., forming a Pt sol for use in a Pt/WO_x catalyst, has not been previously demonstrated.

This paper reports two SG-derived syntheses of WO_x, using $W(OC_2H_5)_6$ as the starting material, and the evaluation of their products. The two syntheses are identical, except that Type 1 sols used ethanol as the solvent, while Type 2 sols employed an aqueous medium. The WO_x sols were combined, for the first time, with a pre-formed Pt sol synthesised using a similar approach. These WO_x/Pt films have been evaluated in terms of the applicability of WO_x as a support material and the effect of the WO_x content on methanol oxidation activity. Type 1 films exhibit poor methanol oxidation behaviour that decreases with higher WO_x loading, while Type 2 films show much more stable methanol oxidation catalysis, with clear evidence for the occurrence of co-catalysis.

2. Experimental methods

2.1. WO_x synthesis

All WO_x films were synthesised via the sol–gel approach, using $W(OC_2H_5)_6$ as the precursor compound. The synthesis of Type 1 sols involved refluxing a mixture of 0.2 g of $W(OC_2H_5)_6$ (Alfa Aesar) and 9 mL of absolute ethanol for 2 h [17]. The volume was brought up to 10 mL with ethanol to yield a 0.044 M WO_x solution. Type 2 sol synthesis was identical to Type 1, except that distilled water was used as the solvent, instead of ethanol.

2.2. Pt sol synthesis [18]

A solution containing 0.2 g $NaOC_2H_5$ and 0.5 g H_2PtCl_6 was refluxed in 6 mL absolute ethanol under Ar for 2 h. An additional 4 mL of ethanol were added and the mixture was then stirred for 18 h at room temperature (20–23 °C). The Pt sol was filtered to remove the precipitate and then diluted to a volume of 10 mL.

2.3. WO_x/Pt catalyst synthesis

A 50 μL aliquot of the Pt sol was placed into a small vial using a micropipette. The appropriate amount of WO_x sol was added to achieve the desired WO_x/Pt molar ratio and then the combined solution was diluted to 1 mL with either ethanol for composite sols made with Type 1 WO_x sols, or water for those made with Type 2 WO_x sols. In all of the WO_x/Pt mixtures, the amount of Pt remained constant and only the amount of WO_x added was altered, in order to generate composite sols with WO_x:Pt molar ratios of 0.5, 1, 1.5, 3, and 5. The W content in both the Type 1 and Type 2 composite films ranged from ∼60 nmol to ∼625 nmol, and the Pt content was constant at ∼125 nmol.

2.4. Electrochemical measurements

A cell consisting of two compartments joined by a Luggin capillary was employed. One compartment contained the working electrode (WE) and a Pt gauze counter electrode, while the second housed a reversible hydrogen reference electrode (RHE). For WO_x film characterisation, the electrolyte was 0.5 M H_2SO_4. Methanol oxidation studies were carried out in a cell solution of 0.5 M H_2SO_4 and 1 M methanol. Data were collected using a PARC EG&G 263A potentiostat, controlled by Corrware 2.0 data acquisition software.

WEs consisted of 1.25 cm^2 glass slides, sputter-coated with a ca. 3 nm layer of Ti and then with a ca. 120 nm layer of Au, using a Denton Vacuum DV-502A High Vacuum Sputter-Coater. WO_x and WO_x/Pt films were made by coating the electrodes with 40 μL aliquots of sol using a micropipette. The film-coated electrodes were dried in air for 2 h at 200 °C. The electrodes were wrapped in Parafilm so that only ∼0.6 cm^2 would be exposed to the electrolyte and then immersed into the electrochemical cell using an alligator clip. The cell solution was deaerated by bubbling continuously with N_2 gas during all experiments. Electrochemical characterisation of the films was carried out using cyclic voltammetry (CV), typically cycling between 0 V and 0.4 V versus RHE at a sweep rate of 25 mV/s. The sweep rate studies were carried out at sweep rates from 20 mV/s to 300 mV/s, between potential limits of 0.05 V and 0.4 V. Methanol oxidation experiments typically consisted of 10 cycles between 0.05 V and 0.75 V versus RHE at 10 mV/s.