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# Tungsten materials as durable catalyst supports for fuel cell electrodes

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## HIGHLIGHTS

- Tungsten carbide and tungsten oxide were used as catalyst support for HT-PEMFC.
- Tungsten oxide showed higher stability compared to carbon materials.
- 1000 h test of tungsten oxide based anode in HT-PEM stack was done.

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## ABSTRACT

Durable platinum catalyst support materials, e.g. tungsten carbide (WC), tungsten oxide ($WO_x$) and self-synthesized tungsten oxide ($WO_{xs}$) were evaluated for the use in High-Temperature Proton Exchange Fuel Cells (HT-PEM) based on phosphoric acid doped polybenzimidazole as electrolyte. The support materials and the catalyst loaded support materials were characterized *ex*-situ by cyclic voltammetry in $HClO_4$, potential cycling, CO-stripping, electron microscopy and X-ray diffraction measurements. The tungsten oxide and tungsten carbide based supported catalysts were compared to High Surface Area Carbon (HSAC), each coated with platinum via the same in-house manufacturing procedures. The in-house manufacturing procedures resulted in catalyst particle sizes on HSAC of 3–4 nm with a uniform distribution.

The *in-situ* Potential Cycling experiments of $WO_x$ or $WO_{xs}$ supported catalysts showed much lower degradation rates compared to High Surface Area Carbons. The formation of $WO_x$ species on WC was proven by *ex*- and *in-situ* cyclic voltammetric studies and thermogravimetric analyses. X-ray diffraction, *ex-situ* cyclic voltammetry and *in-situ* cyclic voltammetry showed that $WO_x$ is formed from WC as starting material under oxidizing conditions. Finally a 1000 h durability test with $WO_x$ as catalyst support material on the anode was done in a HT-PEM fuel cell with reformed methanol on the anode.

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## 1. Introduction

The corrosion of today's widely used high surface area carbon blacks is one of the main reasons of performance degradation in fuel cells, especially under start–stop conditions and high electrochemical potentials on anode and cathode. Because of high potentials and temperatures the carbon catalyst support oxidizes to $CO_2$, which can be detected in the anode and cathode off-gas [1]. A lot of effort was put in the development of more stable carbon compounds as catalyst support material, especially with a more graphitic structure, e.g. carbon nanotubes or carbon nanofibers. These structured carbon materials show lower carbon corrosion rates [2–4], but they cannot prevent carbon oxidation.

Due to this non-carbon materials with high corrosion resistance and high stability under acidic fuel cell conditions are in the focus of interest of research groups worldwide in order to substitute conventional electrode material. However there are several factors which are important for catalyst support materials such as high surface area, porosity, electrical conductivity, electrochemical stability and surface functional groups [5]. These mentioned parameters have to be fulfilled for any successful application.

Tungsten Oxides ($WO_x$) are compounds with very high melting points of 1700 °C and very low vapor pressure [6]. $WO_x$ is formed by

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the reaction of metallic tungsten with oxygen to form stoichiometric tungsten trioxide ($WO_3$) and lower non stoichiometric oxides $WO_x$, with $2 < x < 3$ [7]. $WO_{2<x<3}$ is an *n*-type semiconductor with a band gap of about 2.6–2.8 eV [8]. It has a high conductivity which arises from a donor level formed by oxygen-vacancy defects. This leads to the decrease in the resistivity from 1 Ω cm for $WO_2$ to a minimum of 0.1 Ω cm for $WO_{2.75}$ [8], which is sufficient for the use in fuel cell electrodes.

Hobbs and Tseung [9] observed that the rate for hydrogen oxidation in acidic solution increases by the use of Polytetrafluoroethylene (PTFE) bonded Pt supported on $WO_3$. They explained this behavior with hydrogen that spills over onto the surface of the hydrogen tungsten bronze ($H_xWO_3$), freeing these Pt sites for further chemisorptions of hydrogen. This spill-over mechanism of hydrogen between $WO_3$ and Pt has been suggested as being responsible for the increased activity for the Oxygen Reduction Reaction (ORR) [10]. On the other hand Ota et al. [11] claimed that the observed enhancement of the ORR activity is due to reduced $PtO_2$ formation. This leads to a higher oxide free Pt-surface area, which is more active for the ORR. Further works on the topic of the relationship between structure and activity of Pt on different synthesized $WO_3$ support material were done by Shim et al. [12] and Kulesza and Faulkner [13]. They showed that Pt loaded $WO_3$ nanorods are more stable compared to $WO_3$ bulk when cycling is conducted between −0.2 and 1.0 V in 2 N $H_2SO_4$ for several times.

As discussed before $WO_3$ shows a considerable high proton transfer due to the formation of $WO_3$ hydrates. This is a very attractive property for fuel cell catalyst supports [14] since this has a beneficial impact on the number of three phase reaction zones, where the catalyst is in contact with an electron conducting support and a proton conducting electrolyte.

In contrast to $WO_x$, WC was also evaluated as possible material for fuel cell catalyst supports and even catalyst material for the hydrogen oxidation reaction (HOR). Nikolov and Vitanov [15,16] investigated the corrosion resistance of WC in $H_2SO_4$ and the changes in catalytic activity during corrosion. They discovered that the amount of oxides linearly increases with time, suggesting that during corrosion the catalyst surface was not passivated. In contrast to these findings, Brady et al. [17] reported passivation of WC based catalysts. Depending on the surface stoichiometric ratio of W:C, with higher W content, surface passivation to $WO_3$ in $H_2SO_4$ occurs. This causes a loss of electrocatalytic activity of WC for the HOR.

Chhina et al. [18] claimed that the stability of WC under electrochemical oxidizing conditions is higher compared to High Surface Area Carbons (HSAC). Meng and Shen [19–21] studied the effect of the addition of Pt onto WC. They observed a ten times larger activity for the ORR of Pt–$W_2C$/C than that of Pt/C in an alkali medium and proposed a synergy between $W_2C$ and Pt. In acidic media Santos et al. [22] found that the use of Pt on $W_2C$ as catalyst support material leads to a remarkable enhancement of the ORR activity compared to Pt on carbon, although both catalysts follow the four electron mechanism. Another idea from Shao et al. [23] to get a higher stability of the catalyst support material is to coat the commercial available carbon based catalyst supports with an electrochemical process with phase pure WC and Pt. They achieved a two fold increase of the corrosion resistivity compared to not coated carbon based support materials.

The major drawback of commercial available WC and $W_2C$ is the low Brunauer–Emmett–Teller (BET) surface area (2.1 $m^2\ g^{-1}$) compared to HSAC (about 250 $m^2\ g^{-1}$), which hinders their implementation in fuel cells. Ganesan and Lee [24] synthesized platinum particles on $WO_3$ nanoparticles with controlled oxidation of $W_2C$ microspheres by calcination at 773 K in $O_2$ atmosphere for 3 h. Zhu et al. [25] recently showed that the electrochemical stability of WC is dependent on the specific surface area. The higher the specific surface area, the more WC is prone to get oxidized to $WO_3$ under oxidizing electrochemical conditions (>0.7 V). They also measured very low ORR activity values, which they explained by a high contact resistance between the catalyst and catalyst support. When WC is oxidized it forms an insulating $WO_3$ layer. This layer blocks the electron transfer between the catalyst and catalyst support, and according to that the contact resistance increases significantly [26].

In this study we evaluate the characteristics of WC, self-made $WO_{xs}$ and commercial available $WO_x$ for the use as electrode material in high-temperature proton exchange (HT-PEM) fuel cells. Electrodes are fabricated with and without platinum and their electrochemical properties are investigated and compared to each other.

The materials are evaluated in *in-situ* experiments in HT-PEM fuel cells and *ex-situ* with Cyclic Voltammetry (CV), Potential Cycling (PC), CO-Stripping, Thermogravimetric Analysis (TGA), X-ray diffraction (XRD) and electron microscopy investigations. The resulting degradation effects, the formation of $WO_x$ and tungsten bronzes and the influence of the catalyst support on the CO-oxidation behavior are discussed. Finally a 980 h long term test at constant load in a HT-PEM fuel cell stack was done and no degradation was observed.

## 2. Experimental

### 2.1. Synthesis of $WO_{xs}$

Commercial available WC (WC CRC 010u, Wolfram Bergbau und Hütten AG) with a BET surface area of 2.71 $m^2\ g^{-1}$ and a grain size of 0.47 μm were oxidized in order to obtain a surface oxidized $WO_{xs}$ species.

For this, the raw WC powder (3 g) is dispersed in 50 ml of a mixture (3:2) of $HNO_3$ (65 wt%, BDH Prolabo, AnalaR Normapur) and $H_2SO_4$ (98 wt%, MERCK KGAA, EMSURE) and heated under reflux for 6 h. After this treatment the resulting green powders are washed several times with deionized water until a neutral pH value was obtained.

### 2.2. Catalyst deposition

The deposition of platinum catalyst on the different catalyst supports is realized via electroless deposition methods. $WO_x$, $WO_{xs}$, WC and for comparison HSAC based catalyst supports (0.5 g) are ultrasonicated in a three neck round bottom flask in 30 ml of ethylene glycol and 10 ml deionized water. The deposition of the Pt precursor was done according to the procedure described elsewhere [26]. A platinum loading of 13 wt% on tungsten and HSAC based powders is obtained and confirmed via elemental and Energy-Dispersive X-ray (EDX) measurements.

### 2.3. Determination of catalyst crystallite size and support structure

To investigate the general morphology and to determine the overall chemical composition of the Pt loaded and unloaded electrode materials a JEOL JSM-6500F scanning electron microscope operated at 4.0 kV and equipped with an energy-dispersive X-ray detector from Oxford Instruments (Inca Energy) was used. Using the implemented JEOL standard detector, secondary electron (SE) images were acquired. SEM top view samples were prepared using conventional preparation techniques. Transmission electron microscopy (TEM) investigations were accomplished by using a FEI Titan 80–300 (S)TEM microscope equipped with a Gatan Tridiem image filter and an EDAX EDX detector for analytical measurements. Standard TEM samples were obtained by suspending the

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