

Tungsten Monocarbide (WC) as an Alternative Anode Electrocatalyst in Proton Exchange Membrane Fuel Cells

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Introduction

The motivation of this research is to assess the feasibility of tungsten carbides as alternative electrocatalysts in proton exchange membrane fuel cells (PEMFC). PEMFCs directly convert chemical energy into electrical energy by the electro-oxidation of hydrogen or small oxygenates, such as methanol. Compared to internal combustion engines, PEMFCs offer several attractive features, such as high theoretical efficiency, low operating temperature, and minimum vibration and noise [1]. Current fuel cells require the use of Pt/Ru bimetallic anode catalysts which suffer from CO poisoning and high cost [2]. The commercialization of such technologies requires less expensive and more CO tolerant materials. Transition metal carbides often show catalytic properties similar to the Pt-group metals [3] and recent research suggests that tungsten carbides may be an appropriate substitute [4].

Materials and Methods

The electrochemical properties of platinum foil and carburized tungsten foil were studied using cyclic voltammetry (CV) and chronoamperometry (CA) in an *in-situ* electrochemical half-cell that allowed pre- and post- examination by X-ray photoelectron spectroscopy (XPS) [5]. The different reaction pathways of methanol on the three surfaces were investigated using surface vibrational spectroscopy. Density Functional Theory modeling was also performed to further understand the sequence of bond scission for the O-H, C-H and C-O bonds of methanol on the three surfaces.

Temperature programmed desorption (TPD) was used to study the reactions of CO, H₂, CH₄ and CH₃OH on polycrystalline platinum, tungsten carbide and platinum-modified tungsten carbide foils [5, 6]. Polycrystalline foils were chosen as test materials since their morphological complexity better approaches that of real commercial catalysts.

Results and Discussion

A synergistic effect was observed on tungsten carbide modified by physical vapor deposition with submonolayer platinum, evidenced by an increase in the onset of metal oxidation potentials compared to WC in an acidic environment at anodic potentials [7]. Additionally, both WC and Pt/WC displayed two oxidation features when exposed to methanol in an electrochemical environment, which were attributed to methanol decomposition at intermediate potentials and metal oxidation at high potentials. Both WC and Pt/WC showed higher methanol oxidation current than Pt in the CA measurements. These electrochemical

results suggest that transition metal carbides, and moreover platinum modified tungsten carbides, may be reasonable alternative electrocatalysts for direct methanol fuel cells.

Results from TPD studies show that WC, Pt/WC and Pt surfaces are active to methanol decomposition, with WC being the most active (see table 1). Also, the addition of submonolayer coverages of Pt can eliminate the production of CH₄, which is an undesired reaction occurring over WC.

Table 1. Comparison of activity of methanol reaction pathways on various surfaces [5]

Surface	Complete decomposition activity per metal atom	CO activity per metal atom	CH ₄ activity per metal atom	Total number of CH ₃ OH reacting per metal atom
WC	0.130	0.043	0.055	0.228
0.8 ML Pt/WC	0.010	0.058	0.000	0.068
Pt	0.000	0.059	0.000	0.059

Significance

Commercialization of low temperature fuel cells requires less expensive and more CO tolerant materials. This work has demonstrated that WC is less susceptible to CO poisoning than Pt and capable of methanol electro-oxidation under approximated fuel cell operating conditions. Also, according to the US Department of the Interior *Minerals Yearbook*, as of 2005 platinum was 10,000 times more expensive than tungsten. This saving in material cost, combined with more CO-tolerance compared to Pt, could make WC and Pt/WC promising alternative electrocatalysts for PEMFC applications.

References

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