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Multifunctional composites containing molybdenum carbides as potential electrocatalysts

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Abstract

The aim of the current study is to determine the feasibility of introducing fuel cell functionality on the surfaces of carbon-based composite materials. This can potentially be achieved by the synthesis of molybdenum carbides on the surfaces of carbon foam, which is a light and rigid material that can be used as structural components in aircrafts and vehicles. The current study employed physical vapor deposition (PVD) to deposit molybdenum on the carbon foam substrate. The ratio of surface molybdenum and surface carbon was determined using X-ray photoelectron spectroscopy (XPS). The combination of PVD and in situ XPS allowed for the synthesis of molybdenum-coated carbon foam samples with desirable and reproducible Mo/C ratios. The coated films were then heated in vacuum to promote the reaction between molybdenum and carbon foam to produce surface molybdenum carbides. The carbide-coated samples were further characterized using XPS, near-edge X-ray absorption fine structure (NEXAFS), and scanning electron microscopy (SEM). Platinum metal was also deposited via PVD on carbon foam, both with and without the presence of molybdenum carbide on the foam surface. The electrochemical stability of Pt-coated foams was evaluated using cyclic voltammetry (CV).

Keywords: Molybdenum carbides; Scanning electron microscopy; Cyclic voltammetry

1. Introduction

Carbon foam, or reticulated vitreous carbon foam (RVC), is a potentially useful structural component for light duty aviation applications because of its light, porous, and highly rigid structure [1–3]. Currently, the primary on-board power supply for aviation applications is from batteries. While batteries are presently the most economically feasible source of power for small aircraft, they add a significant amount of net weight to the unit. One of the most likely candidates as alternate power supply to batteries is the direct methanol fuel cell (DMFC). Literature reports show that fuel cells such as DMFC possess an energy density (Wh/kg) approximately 50 times the value of the strongest currently mass-produced batteries [4]. The replacement of batteries with DMFC would represent a significant reduction in the overall weight of the small aircraft. The objective of the current paper is to determine the feasibility of integrating the fuel cell functionality directly onto the carbon foam structural component.

Currently, the most widely used electrocatalysts for DMFC are platinum (Pt) containing alloys such as Pt–Ru [5–7] and Pt–Sn [5–9]. The primary disadvantages of these Pt alloys are their relative scarcity and high cost. In the case of functionalized RVC carbon foam, it is not economically feasible to simply coat the foam surfaces with Pt. Furthermore, because Pt does not bond strongly with carbon foam, Pt would most likely be in the form of clusters instead of being highly dispersed on the foam surfaces. Solutions to these problems are to either produce cost-effective electro-

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catalysts using less expensive components, or to reduce the Pt loading by improving its dispersion on the carbon foam.

Early transition metal carbides have been shown in previous studies [10,11] to behave similarly to the Pt group metals (Pt, Pd, Ir, Rh, Ru). For example, research done by our group has shown that carbide-modified W(1 1 1) and W(1 1 0) surfaces showed high activity toward the dissociation of methanol, although about 14% of the adsorbed methanol decomposed to produce methane [12,13], an undesirable process for the application in DMFC. An additional study from our research group on the carbide-modified Mo(1 1 0) surface showed that the methane formation pathway was not present on C/Mo(1 1 0) [14]. In addition, this study indicated that the C/Mo(1 1 0) surface was more active toward the dissociation of water than the C/W(1 1 1) or C/W(1 1 0) surfaces. Overall, these surface science studies indicate the molybdenum carbides are very active toward the dissociation of methanol and water, suggesting the possibility of using molybdenum carbides as alternative electrocatalysts for DMFC. One of the objectives of the current manuscript is to bridge the findings from single crystal surfaces under ultrahigh vacuum (UHV) conditions [14] to more realistic electrochemical studies.

In the present study, we begin to examine molybdenum carbides and platinum-modified molybdenum carbides as potential electrocatalysts for proton exchange membrane (PEM) type fuel cells. For simplicity, our initial probe electrochemical reaction is the electrooxidation of hydrogen, which will lead to additional studies of the electrooxidation of methanol for DMFC applications. In particular, we are interested in determining the feasibility of the integration of the electrocatalytic functionality on the surfaces of carbon foam. If successful, the multifunctional composite materials would provide the fuel cell functionality to otherwise unused volume within the vehicles and thus reduce the weight demands upon the overall structural components.

In this study, thin films of molybdenum carbide (Mo-C) and platinum-modified Mo-C were synthesized on carbon foam substrates by a combination of physical vapor deposition (PVD) and in situ annealing. For simplicity, Mo-C will be used in the current paper as an abbreviation for molybdenum carbides; although, the exact stoichiometry of the molybdenum carbide film is not determined in the current study due to C signals from the foam substrate. The Mo-C and Pt/Mo-C samples were characterized by X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS), and scanning electron microscopy (SEM) to determine the thin film surface composition and to verify the presence of molybdenum carbides. Cyclic voltammetry (CV) was used to obtain a preliminary assessment of the electrocatalytic stability and activity of RVC foam modified with Mo-C and Pt/Mo-C, which demonstrated the possibility of a synergistic effect by combining Pt and Mo-C on the RVC foam surfaces.

2. Experimental

2.1. Deposition

Sample preparation was performed in a stainless steel vacuum system with a typical base pressure of 3×10^{-8} Torr. The system was equipped with Mo and Pt metal sources for physical vapor deposition. The Mo source was composed of a thin Mo foil (0.0125 mm, 99.99% pure, from Goodfellow) wrapped around two copper feedthroughs. The Pt source was constructed from a Pt metal wire wrapped around a tungsten wire (0.5 mm), which served as a heating filament. Either filament was heated resistively until the metal evaporation temperature was reached. The metal beams were directed onto the foam substrate through an aperture of tantalum (Ta) shields surrounding each respective filament. During PVD experiments with Mo or Pt, the sample was maintained at a distance of approximately 8 cm from the metal source aperture.

The PVD deposition was conducted on nanoporous carbon (NPC, supported on stainless steel) and RVC foam. For the XPS, NEXAFS and SEM characterization, samples were cut to dimensions of 1 cm × 1 cm and resistively heated in a tantalum foil sample boat. Foam samples to be used for electrochemical testing were cut to an approximate length, width and thickness of 5 cm × 1 cm × 0.5 cm, respectively. Resistive heating of these longer samples was achieved by means of a co-axial Inconel wire fed through the center of the sample volume. The RVC foam was purchased from Ultramet and the NPC film supported on stainless steel was provided by the Foley research group at Pennsylvania State University.

Samples were introduced into the vacuum chamber individually and coated with Mo and/or Pt by PVD to produce samples of Mo-C/foam, Pt/foam and Pt/Mo-C/foam. For all samples to be tested in the electrochemical cell, exposure time and metal source current were adjusted such that the surface ratio of Mo/C was approximately 0.17, based on standard XPS sensitivity factors [15]. Molybdenum carbides were formed on the surface of the carbon samples by resistive heating the Mo/C samples in vacuum to temperatures between 823 and 973 K. Pt-modified surfaces were prepared by PVD of Pt on either foam or Mo-C/foam surfaces. The Pt PVD deposition current and time were controlled to achieve a surface atomic ratio of 0.17 Pt/C.

2.2. Techniques

The PVD system was equipped with an Al/Mg dual anode X-ray source and a concentric hemispherical analyzer (CHA) for in situ XPS. Studies using XPS enabled us to control the surface concentrations of Mo and Pt as well as to verify carbide formation. Other characterization techniques used to examine the synthesized samples were NEXAFS at Brookhaven National Laboratory and SEM. These two

techniques provided additional and complementary information about the Mo-C thin films.

The Pt/foam and Pt/Mo-C/foam samples were also evaluated using cyclic voltammetry (CV). The CV measurements were performed in an electrochemical half-cell. The half-cell was a glass vessel containing 1 l of 0.05 M H_2SO_4 electrolyte, equipped with a saturated calomel electrode (SCE) and a platinum foil counter electrode of length, width, and thickness of 5 cm × 1 cm × 0.01 cm. The functionalized carbon foam samples were installed as the working electrode (anode). The electrochemical half-cell was connected to a gas handling system supplied with N_2 and H_2 gas. These gases were introduced individually into solution by a sparger or above the solution surface. During CV experiments, the system was enclosed and purged with gas (either N_2 or H_2) via the sparger for 10 min. Gas flow was routed to the solution surface and the system was allowed to equilibrate for 2 min prior to initiating the CV sweep. Potential sweeps were conducted within a range of 0–0.6 V.

3. Results and discussion

3.1. Deposition on nanoporous carbon (NPC)

The initial PVD deposition was performed on a flat NPC thin film to confirm the proof of principle of carbide formation via the deposition of Mo followed by annealing in vacuum. Fig. 1 shows the XPS spectra following the formation of molybdenum carbides on NPC. The bottom spectrum shows the XPS of the clean NPC surface, which is characterized by the graphitic C 1 s peak at 284.9 eV. A thin film of Mo was deposited to the surface using the aforementioned PVD method to obtain a Mo/C ratio of 0.13. As expected, following deposition the C 1 s signal decreased and there was no significant shift of the C 1 s peak.

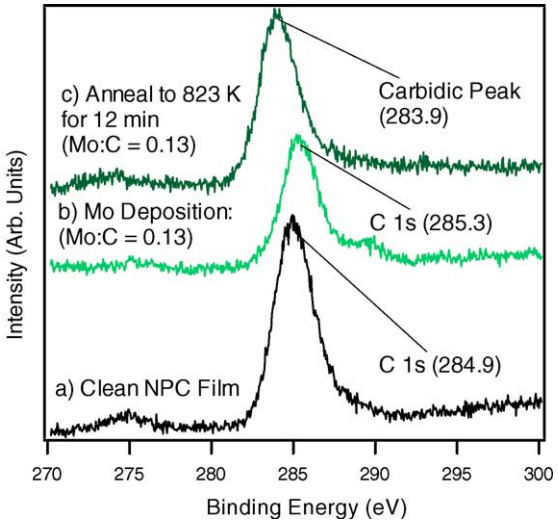

Fig. 1. C 1 s XPS spectra of NPC (a) and Mo/NPC surfaces before (b) and after (c) heating the sample to 823 K for 12 min.

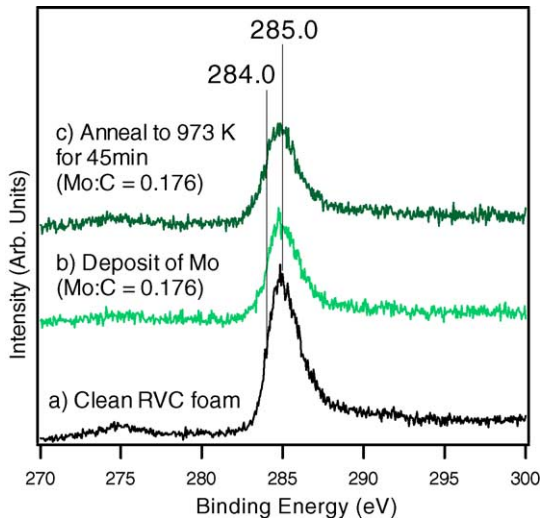

Fig. 2. C 1 s XPS spectra of RVC foam (a) and Mo-modified foam surfaces before (b) and after (c) annealing at 973 K for 45 min.

Annealing the sample to 823 K for a 12-min period caused the C 1 s peak to shift by approximately 1.4 eV. This shift of the C 1 s signal indicates the presence of carbidic carbon on the sample surface, as has been observed in previous studies where XPS was used to verify the formation of carbides on Mo based on the C 1 s peak position [16,17]. The detection of the carbidic peak in Fig. 1 demonstrates that the NPC surfaces can be uniformly functionalized with Mo-C thin films via the deposition of Mo and subsequent annealing.

3.2. Deposition on RVC foam

The XPS results following the deposition and annealing of Mo on RVC foam are shown in Fig. 2. Data shown in this figure are representative of a foam sample with a Mo/C surface ratio of 0.176. Sample annealing was allowed to continue for an extended period of time at 973 K to ensure uniform heating of the sample, because the RVC foam was much less dense and thicker than the NPC samples. The results from Fig. 2 show no clear evidence of carbide formation on the Mo-modified RVC surface, as suggested by the observation that the C 1 s signal does not shift significantly after sample heating.

It was unclear whether the lack of a characteristic carbide peak at 284.0 eV was the result of insufficient sample heating, insufficient surface coverage of Mo, or a dominance of the graphitic C 1 s signal from the channels in the carbon foam. As described in a review, NEXAFS is much more sensitive than XPS in detecting the carbidic carbon in transition metal carbides [18]. Newly prepared samples of RVC foam were analyzed with NEXAFS. The spectra of these studies are shown in Fig. 3. Spectrum (c) in Fig. 3 is a NEXAFS spectrum from an earlier study [19] of molybdenum carbides which were formed on the surface of a Mo(1 1 0) single crystal. The presence of the carbon K-edge feature at 285.5 eV in spectrum (b) is indicative of carbidic

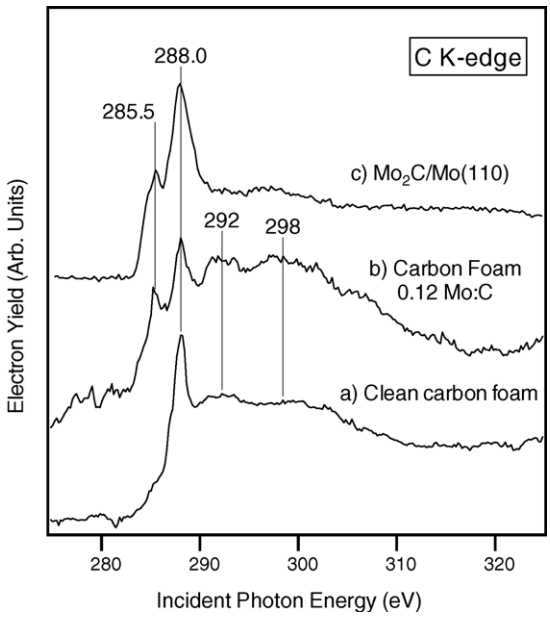

Fig. 3. NEXAFS spectra of RVC foam (a), Mo-modified RVC foam (b) and molybdenum carbides (c).

carbon, confirming the formation of Mo-C on the foam surface. The comparison of the NEXAFS spectra also indicates that the graphitic signals at 292 and 298 eV are present on the Mo-C/foam sample, most likely due to signals from the channels of the foam substrate.

3.3. Scanning electron microscopy (SEM) characterization

In order to determine whether the foam surface was uniformly coated following deposition, a Mo-C/foam sample (Mo/C ratio of 0.17) was prepared and annealed in vacuum for 30 min at 900 K. SEM analysis was employed to obtain information about the sample surface morphology and the distribution of Mo. A low magnification image (110× magnification), seen in Fig. 4, shows the porous sample surface. A sample surface of this nature suggests that PVD of Mo on foam will be more challenging than for a flat substrate. One could expect the Mo beam to deposit within the sample volume in addition to the surface. More deposition time was needed to accumulate Mo because of the shadowing effect in PVD deposition. For example, due to equipment constraints, the PVD beam (for Mo and Pt) was oriented at an angle of ∼130° to the sample surface, and therefore, the shadowing effect to depositions inside the foam channels should be enhanced. Fig. 5 shows a higher magnification image of the same Mo-C/foam sample, at the ridge of the porous carbon foam. A parallel image by X-ray energy dispersive spectroscopy (XEDS) verified the presence of Mo throughout the ridge surfaces (not shown). Overall, the SEM measurements provide evidence that the RVC surface was relatively uniformly coated with Mo after deposition and annealing.

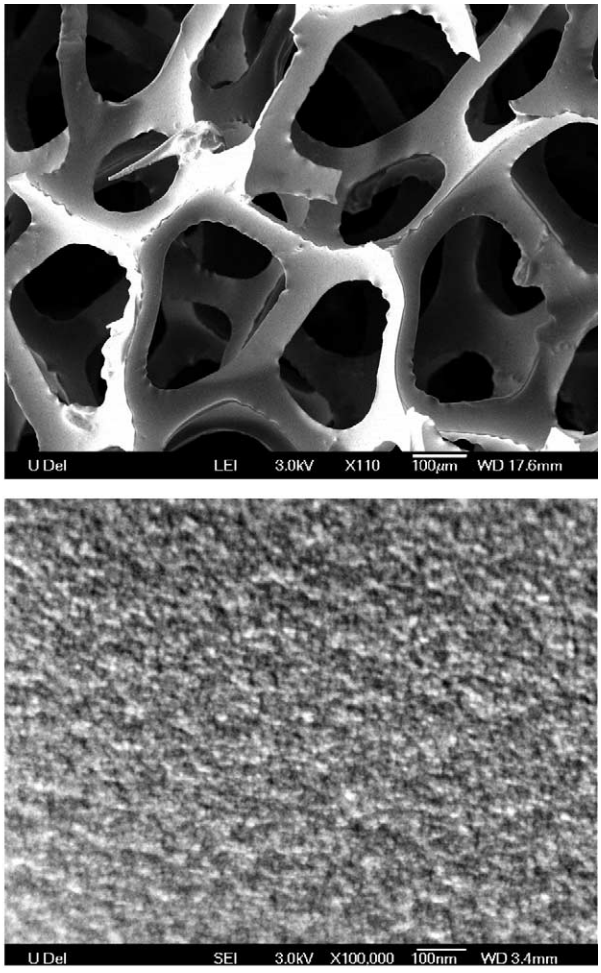

Fig. 4. SEM image of RVC foam at 110× magnification (a) and at 100,000× magnification (b).

3.4. Cyclic voltammetry (CV) characterization of electrochemical stability

Fig. 5 shows results of a preliminary study conducted on Pt/foam and Pt/Mo-C/foam samples to determine their electrochemical stability. Each sample, partially immersed in a dilute H_2SO_4 environment, purged with either N_2 or H_2 gas, was subjected to a voltage sweep between −0.05 and 0.8 V with respect to the SCE. It is readily apparent from the CV curves that there is an increase in magnitude of the current when the surface is modified with Pt. This increase is further enhanced by the modification of carbon foam with both Mo-C and Pt. All CV data were collected with the assumption that the sample surface was uniform. The active surface area of the functionalized sample was calculated using the geometric dimensions of the immersed portion of the sample. The identical CV curves between sweeps 2 and 3 indicated that the Pt/foam and Pt/Mo-C/foam were electrochemically stable during the CV measurements. More detailed post-CV analysis will be performed using an XPS facility equipped with in situ CV measurements.

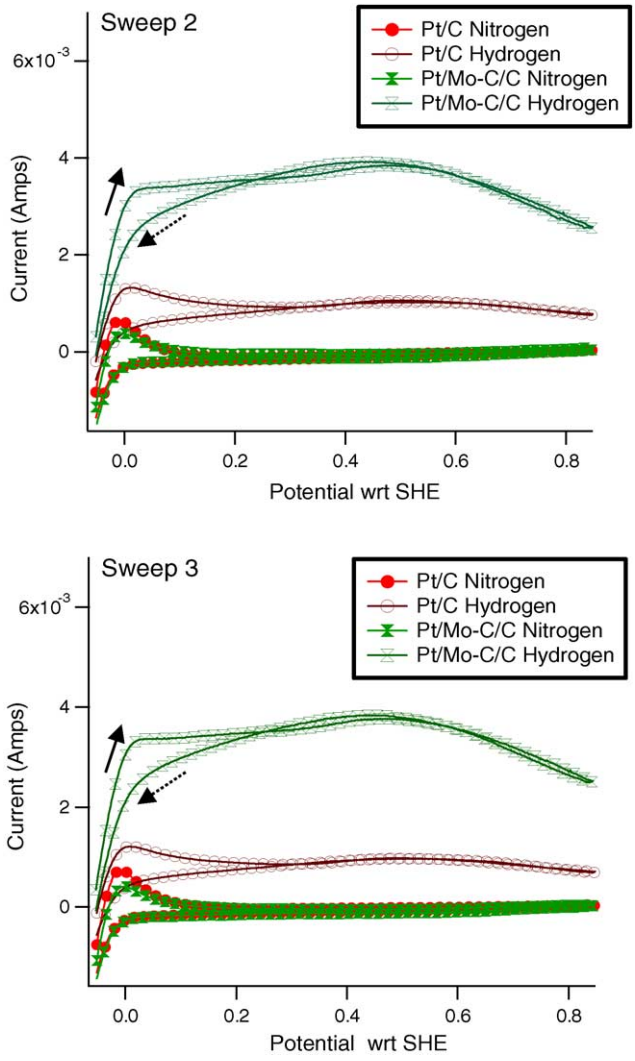

Fig. 5. Cyclic voltammograms of Pt/foam and Pt/Mo-C/foam partially immersed in a 0.05 M H_2SO_4 solution. Arrows indicate the forward (solid) and reverse (dashed) direction of the potential sweep. Potential sweeps were conducted at a rate of 10 mV/s.

The dissimilarity of these CV curves to those obtained from other studies on Pt-modified carbon surfaces [20,21] is not well understood at this time. More systematic electrochemical studies are underway to further understand the CV behavior, as well as the potential synergistic effect of combining Pt and Mo-C. Overall, the initial electrochemical study suggests that the Pt/foam and Pt/Mo-C/foam samples have significantly distinguishable performances, and that they possess some level of electrochemical stability in the sulfuric acid electrolyte solution.

There are two possible causes for the enhancement of the electrooxidation of hydrogen dissociation on Pt/Mo-C/foam as compared to Pt/foam. The first one could be the improved dispersion of Pt on the molybdenum carbide surface, thereby increasing the total active surface sites available for hydrogen oxidation. Another contribution to this enhancement could possibly lie in a synergistic effect occurring between the surface Pt and Mo-C, as has been observed previously in our surface science studies of the dissociation of hydrogen and methanol on Pt-modified tungsten carbide surfaces [22]. More detailed characterization of the Pt/Mo-C/foam as compared to Pt/foam surfaces, such as the chemisorption of CO, is necessary to determine whether the enhancement is from either the improved Pt dispersion or the synergistic effect of Pt/Mo-C interaction.

4. Conclusions

From the results described above, the following conclusions can be made regarding the functionalization of carbon foams by molybdenum carbides:

(1) The formation of molybdenum carbides on the surface of graphitic carbon substrates has been found using XPS for the NPC film, and using NEXAFS for the RVC foam.
(2) SEM images along with XEDS results show that the molybdenum is relatively uniformly distributed on the carbon surface of the RVC foam.
(3) Preliminary CV measurements on the Pt/foam and Pt/Mo-C/foam samples indicate that there is an increase in the electrocatalytic activity when the carbon foam surface is functionalized with Pt and Pt/Mo-C. Multiple sweeps of the CV experiments show identical CV curves, indicating the electrochemical stability of the PVD films.
(4) The results show that Pt/foam and Pt/Mo-C/foam demonstrate electrocatalytic activity and warrant the synthesis and more detailed electrochemical testing of the modified RVC foam as potential electrocatalysts.

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