Facile Synthesis of High Surface Area Molybdenum Carbide and Nitride: An Application in Support Materials for Oxygen Reduction Reaction

Aaron Roy

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THESIS

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Abstract

A method to synthesize high surface area α-MoC\(_{(1-x)}\) without the temperature programmed reduction (TPR) of MoO\(_3\) is described. This method was then used, in conjunction with a novel \textit{in situ} method to obtain highly dispersed PtMo\(_x\) supported on α-MoC\(_{(1-x)}\), to explore the suitability of such materials as catalysts for oxygen reduction reaction (ORR) in a proton exchange membrane fuel cell (PEMFC). Mg\(_2\)(Mo\(_3\)O\(_8\)) and Zn\(_2\)(Mo\(_3\)O\(_8\)), alternative tetravalent Mo intermediates to MoO\(_2\), were obtained through the thermal decomposition of Mg(MoO\(_4\)) and Zn(MoO\(_4\)) in mixtures of CO and H\(_2\). A novel sacrificial support method was developed where MgO and ZnO were investigated sacrificial support materials formed \textit{in situ} as decomposition products of the Mo precursor. Reaction conditions were explored: including feed composition, synthesis temperature, and synthesis duration. X-Ray powder diffraction (XRD) was used to determine the time dependence on conversion, where 30 to 140 minutes at a temperature of \(\sim\)700 °C was required to reach full conversion of the precursors. Scanning electron microscopy (SEM) revealed an equiaxed microstructure with primary particle
sizes between approximately 15-30 nm, depending on the duration of high temperature exposure. Rapid heating rates along with limited exposure to high temperature required by this method resulted in gravimetric surface areas as high 45 m$^2$/g, measured using four point Brunauer-Emmett-Teller (BET) analysis. A similar, ammonia-free, synthesis of $\beta$-MoN$_{(1-x)}$ in mixtures of N$_2$ and H$_2$ is also described.

The ability of these precursors to be decomposed rapidly, in comparison to the time requirements for TPR, was utilized in the development of an in situ method for the preparation of PtMo$_z$ composite phases supported on $\alpha$-MoC$_{(1-x)}$. Ammonium magnesium molybdate, (NH$_4$)$_2$Mg(MoO$_4$)$_2$, was developed as a precursor to $\alpha$-MoC$_{(1-x)}$ which was found to form favorable interactions with ammonium derived (PtCl$_6$)$^{+2}$ species when co-precipitated in NH$_4$(OH). When this co-precipitated, and amorphous, precursor was treated under the carbiding conditions developed for the synthesis of $\alpha$-MoC$_{(1-x)}$, highly dispersed PtMo$_z$ on $\alpha$-MoC$_{(1-x)}$ was obtained. Crystalline platinum phases were not observed by XRD and Transmission Electron Microscopy (TEM) revealed platinum phases with crystalline domains on the order of approximately 5 nm, homogeneously dispersed throughout the observed samples. The materials, as prepared, were found to be catalytically inert for ORR, leading to the development of an additional treatment designed to redistribute platinum phases in a manner conducive for yielding more labile surface species. In particular, it was found that a thermal treatment in a pure CO atmosphere directly following the initial material synthesis resulted in significant development of electrochemical surface area (ECSA). Materials were characterized using cyclic voltammetry (CV) in a rotating disc electrode setup. CV measurements were performed in both O$_2$ and N$_2$ saturated solutions of 0.1 M HClO$_4$. The ECSA of this material was measured at $\sim$36 m$^2$/g and the specific mass activity for ORR was measured to be $\sim$ 137 A/g$_{pt}$. Catalyst durability measurements were also
performed and the results are reported. The gravimetric surface area of the α-MoC(1-x) support was measured using BET N2 adsorption, measuring ~32 m²/g. The catalysts microstructure was also characterized using SEM. Transmission electron microscopy (TEM) was employed for the identification of various possible composite phases ranging from : α-Pt, α-PtMoz, β-Pt3Mo, and, α-(Pt2Mo3C)0.66. TEM results indicate a more broad distribution of these platinum phases, with the addition of what is likely β-MoC(1-x), in the materials following the CO surface treatment. X-ray photoelectron spectroscopy (XPS) was also used for surface analysis and the results are discussed.
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Introduction

Beginning in the latter part of the 20th century, hydrogen fuel cell technology has received much attention as a promising avenue for providing unconventional forms of energy in a variety of applications, most notably the automotive industry. However, high costs associated with fuel cell catalysts, as well as the durability of these materials, have proven to be a substantial economic constraint. Of particular interest is the low durability of state-of-the-art Pt/C_{black} catalysts due to electrochemical oxidation, and subsequent corrosion, of the carbon support. Specifically, cathode materials supported on carbon are exceptionally vulnerable to corrosion due to electrochemical oxidation of carbon in the presence of water to form CO\_2 (E^\circ=0.207 \text{ V vs. SHE}) [1]. The loss of the support results in the detachment of Pt particles which can then, through the process of Ostwald Ripening, agglomerate on the surface which effectively decreases the electrochemical surface area (ECSA) of the catalyst. Pt nano-particles may also be soluble in acidic electrolytes at cell potentials near the upper operating range of a PEMFC [2]. Other phenomena, such as the migration and subsequent sintering of high energy Pt surface particles, also contribute to the loss of ECSA. Another mode of corrosion at the cathode is due to the heterogeneous water gas reaction. Here, Pt can catalyze the oxidation of carbon to form CO and H\_2 stoichiometrically, again resulting in a loss of ECSA. As such, it has been proposed to replace carbon with high surface area materials such as transition metal carbides and nitrides which possess high electrical conductivity and corrosion resistant properties under the range of PEMFC operating conditions [3]. Of particular interest is \alpha-MoC_{(1-x)}, which has been shown to have a large region of
stability under an applied potential at low pH [4].

Contemporary methods of preparing high surface area $\alpha$-MoC$_{(1-x)}$ and MoN$_{(1-x)}$ typically require extensive temperature programmed reduction reaction designed to control particle morphology. This, when coupled with the oxophilicity of $\alpha$-MoC$_{(1-x)}$, create specific engineering challenges involving the dispersion of catalyst phases on the surface of these materials. Therefore, it has been the objective of this work to develop methods of preparing both, high surface area $\alpha$-MoC$_{(1-x)}$, as well as methods of dispersing active Pt phases on $\alpha$-MoC$_{(1-x)}$, in ways which address the specific technical challenges associated with the preparation of this specific class of materials. This work describes the methods developed for a more facile preparation of these materials as well as an assessment, via electrochemical characterization, of the suitability of these materials in the application for catalysis of oxygen reduction reaction in a proton exchange membrane fuel cell (PEMFC).
Chapter 1

Synthesis of High Surface area $\alpha$-MoC$_{(1-x)}$ and $\beta$-MoN$_{(1-x)}$

1.1 Introduction

High surface area ceramic materials, such as Mo$_2$N and Mo$_2$C, have been investigated for their useful material properties which include, but are not limited to: catalysts for methane reforming, ammonia synthesis, alcohol synthesis from syngas, hydrodesulfurization, and electrocatalysis for hydrogen evolution reaction [5-10]. Additionally, Mo$_2$C and Mo$_2$N are known to possess high electrical conductivity, which in combination with their notable material hardness provide the potential to function as corrosion-resistant supports for platinum in PEM fuel cells [3].

Synthesis methods of high surface area Mo$_2$N and Mo$_2$C have been reported using a variety of methods, which can be summarized by three main reaction categories: carbothermal reduction, carburization, and ammonolysis of MoO$_3$ [11-17]. In all three cases the molybdenum precursors are typically MoO$_3$, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (AHM), or (NH$_4$)$_2$MoO$_4$ (AM), where molybdenum is initially hexavalent. During the reduction of the precursor, an intermediate tetravalent phase (MoO$_2$) is formed which is the species directly converted to nitride or carbide. High rates of solid state diffusion of the intermediate oxide phase, along with slow reduction kinetics, often result in extensive grain growth and low surface area carbides and nitrides [18]. To avoid this, these methods routinely employ temperature programmed reduction reaction (TPR) as a means of minimizing grain growth and maximizing surface area. Although effective,
TPR typically requires long synthesis times at elevated temperature due to slow ramp rates involved in the TPR profile. As a result, TPR may be cost prohibitive to the scaling of these methods and alternative reaction pathways which yield high surface area materials are of interest.

This work focuses on the deliberate selection of molybdenum precursors which decompose in reductive atmospheres resulting in nanocrystalline Mo$_2$C or Mo$_2$N, selectively and without the formation of intermediate MoO$_2$. However, considerable attention has been placed on the synthesis of the cubic phase of Mo$_2$C, $\alpha$-MoC$_{(1-x)}$.

The approach has been to achieve rapid conversion of the Mo precursor by arresting certain tetravalent molybdate intermediates, using high temperature along with rapid ramp rates to maximize rates of formation of desired phases while minimizing sintering processes. A sacrificial support method has also been adopted in which a sacrificial material is used to minimize contact between grain boundaries, thus preventing sintering and agglomeration of both molybdate intermediates as well as the carbide/nitride reaction products. In a slight variation of the sacrificial support method (SSM) commonly reported [19-24], reported here is a novel approach in which the sacrificial material is formed in situ as a decomposition product of the molybdenum precursor.
1.2 Experimental

1.2.1 Preparation of Mg(MoO$_4$) and Zn(MoO$_4$)

Molybdic acid, H$_2$(MoO$_4$), was prepared by adding MoO$_3$ powder (Sigma-Aldrich) to an excess amount of 30 wt% H$_2$O$_2$ (Sigma-Aldrich). The mixture was heated on a hot plate until the MoO$_3$ was fully dissolved and the solution, yellow in color, became transparent. The solution of H$_2$(MoO$_4$) and excess H$_2$O$_2$ was brought to a boil to decompose excess peroxide. Next, the H$_2$(MoO$_4$) was removed from the hot plate and an excess amount of MgO powder (UBE Material Industries, Ltd.) was added directly to H$_2$(MoO$_4$). The resulting acid/base reaction produces magnesium molybdate, Mg(MoO$_4$). Water soluble Mg(MoO$_4$) was then isolated by the filtration of insoluble MgO, which was added in excess to insure complete conversion of H$_2$(MoO$_4$). The solution of Mg(MoO$_4$) was then brought to a boil on a hot plate until dried and the crystalized Mg(MoO$_4$) was collected.

For the preparation of Zn(MoO$_4$), the procedure for Mg(MoO$_4$) synthesis was modified slightly. As Zn(MoO$_4$) is insoluble in water, high purity ZnO (Sigma-Aldrich) was added to an excess amount of H$_2$(MoO$_4$). The precipitate, Zn(MoO$_4$), was then isolated by centrifuging the reaction mixture, decanting the excess H$_2$(MoO$_4$), and then adding deionized water. This step was repeated until all excess H$_2$(MoO$_4$) was removed. The Zn(MoO$_4$) precipitate was then placed in an oven and dried in air at ~100 °C for several hours. It is important to note that this procedure yields a monoclinic phase of Zn(MoO$_4$), where a triclinic phase can be prepared by slight modification of this procedure. In the case of Zn(MoO$_4$) and Mg(MoO$_4$) the monoclinic structures were used explicitly in this study.
1.2.2 Synthesis of $\alpha$-MoC$_{(1-x)}$ in Syngas

For the preparation of $\alpha$-MoC$_{(1-x)}$, 0.4 g of Mg(MoO$_4$) or Zn(MoO$_4$) was placed in a 7 mL porcelain combustion boats inside of a 1 inch diameter quartz tube. The quartz tube was then heated using a 14 inch single zone tube furnace in a 1:4 molar mixture of CO-H$_2$ at a total volumetric flow rate of 200 mL/min. The reactor temperature was ramped from ambient temperature to 700 °C at a rate of $\sim$40 °C/min.

In the case of Mg(MoO$_4$), the synthesis temperature of 700 °C was held for 2.0 hours under continuous flow of a 1:4 molar mixture of CO-H$_2$ at a rate of 200 mL/min, followed by a treatment in pure H$_2$ at a flow rate of 120 mL/min at 700 °C for 20 minutes. For the synthesis of $\alpha$-MoC$_{(1-x)}$ using Zn(MoO$_4$), the synthesis temperature of 700 °C in a 1:4 molar mixture of CO-H$_2$ was maintained for only 30 minutes, there was no addition H$_2$ treatment. After the heat treatment, all samples were cooled to $\sim$400 °C under syngas where the carrier was then switched to a flow of industrial grade argon. The quartz reactor tubes were then removed from the furnace and allowed to cool to ambient temperature under argon flow. Once at ambient temperature, the flow was switched to 2 mol% O$_2$ with a He balance for $\sim$1 hour. This step is intended to passivate the $\alpha$-MoC$_{(1-x)}$ surface with oxide to inhibit bulk oxidation of the material upon exposure to atmospheric partial pressures of O$_2$.

In both cases, the decomposition products, MgO and ZnO respectively, were removed by etching in 7M HCl. The products were then washed in deionized water by centrifuging followed by decanting of soluble phases. This process was repeated until a neutral pH was achieved, approximately 6 wash cycles, and the samples were then dried at $\sim$85 °C in air for 12-18 hrs.
1.2.3 Characterization

Materials morphology, purity, and surface area were characterized using scanning electron microscopy (SEM), powder X-ray diffraction (XRD), and Brunauer–Emmett–Teller N\textsubscript{2} adsorption (BET).

Powder X-ray diffraction analysis was performed using a Rigaku Smartlab with Bragg-Brentano focusing and Cu K\textsubscript{α} radiation (40 kV, 40 mA). The detector used was the Rigaku D/teX Ultra 250 1D silicon strip detector. Scanning Electron Microscopy was performed using a Hitachi S-5200 SEM where powder samples were disbursed onto carbon tape adhered to an aluminum sample plate. The accelerating voltage used was 2 kV. Surface areas were measured using N\textsubscript{2} adsorption via four point BET analysis, carried out in a Micrometrics 2360 Gemini Analyzer.

1.3 Results and discussion

1.3.1. Sacrificial Support Method and Non-Oxide Reaction Pathway

The sacrificial support method (SSM) has been extensively used as a generalized method for creating a variety of high surface area materials. In many cases high surface area silica is used as the sacrificial material, which is removed by post processing in either KOH or HF. In the present work, we present a modification to the SSM method where the sacrificial support is formed in situ as a decomposition product of the Mo precursor, eliminating lengthy pre-processing methods required by the SSM method. A reaction mechanism was proposed where various sheelite salts with the general formula M(MoO\textsubscript{4}) were used as Mo precursors; where M may be any
divalent metal cation (Be, Mg, Ca, Sr, Ba, Mn, Zn). These salts were selected on a basis of two criteria. The first being that the metal, M, must form a stable oxide, thus satisfying the general redox reaction described by Equation (1).

\[ M(MoO_4) + R + 3H_2 \rightarrow MO + 3MoR_{(1-x)} + 3H_2O \]  
\[ R = \text{carbon or nitrogen source} \]

Equation (1) is written in a general form intended to balance only those species directly involved in the reduction of molybdenum. R may contain other species, not being C or N, which may be balanced with H\(_2\) in stoichiometric proportions not shown. Also, the variable “x” is bound between 0 and 0.5 for \(\alpha\)-MoC as well as between 0.67 and 0.72 for \(\beta\)-MoN; see the phase diagrams for molybdenum carbide and nitride in Appendix-C.

The intended role of the oxide product is to provide resistance to solid-state mass transfer, effectively preventing the coarsening of grain boundaries. The result of which is likely to produce smaller grain sizes, smaller primary particle sizes, and greater specific surface area of molybdenum carbide and nitride.

As previously described, the reaction pathway to molybdenum carbide and nitride commonly proceeds through a tetravalent molybdenum oxide intermediate, MoO\(_2\) [6,16,18]. As it has been suggested that MoO\(_2\) is an undesired intermediate phase to high surface area molybdenum carbide and nitride, a second criterion to the proposed reaction mechanism was established. This criteria states that these M(MoO\(_4\)) salts must decompose reductively to form a tetravalent molybdate. This criteria acknowledges the fact that Mo\(^{IV}\) is the common valency between oxide, carbide, and nitride. Therefore, a tetravalent molybdate is required for the proposed reaction pathway to carbide or nitride.
that is not to proceed through MoO₂.

Based on the first criteria, Mg and Zn were selected as the most promising cations to be used in this method due to the stability of MgO and ZnO. To identify possible intermediate species, Mg(MoO₄) was partially decomposed at 500 °C in a 5 mol% flow of NH₃, N₂ balance, for ~30 minutes. The decomposition products of Mg(MoO₄) were compared to that of AHM treated under identical conditions. XRD patterns in Figure-1, for both cases, show the reduction of molybdenum, initially Mo⁶⁺, to a valence state of four.

**Figure 1.1** XRD patterns of intermediate species from the decomposition of (A) Mg(MoO₄) to MgO (+) and Mg₂(Mo₃O₈) (*), and (B) AHM to MoO₂ in a 5 mol% flow of NH₃ at 500 °C for ~30 min. All peak intensities are normalized to the (200) reflection of MgO in (A).

This result suggests that dimagnesium-trimolybdate, Mg₂(Mo₃O₈), can replace MoO₂ as the intermediate phase to carbide or nitride when starting from Mg(MoO₄). It
was also verified that Zn(MoO4) decomposes to an analogous Zn2(Mo3O8) and ZnO under identical conditions. Thus, Mg(MoO4) and Zn(MoO4) satisfy both criteria, establishing these salts as possible precursors to α-MoC(1-x) and β–MoN(1-x).

From this, an overall two-step reaction pathway was proposed and is described by Equations (2) and (3) for the case of Mg(MoO4) reacting to α-MoC(1-x) using CO as a carbon source.

$$3Mg(MoO_4) + 3H_2 \longrightarrow MgO + Mg_2(Mo_3O_8) + 3H_2O$$  \hspace{1cm} (2)

$$Mg_2(Mo_3O_8) + 3CO + 9H_2 \longrightarrow 2MgO + 3MoC_{(1-x)} + 9H_2O$$  \hspace{1cm} (3)

1.3.2 Synthesis of α-MoC(1-x) from MgMoO4

α-MoC(1-x) was prepared by the reaction of Mg(MoO4) in mixtures of CO and H2. The molar ratio of CO to H2 was held constant at 1:4 and synthesis temperatures were varied from the approximated thermodynamic minimum of 469 °C, where ΔrG°=0, to ~ 25 °C below an upper limit determined experimentally [17]. The upper limit was defined as the onset temperature when the formation of hexagonal phase molybdenum carbide, β-Mo2C, was observed. The purpose for this was to selectively exclusively produce cubic α-MoC(1-x) at a maximum rate of reaction. The upper temperature limit was found to be ~ 725 °C.

XRD was used to study the effect of synthesis time on conversion. Samples were heat treated at 700 °C from 1.0 - 2.5 hours, followed by passivation in a low concentration of O2 then post processing in HCl to etch MgO. Whole pattern fitting (WPF) using MDI JADE 2010™ analytical software was used to determine relative
ratios of α-MoC\textsubscript{(1-x)} and Mg\textsubscript{2}(Mo\textsubscript{3}O\textsubscript{8}). This data was then used to calculate total molar conversion. Conversion was also calculated through a material balance based on experimental and theoretical yield. Material balance calculations were in agreement with XRD WPF calculations within approximately ± 5%. Figure 1.2 shows XRD patterns for samples heat treated for 1.0 hr, 1.5 hr, 2.0 hr, and 2.5 hr under identical conditions. Molar conversions of Mg\textsubscript{2}(Mo\textsubscript{3}O\textsubscript{8}) were calculated to be ~ 10, 35, 60, and 65\% respectively. Results show the observed rate of reaction (3) slows significantly with increased conversion and that the rate limiting step is the decomposition of Mg\textsubscript{2}(Mo\textsubscript{3}O\textsubscript{8}), not the decomposition of Mg(MoO\textsubscript{4}).

Figure 1. 2 XRD patterns showing conversion of Mg\textsubscript{2}(Mo\textsubscript{3}O\textsubscript{8}) to α-MoC\textsubscript{(1-x)} at 700°C: (A) ~10\% conversion after 1.0 hr, (B) ~35\% after 1.5 hr, (C), ~60\% after 2.0 hr, and (D) ~65\% after 2.5 hr. In all samples MgO was etched using HCl. All peaks are normalized to the (002) reflection of Mg\textsubscript{2}(Mo\textsubscript{3}O\textsubscript{8}) in “A”, of which reflections are denoted by “x”. α-MoC\textsubscript{(1-x)} reflections denoted by (*).
An additional reaction where $\alpha$-MoC$_{1-x}$ can be used as a carbon source was investigated. Here, the reduction of Mg$_2$(Mo$_3$O$_8$) by $H_2$ provides the necessary redox potential for the direct reaction of solid species $\alpha$-MoC$_{1-x}$ and Mg$_2$(Mo$_3$O$_8$).

\[
Mg_2(Mo_3O_8) + 3MoC_{1-x} + 6H_2 \rightarrow 2MgO \\
+3MoC_{1-y} + 6H_2O ; \ x < y
\]  

(4)

Reaction (4) allows for a carbon rich phase of $\alpha$-MoC$_{1-x}$ to be converted to a molybdenum rich phase by the removal of the carbon source from the feed. An assumption was made that $\alpha$-MoC$_{1-x}$ produced from Reaction (3) serves as the sole carbon source for reaction (4) and that $x=0$. These assumptions then set a minimum intermediate molar conversion, based on Reaction (3), of Mg$_2$(Mo$_3$O$_8$) at 50 %, prior to the use of Reaction (4). At intermediate conversions of Reaction (3) less than 50 %, Mg$_2$(Mo$_3$O$_8$) will be reduced to molybdenum as the available carbon is becomes depleted. This corresponds to $x=0.5$. Once this minimum conversion was reached, the CO feed was stopped and pure H$_2$ was used to carry out the additional heat treatment, again at 700 °C.
Figure 1. 3 XRD patterns showing conversion of Mg$_2$(Mo$_3$O$_{12}$) to (A) $\alpha$-MoC$_{(1-x)}$ at 60 % conversion after 2 hr of reaction (2) at 700 °C, and (B) $\alpha$-MoC$_{(1-y)}$ at 95 % conversion after 2 hr of Reaction (2) at 700 °C followed by 10 min of reaction (3). In both samples, MgO was etched using HCl.

Figure-1.3 shows the rapid conversion reached, from an intermediate conversion 65 % to 95 % after only 10 minutes in pure H$_2$. Further evidence of this reaction can be seen by XRD as subtle shifts in the peak positions to slightly lower values of 2θ. This is an expected result for a shift from a carbon rich phase to a Mo rich phase of $\alpha$-MoC$_{(1-y)}$, indicating a decreasing lattice parameter with decreasing carbon content.
SEM image of $\alpha$-MoC$_{(1-x)}$ prepared using Mg(MoO$_4$) in a 1:4 molar flow of CO-H$_2$ at 700 °C for 2 hours followed by treatment in pure H$_2$ for 20 minutes. MgO was etched by HCl.

Additional samples were prepared under the conditions described by Reaction (4) where it was found that a total of 20 minutes were required to obtain complete conversion of Mg$_2$(Mo$_3$O$_8$) to $\alpha$-MoC$_{(1-y)}$. Sample purity was confirmed by XRD. SEM images in Figure-1.4 show this material to possess a relatively uniform and equiaxed primary particle size between approximately 15 nm and 30 nm, with agglomerates on the order of several microns. The specific surface area was measured, using four point BET analysis, to be 35 m$^2$/g. This result is consistent with an average particle size of 20 nm.

1.3.3 Synthesis of $\alpha$-MoC$_{(1-x)}$ from Zn(MoO$_4$) in Syngas

Zn(MoO$_4$) was studied as an alternative precursor to Mg(MoO$_4$). Initially, Zn(MoO$_4$) was used in an attempt to eliminate post processing in HCl by making use of the volatile decomposition of ZnO, occurring in a H$_2$ atmosphere and at temperatures
near 650°C [25]. Analogous to the synthesis of $\alpha$-MoC$_{1-x}$ using Mg(MoO$_4$), Zn(MoO$_4$)$_2$ was found to decompose to an intermediate dizinc-trimolybdate phase, Zn$_2$(Mo$_3$O$_8$). This intermediate was then treated in a 1:4 molar ratio of CO to H$_2$ at 700 °C where the observed rate of reaction was found to be much greater than in the case of Mg$_2$(Mo$_3$O$_8$). Unlike Mg$_2$(Mo$_3$O$_8$), where conversion to $\alpha$-MoC$_{1-x}$ was less than 10% after 1.0 hours, Zn$_2$(Mo$_3$O$_8$) was converted entirely to $\alpha$-MoC$_{1-x}$ in as little as 0.5 hours. Figure-1.5A shows the rapid conversion of Zn$_2$(Mo$_3$O$_8$) to $\alpha$-MoC$_{1-x}$ obtained after only 30 minutes at 700 °C.

\[ \text{Figure 1.5 XRD patterns showing (A) conversion of Zn}_2\text{(Mo}_3\text{O}_8)\text{ to } \alpha\text{-MoC}_{1-x} \text{ and ZnO at in a 1:4 molar flow of CO-H}_2 \text{ at 700 °C for 30 minutes, and (B) thermal removal of ZnO in a 1:4 molar flow of CO-H}_2 \text{ at 700 °C for 5 hours.} \]

$\alpha$-MoC$_{1-x}$ reflections are not labeled.

ZnO was successfully removed by volatilization of Zn produced by the thermal decomposition of ZnO in H$_2$, Equation (5). This process was carried out under the
synthesis conditions of a 1:4 molar ratio of CO to H₂ at 700 °C. A total of ~5 hours were required to remove ZnO below trace amounts found by XRD, Figure-1.5B. Attempts were made to accelerate the decomposition of ZnO in pure H₂ and at higher temperature; however these attempts resulted in the formation of hexagonal carbide, β-Mo₂C. It is unclear as to what role CO plays in the inhibition of this phase transition.

\[
ZnO + MoC_{(1-x)} + H₂ \rightarrow Zn(v) + MoC_{(1-x)} + H₂O
\]  

(5)

No evidence of Zn₂(Mo₃O₈) was found in either sample prepared with and without the thermal removal of ZnO described by Reaction (5). Although ZnO was successfully removed in situ, bulk sintering at these temperatures is a concern and HCl was favored for the etching of ZnO to yield higher surface area materials. SEM images shown in Figure-1.6 reveal a more nanocrystalline morphology of α-MoC_{(1-x)} than was achieved using Mg(MoO₄). Primary particle sizes were found to be approximately < 20 nm which is consistent with the surface area measured by BET, ~45 m²/g. The significant increase in surface area obtained using Zn(MoO₄) is directly attributed to the rapid rate of reaction, and low overall synthesis time, reducing the effects of sintering and grain coarsening.
Figure 1.6 SEM image of α-MoC\(_{(1-x)}\) prepared by the reaction Zn(MoO\(_4\)) in a 1:4 molar flow of CO-H\(_2\) at 700 °C for 30 minutes. ZnO was etched by HCl.

1.3.4 Synthesis of β-MoN\(_{(1-x)}\) from MgMoO\(_4\) in Forming Gas

The most effective method for synthesizing high surface area molybdenum nitride was developed by Leo Volpe by the temperature programmed reduction of MoO\(_3\) in NH\(_3\) [11]. To address the logistical difficulties associated with this method, it was attempted to eliminate TPR from the synthesis of high surface area β-MoN\(_{(1-x)}\) and simultaneously demonstrate the capability to do so using an ammonia-free synthesis. Reaction (1) was again applied using Mg(MoO\(_4\)), where R = N\(_2\). An overall pathway to β-MoN\(_{(1-x)}\) in a mixture of N\(_2\)-H\(_2\) is described by Reactions (6) and (7).

\[
3Mg(MoO_4) + 3H_2 \rightarrow MgO + Mg_2(Mo_3O_8) + 3H_2O \tag{6}
\]

\[
Mg_2(Mo_3O_8) + N_2 + 6H_2 \rightarrow 2MgO + 3MoN_{(1-x)} + 6H_2O \tag{7}
\]
Initially, the molar ratio of N₂-H₂ was chosen to be 1:4 at a synthesis temperature of 700 °C, modeled after the synthesis of α-MoC₃₋₋. Under these conditions, it was found that this reactive atmosphere was insufficient for nitride formation of for significant decomposition of Mg₂(Mo₃O₈), where Mo metal was the primary decomposition product observed, shown in Figure-1.7A. Temperatures were gradually increased, using a 1:4 molar ratio of N₂-H₂, until β-MoN₁₋₋ was observed as a reaction product. At 900 °C Mg₂(Mo₃O₈) was seen to form β-MoN₁₋₋ as a minor product with Mo metal being the dominant product, Figure-1.7B.

**Figure 1.7** XRD patterns showing (A) conversion of Mg₂(Mo₃O₈) to Mo metal in a 1:4 molar flow of N₂-H₂ at 700 °C for 30 minutes, and (B) conversion of Mg₂(Mo₃O₈) to β-MoN₁₋₋ and Mo metal under identical flow conditions at 900 °C for 1 hour, MgO was etched by HCl in the sample shown in (B). All peaks are normalized to the Mo (110) reflection in (A). Reflections of specific phases are denoted as follows: Mg₂(Mo₃O₈) “x”, MgO “^”, Mo “+”, and β-MoN₁₋₋ “*”.
Next, the concentration of N\textsubscript{2} was gradually increased, at a temperature of 900 °C, until the hexagonal phase, β-MoN\textsubscript{(1-x)}, was produced without evidence of Mo metal. This occurred when the molar ratio of N\textsubscript{2}-H\textsubscript{2} used was 7:3 and at a temperature of 900 °C for 2 hours, shown in Figure-1.8. After etching MgO in HCl, BET surface area was measured to be ~12 m\textsuperscript{2}/g, where SEM images (inset on Figure-1.8) show primary particle sizes on the order of ~50-100 nm. Lower temperatures were explored in attempts to increase surface area by reducing the effects of sintering, however slow rates of conversion and lengthy synthesis durations resulted in the production of metallic Mo. Further experimentation is needed to establish whether the use of Zn(MoO\textsubscript{4}) as a nitride precursor will allow for lower temperature, shorter synthesis, and the production of higher surface area nitride phases.
Figure 1.8 XRD patterns showing conversion of Mg$_2$Mo$_3$O$_8$ to Hexagonal $\beta$-MoN$_{(1-x)}$ in a 7:3 molar flow of N$_2$-H$_2$ at 900 °C for 2 hours. Sample was washed in HCl to remove MgO. Inset shows SEM image of $\beta$-MoN$_{(1-x)}$

1.4 Conclusion

High surface area $\alpha$-MoC$_{(1-x)}$ was synthesized in mixtures of CO and H$_2$ at 700 °C without the aid of temperature programmed reduction. Mg(MoO$_4$) and Zn(MoO$_4$) were used as Mo precursors where the resulting $\alpha$-MoC$_{(1-x)}$ possessed surface areas, measured by BET analysis, of 35 m$^2$/g and 45 m$^2$/g respectively. MoO$_2$ was successfully replaced as a reaction intermediate by the tetravalent molybdenum compounds Mg$_2$(Mo$_3$O$_8$) and Zn$_2$(Mo$_3$O$_8$), which form MgO and ZnO as partial decomposition products. An equiaxed and porous morphology was observed in the $\alpha$-MoC$_{(1-x)}$ samples prepared using this method, with primary particle sizes typically ranging from
15-30 nm. Reaction conditions were explored: including feed composition, synthesis temperature, and synthesis duration, in efforts to maximize the rate of conversion to α-MoC\(_{(1-x)}\). A high surface area hexagonal phase of β-MoN\(_{(1-x)}\) was also produced without TPR using Mg(MoO\(_4\)), although a much higher temperature was required for this synthesis (900 °C). This high temperature, compared to the carbide synthesis temperature of 700 °C, resulted in significantly less surface area in the β-MoN\(_{(1-x)}\) samples, ~12 m\(^2\)/g. The key result in the synthesis of β-MoN\(_{(1-x)}\) was the use of N\(_2\)-H\(_2\) mixtures as the reactive atmosphere. This demonstrates that high surface area molybdenum nitride phases can be prepared without TPR, and perhaps more useful, without using NH\(_3\) as a nitrogen source.
Chapter 2

Oxygen Reduction on $\alpha$-MoC$_{(1-x)}$ Supported PtMo$_z$

2.1 Introduction

Platinum and platinum composite materials have been extensively used in the field of catalysis due to the various inherent catalytic properties of platinum [24, 26-31]. More specifically, proton exchange membrane fuel cells (PEMFC’s) have exploited platinum as a catalyst for oxygen reduction reaction (ORR); a four-electron transfer reaction which platinum is able to catalyze in a single step. Efficient kinetics and a low overpotential for ORR make platinum the state-of-the-art catalyst for ORR, thus setting the performance benchmark for ORR catalyst design [32-37]. The cost of platinum, and significant performance degradation due to the electrochemical corrosion of traditional support materials, specifically carbon, gives rise to the basis of several design considerations necessary for the efficient use of platinum as an ORR catalyst. Considerations such as increasing the durability of platinum catalysts by the proposed use of durable support materials such as transition metal nitride or carbide based ceramics. Another important consideration is to maximize the mass activity of platinum. This can be accomplished by achieving highly dispersed platinum particles on the surface of the support, thus maximizing the surface to volume ratio of platinum.

In the present work, cubic phase $\alpha$-MoC$_{(1-x)}$ was used as a support due to its high electrical conductivity as well as the large region of stability of $\alpha$-MoC$_{(1-x)}$ in acidic media predicted by previous studies [38]. However, passivation oxide on the surface of $\alpha$-MoC$_{(1-x)}$ complicates traditional chemical and thermal reduction methods commonly
employed for platinum dispersion. To overcome such difficulties an *in situ* method of platinum dispersion was pursued. This approach regards the catalyst, a PtMo$_x$ composite, and catalyst support as a single multi-component system, where certain components of the catalyst species are derived directly from the support itself. In chapter 1, high surface area molybdenum carbide and nitride ceramics were prepared using a novel method which does not rely on temperature programmed reduction as the mode of achieving surface area, rather on the use Mg(MoO$_4$) and Zn(MoO$_4$) which decompose reductively in a manor found to favor the formation of high surface area products. Here, this method has been modified by using (NH$_4$)$_2$Mg(MoO$_4$)$_2$, which further reduces the time duration, as well as temperature requirement, to obtain full conversion of the ceramic precursor.

This modification, in combination with a chemical method of obtaining desirable interactions between platinum and molybdenum precursors, allows for an *in situ* method of creating a highly dispersed PtMo$_x$ composite catalyst supported on α-MoC$_{(1-x)}$. This method has, with platinum loadings as low as 7.5 wt%, resulted in catalysts with an electrochemical surface area of ~36 m$^2$/g and a platinum mass activity of 137 A/g, comparable to that of commercially available platinum supported on carbon black [39, 40]. Although these catalysts do not possess the desired improvement in durability for ORR, this work demonstrates the capability of producing highly dispersed, platinum or platinum composite catalysts, using a simple *in situ* synthesis.
2.2 Experimental

2.2.1 Synthesis of PtMo supported on α-MoC_{(1-x)}

The molybdenum precursor, (NH₄)₂Mg(MoO₄)₂, was prepared by a slight modification of a method described in Chapter 1 for preparing Mg(MoO₄). Upon the formation of molybdic acid, H₂(MoO₄), MgO (UBE Material Industries, Ltd) was added in a 2:1 molar ratio of Mo to Mg. Next, an excess of saturated NH₄(OH) solution was added during continuous heating on a hot plate. Once the reaction appeared to reach completion the product was dried in air at 85 °C. Next, a known amount of (NH₄)₂Mg(MoO₄)₂ was dissolved in deionized water and brought to a boil. An appropriate amount of H₂(PtCl₆) was dissolved in deionized water then added to the boiling solution of (NH₄)₂Mg(MoO₄)₂; the amount of H₂(PtCl₆) added was based on a desired mass loading of Pt on α-MoC_{(1-x)}. An excess of saturated (NH₄)OH solution was then added to the boiling mixture where continuous heat was applied until a white precipitate was formed. The precipitate was allowed to dry completely in air at 85°C. Once dried the precursor was finely ground using a mortar and pestle.

Approximately 0.5 g of the ground precursor was then placed in a 7 mL porcelain combustion boat then placed inside of a 1 inch diameter quartz tube. The quartz tube was then heated using a 14 inch single zone tube furnace. A 1:4 molar mixture of CO-H₂ at a total volumetric flow rate of 200 mL/min was used as the reaction atmosphere. The reactor temperature was ramped from ambient temperature to 675 °C at a rate of ~40 °C/min. After 1.5 hours at 675 °C, the reactor was cooled to 650 °C and the feed was switched to a pure CO atmosphere at a rate of 100 mL/min. After 2 hours, the reactor was cooled to room temperature, the feed was
switched to 2% O₂ with a He balance, and these conditions were maintained for ~12-18 hours in order to passivate the α-MoC_{(1-x)} catalyst surface. The powder was then removed from the furnace and was etched in 7 M HCl to remove MgO. The product was then washed in deionized water by identical procedures described in section 1.2.1. Samples were then washed, 2 additional cycles, in 200 proof ethanol then dried in vacuum (~ 30 inHg) at room temperature for ~12-18 hours.

### 2.2.2 Catalyst Characterization

As described in chapter 1.2.3, the catalysts were characterized using powder X-ray diffraction analysis, SEM imaging, and BET surface area measurements. Additional characterization was performed using X-ray photoelectron spectroscopy for surface composition analysis (XPS), transmission electron microscopy (TEM), and electrochemical measurements conducted in a three electrode half-cell using cyclic voltammetry.

Surface analyses of the catalysts by X-ray photoelectron spectroscopy (XPS) utilized a Kratos Analytical AXIS Ultra DLD Imaging System with an Al K-alpha X-ray source operating at 225 W. High-resolution C 1s, O 1s, Mo 3d and Pt 4f spectra were acquired at 20 eV pass energy for 2, 2, 5 and 10 min respectively. Data analysis and quantification were performed using Casa XPS software.

Electrochemical measurements of ORR performance were conducted in a three electrode cell with 0.1M HClO₄ as the electrolyte. A rotating disk electrode (RDE) was used as the working electrode and a real hydrogen electrode (RHE) as the reference electrode. Forming gas, consisting of 6% H₂, was used at the reference electrode for
which a correction of +39 mV to all experimentally collected data was applied. A Pine Instrument Company rotator was used to collect ORR data at 100, 225, 400, 625, and 900 RPM at a scan rate of 5 mV/s and 100 mV/s in both O₂ and N₂ saturated electrolyte.

TEM images were acquired using a JEOL 2010 instrument with an accelerating voltage of 200kV. Data analysis was performed using GATAN Digital Micrograph software where TEM images were digitally converted into spot diffraction patterns using the built-in script files “diffractogram3.s”. These diffraction patterns were then used to measure crystallite d-spacing values by utilizing the built-in script file “peak4.s”.

2.3 Results and Discussion

2.3.1 Synthesis of α-MoC₁₋ₓ from (NH₄)₂Mg(MoO₄)₂ in Syngas

As described in Chapter 1, Mg(MoO₄) and Zn(MoO₄) have been shown to be useful precursors in the synthesis of α-MoC₁₋ₓ and β-MoN₁₋ₓ phases in mixtures of CO-H₂ and N₂-H₂ respectively. The primary advantage being the ability of these precursors to decompose to high surface area (30-45 m²/g) α-MoC₁₋ₓ without the necessity of TPR as the primary means of producing surface area. Here, the co-crystallized product of Mg(MoO₄) and (NH₄)₂(MoO₄), (NH₄)₂Mg(MoO₄)₂, has been found to decompose to α-MoC₁₋ₓ and β-MoN₁₋ₓ phases more rapidly than Mg(MoO₄), described by the following redox reactions:

\[(NH₄)₂Mg(MoO₄)₂ + CO + 8H₂ \rightarrow MgO + 2MoC₁₋ₓ + 8H₂O \quad (8)\]

\[(NH₄)₂Mg(MoO₄)₂ + N₂ + 7H₂ \rightarrow MgO + 2MoN₁₋ₓ + 7H₂O \quad (9)\]
Equations (8) and (9) are written in a form intended to balance only those species directly involved in the reduction of molybdenum. The N species on the reactant side may be balanced with H₂ in stoichiometric proportions not shown.

XRD patterns in Figure-2.1 show the reaction products described by Reactions (8) and (9). The rate of α-MoC₁₋ₓ production was found to be approximately twice that which was observed when pure Mg(MoO₄) was used, while at a temperature lower by 25 °C. This rapid rate of α-MoC₁₋ₓ production is considered an integral factor in the in situ platinum dispersion method described in section 2.3.2. More notably, β-Mo₂N was prepared at 750 °C, a temperature 150 °C lower than the minimum nitriding temperature attainable using pure Mg(MoO₄).

**Figure 2.1** XRD patterns showing the reaction products of (NH₄)₂Mg(MoO₄)₂ decomposed in (A) a 1:4 molar ratio of CO-H₂ at 675 °C for ~1.0 hours and (B) a 4:1 molar ratio of N₂-H₂ at 750 °C for ~ 1.5 hours. All peaks are normalized to the α-MoC₁₋ₓ (111) reflection in (A). Reflections of specific phases are denoted as follows: β-MoN₁₋ₓ “+”, α-MoC₁₋ₓ “*”. The sample in (A) was not etched by HCl.
SEM images in Figure-2.2 shows a similar morphology as the materials obtained by the method in Chapter 1, with average particle sizes on the order of ~30 nm. The surface area of \( \alpha\text{-MoC}_{(1-x)} \) prepared by this method was measured by BET analysis to be ~32 m\(^2\)/g. This result is consistent with the observed particle size.

\[ \text{Figure 2.2} \text{ SEM image of } \alpha\text{-MoC}_{(1-x)} \text{ prepared the reaction } (\text{NH}_4)_2\text{Mg(MoO}_4)_2 \text{ in a 1:4 molar flow of CO-H}_2 \text{ at 675 °C for 1.5 hours. MgO was etched by HCl.} \]

### 2.3.2 In Situ Synthesis of PtMo\(_2\)/\( \alpha\)-MoC\(_{(1-x)}\)

For the in situ synthesis of PtMo\(_2\)/\( \alpha\)-MoC\(_{(1-x)}\), H\(_2\)(PtCl\(_6\)) and (NH\(_4\))\(_2\)Mg(MoO\(_4\))\(_2\) were found to form an amorphous white solid when an aqueous solution of the two compounds were precipitated using an excess of NH\(_4\)(OH). This amorphous compound is likely a co-precipitated product of (NH\(_4\))\(_2\)Mg(MoO\(_4\))\(_2\) and (NH\(_4\))\(_2\)(PtCl\(_6\)), although the exact nature of this compound remains undetermined. When heat treated under the carbidizing conditions described previously, this amorphous compound was found to decompose to a platinum containing \( \alpha\)-MoC\(_{(1-x)}\) composite material. There was no metallic Pt or PtMo\(_2\) phases observed in XRD, shown in Figure-2.3. The theoretical platinum loading of 8 wt% was consistent with X-ray fluorescence measurements.
(XRF) showing an actual loading of ~7.5 wt% Pt. These results suggest the presence of highly dispersed PtMoₓ phases.

![XRD patterns showing reaction products](image)

**Figure 2.3** XRD patterns showing the reaction products of (A) the precipitated product of (NH₄)₂Mg(MoO₄)₂ and Mg(MoO₄) in an excess of NH₄(OH) and (B) (NH₄)₂Mg(MoO₄)₂ and Mg(MoO₄) crystallized from solution without precipitation in NH₄(OH). *MgO in the catalyst shown in (A) was not etched by HCl*

Cyclic voltammetry in deaerated 0.1M HClO₄, however, showed no evidence of platinum oxidation/reduction, H₂ underpotential deposition (UPD), or H₂ adsorption/stripping (HAD) peaks suggesting the absence of catalytically active Pt surface species. RDE experiments in O₂ saturated 0.1M HClO₄ revealed no cathodic activity and confirmed this material to be catalytically inert for ORR.

2.3.3 Catalyst activation by CO Surface Treatment

Since the as produced catalyst was found to be inactive for ORR, an activation
procedure was developed involving a surface treatment in pure CO directly following the thermal synthesis of the composite material in syngas (1:4 ratio of CO-H₂). The use of CO as an adsorbate which can induce the segregation of certain species within an alloy have been reported, typically applied to platinum by electrochemical adsorption of CO in saturated electrolyte [41]. Although electrochemical adsorption of CO was attempted to activate Pt phases within these materials, this was only found to have limited effect. A thermal method was attempted in which samples were cooled from the synthesis temperature of 675 °C to a slightly lower temperature, ranging from 450 °C to 650 °C, where the CO surface treatment would be administered. Once the new target temperature was reached the feed was switched to a pure CO atmosphere. Samples were then treated for an additional 2 hours under these conditions. XRD patterns for the catalysts prepared after the surface treatment, Figure-2.4, show no evidence of Pt or PtMo₂ phases found in the region between 36 ° - 40 ° in two-theta, the region where the (111) reflections of these species would be observed. A subtle decrease in the peak width at half maximum for the (111) reflection of α-MoC₁₋ₓ was found with increasing surface treatment temperature, being most pronounced for samples treated at 650 °C. This result is attributed grain coarsening due to high temperature sintering of the α-MoC₁₋ₓ domains. Crystallite domain size (XS) was calculated using whole pattern refinement in MDI JADE analytical software, where the domains were calculated to be approximately 1.5 nm larger for the sample treated in CO at 650 °C compared to the sample treated at 450 °C.
Figure 2.4 XRD patterns showing 8 wt% Pt/α-MoC_{(1-x)} prepared from the precipitate formed by the reaction of H_2(PtCl_6) and (NH_4)_2Mg(MoO_4)_2 in NH_4(OH). Samples were treated in a 1:4 molar ratio of CO-H_2 at 675 °C for 1 hour followed by a surface treatment in pure CO for 2 hours at (A) 650 °C, XS = ~6.8 nm and (B) 450 °C, XS = ~5.3 nm.

2.3.4 Electrochemical Characterization

Following the CO surface treatment, these materials were found to possess characteristic Pt features in cyclic voltammetry, including: H_2 UPD, H_2 adsorption, and H_2 stripping when cycled in N_2 saturated perchloric acid, Figure-3. Using the H_2 adsorption peak from CV data, the electrochemical surface area was calculated from the following equation:

\[
ECSA = \frac{Q_{p_2}}{210 \frac{\mu C}{cm^2_{Pt}} \times L}
\]
Here, $Q_{pt}$ is the charge density calculated by the integration of the HAD peak (C/cm$^2$), 210 is the charge required to reduce a monolayer of protons on the electrode, and $L$ is the catalyst loading on the electrode (g$_{pt}$/cm$^2$).

![Graph](image_url)

**Figure 2.5** Cyclic voltammogram at 100 mV/s of 8 wt% Pt/α-MoC$_{(1-x)}$ in deaerated 0.1M HClO$_4$ after CO surface treatment at 650 °C for 2 hours.

From this, it was found that samples treated in CO at 650 °C had an ECSA of ~36 m$^2$/g$_{pt}$, indicating significant development of catalytic surface area as a direct result of the surface treatment in CO. ORR activity was measured using RDE experiments in a half cell configuration with O$_2$ saturated 0.1M HClO$_4$ at 100, 225, 400, 625, and 900 RPM at a scan rate of 5 mV/s (Figure-2.4). The half wave potential, $E_{1/2}$, was calculated as the potential corresponding to 50 % of the diffusion limited current, found to be 0.78 V vs RHE. The corresponding onset potential was found to be 1.01 V.
vs RHE, an approximate overpotential of 50-100 mV for ORR when compared to values typically reported for that of platinum supported on carbon black [42-45].

Figure 2.6 RDE measurements at 5 mV/s in O₂ saturated 0.1M HClO₄ for Pt/α-MoC₁₋ₓ following CO surface treatment at 650 °C for 2 hours.

The Levich equation was used to estimate the number of electrons in the reaction transfer mechanism, ~3.8 e⁻, calculated from the mass transfer limited current density, jₐ:

\[ n = \frac{j_{Lev}^{(1/6)}}{0.62FD^{(2/3)}\omega^{(1/2)}C_{O₂}} \]  

(11)

where \( j_{Lev} \) is the limited current density (A/cm²), \( \nu \) is the kinematic viscosity of the electrolyte solution (St), \( F \) is the Faraday constant (C/mol), \( D \) is the diffusion coefficient for O₂ in the electrolyte (cm²/s) \( \omega \) is the angular frequency of the electrode (rad/s), and \( C \) is the concentration of O₂ in the electrolyte (mol/cm³). Additionally, the platinum mass
activity, $i_m$, was calculated from RDE data using the following equation corrected for the mass transfer limited current density:

$$i_m = \frac{j_L \times j}{(j_L - j) \times L}$$  \hspace{1cm} (12)$$

The result is shown in Figure-2.6 for data collected at 900 RPM, were the mass activity evaluated at 0.9 V vs RHE was found to be $\sim 137 \text{ A/g}_{pt}$. Again, this result is consistent with values of mass activity for Pt/C$_{\text{black}}$ commonly reported [39-40].

![Figure 2.7](image.png)

Figure 2.7 Platinum mass activity calculated from RDE data at 900 RPM and a scan rate of 5 mV/s in O$_2$ saturated 0.1M HClO$_4$ for Pt/$\alpha$-MoC$_{(1-x)}$ following CO surface treatment at 650 °C for 2 hours.

2.3.5 XPS Analysis

Although bulk composition of the catalyst was seen to be unaffected by the CO surface treatment, substantial development in catalytic activity and surface area confirms either morphological or chemical changes in the surface environment of the $\alpha$-MoC$_{(1-x)}$.
supported PtMo<sub>2</sub> composite phases, however subtle these changes may be. To investigate the effect of surface treatment temperature, four catalysts were prepared and characterized using XPS surface analysis where the surface treatment temperatures were incremented as follows: 450 °C, 550 °C, 600 °C, and 650 °C. All samples were treated for the same duration, 2 hours, in pure CO.

![Figure 2.8](image_url)

**Figure 2.8** XPS spectra showing the binding energies of the Pt 4f orbital for (A) 8 wt% Pt/α-MoC<sub>(1-x)</sub> CO treated at 650 °C and (B) Pt<sub>2</sub>Mo, and for the C 1s orbital for (C) 8 wt% Pt/α-MoC<sub>(1-x)</sub> CO treated at 450 °C, and (D) 8 wt% Pt/α-MoC<sub>(1-x)</sub> CO treated at 650 °C

Platinum 4f binding energies were compared to a Pt<sub>2</sub>Mo reference prepared by the high temperature reduction of MoO<sub>2</sub> and H<sub>2</sub>(PtCl<sub>6</sub>), shown in Figure-2.8A and 2.8B respectively. The platinum environment for the 8 wt% Pt/α-MoC<sub>(1-x)</sub> catalysts CO treated
at temperatures from 450 °C to 650 °C were found to be similar to the Pt environment of the Pt₂Mo reference, with a dominant binding energy of 71.8 eV. The absence of a Pt-Pt binding energy, typically found near 71.2 eV for bulk Pt materials, suggest the presence of PtMo₂ intermetallic and solid solution phases by direct comparison of the Pt₂Mo reference. The dominant Pt 4f binding energy and corresponding distributions were found to remain relatively constant with increased CO treatment temperature. However, it is possible that the only observed Pt 4f binding energy, 71.8 eV, is a result of platinum oxide, Pt²⁺, where a monolayer of platinum oxide is responsible for the observed binding energy. This would suggest that the similarity in the Pt 4f binding energies of the 8 wt% Pt/α-MoC₁₋ₓ catalyst and the Pt₂Mo reference is coincidental and not evidence that the two materials are of similar or identical composition [46].

Analysis of the C 1s spectra, Figure-2.8C and 2.8D, revealed a trend correlating the C-Mo ratio as a function of increasing surface treatment temperature. Figure-2.9 plots the ratio of MoC to Mo₂C calculated from the C 1s spectra, deconvoluted into the XPS spectra for MoC, Mo₂C, and C-C, as a function of surface treatment temperature.
It was found that increasing the CO surface treatment temperature results in a shift to a more carbon rich phase of $\alpha$-MoC$_{(1-x)}$ on the catalyst surface. An initial ratio of MoC:Mo$_2$C of 1:1 was significantly increased to $\sim$ 3.5:1 following the CO treatment at 650 °C. Although this result may be expected for an additional heat treatment of molybdenum carbide in a carbonaceous atmosphere, it is unclear if this result has any significance in the dramatic development of surface activity following the CO treatment.

### 2.3.6 TEM Analysis

TEM analysis, shown in Figure-2.10, reveals crystallite domains for $\alpha$-MoC$_{(1-x)}$, as well as various platinum phases of various domain size, on the approximate order of 5-10 nm. The observed polycrystalline particle structure is consistent with XRD observations of particle domain size. To confirm the existence of specific PtMo$_x$ phases,
lattice fringes were indexed using spot diffraction patterns created by Fourier Form Transform using GATAN Digital Micrograph software. Lattice d-spacings were indexed in the region of 2.22 Å to 2.35 Å due to the increased resolution between (111) reflections of α-Pt phases, the (210) reflection of cP α-PtMo$_x$ phases, (111) reflections of the cF α-PtMo$_x$, and the (111) reflection of the tetragonal PtMo$_z$ phase found in this region. Additionally, this is the region in which the 100% lines of these phases, again typically the (111) reflections, would be observed in XRD.

Figure 2.10 TEM images and corresponding histograms showing the distribution of Pt and PtMo$_x$ phases for (A) 8 wt% Pt/α-MoC$_{(1-x)}$ prior to a CO surface treatment 650 °C for 2 hours and (B) 8 wt% Pt/α-MoC$_{(1-x)}$ after a CO surface treatment at 650 °C for 2 hours.
The results show that prior to the CO surface treatment there was a broad distribution of Pt and/or PtMo\textsubscript{z} phases observed, with a majority concentrated in the region of 2.26 Å and 2.31 Å. Identification of specific phases was not possible due to a large overlap in the d-spacing of various Pt and PtMo\textsubscript{z} phases in this region, a result of the isostructural nature of these materials. Following the CO surface treatment, the distribution of PtMo\textsubscript{z} phases was found to be spread more broadly throughout the entire region. Although there is no clear evidence of a shift from one phase in particular to another, it is clear that the CO surface treatment is inducing a redistribution of the PtMo\textsubscript{z} phases. It is hypothesized that this redistribution results in the exposure of certain Pt or PtMo\textsubscript{z} facets on the surface of the material. This result is consistent with the development of catalytic activity confirmed by CV measurements, where catalytic activity is strictly a surface phenomenon.

Evidence of a ternary Pt-Mo-C phase can also be found in the region of 2.33 Å, corresponding to a lattice parameter too large to be associated with any cubic Pt or PtMo\textsubscript{z} compound published in various crystal structure databases, as shown in Figure-2.10B. The preparation of this particular ternary phase is consistent with the direct high temperature reaction of the constituent species [47]. This phase was found in slightly higher concentrations following the CO surface treatment, yet it is unclear if this phase contributes to the developed catalytic activity resulting from the surface treatment.

The most significant observation found in the materials following the CO surface treatment is the formation of a phase with the corresponding d-spacing of 2.35 Å. This phase is attributed to the (103) reflection of hexagonal β-MoC\textsubscript{(1-x)}, a transition within the
molybdenum carbide species which may be related to the segregation of carbide and PtMo$_z$ phases. This determination is supported by XRD analysis which reveals no bulk shift from cubic to hexagonal $\beta$-MoC$_{(1-x)}$, which when compared to TEM analysis suggests an extent of phase transition within the carbide phase on the same order as the transitions within the PtMo$_z$ phases.

### 2.4 Conclusion

An in situ method of dispersing PtMo$_z$ on $\alpha$-MoC$_{(1-x)}$ was successfully developed which involves the integration of Pt and Mo precursors, allowing for the simultaneous synthesis of catalyst and catalyst support species without significant sintering and agglomeration of the Pt phases. A CO surface treatment was successfully used to tune the surface properties/composition of the material transforming it from an inert to an active catalyst for ORR. The development of ECSA following the surface treatment, $\sim 36$ m$^2$/g$_{pt}$, and Pt mass activity of $\sim 137$ A/g$_{pt}$, demonstrates the success of this method in creating an active catalyst for ORR. The lack of crystalline PtMo$_z$ phases observed in XRD as well as TEM analysis suggests a particles size of the PtMo$_z$ phases estimated to be on the order of $\sim 5$ nm, further demonstrating the success of the method for dispersing PtMo$_z$ nano-particles on the surface of the the $\alpha$-MoC$_{(1-x)}$ support. However, kinetic measurements for ORR, $E_{1/2}$ of $\sim 0.78$ V vs. RHE with an onset potential of $\sim 1.01$ V vs. RHE, show this catalyst suffers from an overpotential for ORR approximately 50-100 mV greater than that of P/C$_{black}$. Additionally, preliminary durability studies (see Appendix-B) suggest this catalyst does not possess any improvement in durability compared to P/C$_{black}$. Although catalyst degradation is observed, the mode of degradation
remains unidentified (dissolution of the $\alpha$-MoC$_{(1-x)}$ support, dissolution of PtMo$_z$, or a combination of the two processes).
**Thesis Conclusion**

Pertaining to the objectives identified within the scope of this project, a method for preparing high surface area $\alpha$-MoC$_{(1-x)}$, and $\beta$-MoN$_{(1-x)}$, without the requirement of temperature programmed reduction (TPR) has been achieved. Mg(MoO$_4$) and Zn(MoO$_4$) have been demonstrated to decompose, through a preferred non-oxide (MoO$_2$) reaction pathway, to high surface area $\alpha$-MoC$_{(1-x)}$ (35 m$^2$/g and 45 m$^2$/g respectively) using syngas as a carbon source. The capability of producing $\beta$-MoN$_{(1-x)}$ without TPR and in an NH$_3$ free synthesis (using forming gas as a N$_2$ source) has also been demonstrated.

This result led to the development of a more effective precursor, (NH$_4$)$_2$Mg(MoO$_4$)$_2$, which was found to decompose to $\alpha$-MoC$_{(1-x)}$ in syngas at a rate two times greater, while at lower temperature, than Mg(MoO$_4$). $\beta$-MoN$_{(1-x)}$ was also found to form more readily when this ammonium molybdate derived precursor was used.

A facile method of producing highly dispersed Pt phases, active for oxygen reduction reaction, on $\alpha$-MoC$_{(1-x)}$ has also been accomplished. The integration of Pt and Mo precursors using a chemical precipitation method made possible the simultaneous synthesis of $\alpha$-MoC$_{(1-x)}$, the support species, and PtMo$_z$, the catalyst species. The simultaneous synthesis of the catalyst and support address the logistical difficulties of dispersing Pt on $\alpha$-MoC$_{(1-x)}$ without the exposure of $\alpha$-MoC$_{(1-x)}$ to air.

Although the PtMo$_z$ composite catalyst supported on $\alpha$-MoC$_{(1-x)}$ was found to be active for ORR, as characterized by cyclic voltammetry, the durability of this catalyst does not appear to offer any improvements to the limited durability of Pt/C$_{black}$.
References


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47. Lawson, A. C., Superconductivity of the f.c.c. transition metals, and of their alloys and f.c.c. carbides. *Journal of the Less Common Metals* 1971, 23 (1), 103-106.


Appendix A

Appendix A. 1 XRD diffraction pattern for (NH$_4$)$_2$Mg(MoO$_4$)$_2$ obtained by the co-precipitation of (NH$_4$)$_2$(MoO$_4$) with Mg(MoO$_4$) in stoichiometric proportions. See Appendix A.2 for phase reflection data.
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**Appendix A.** 2 XRD diffraction data for (NH₄)₂Mg(MoO₄)₂. Phase PDF # [97-002-3001] taken from ICSD database.
Appendix B

Appendix B. 1 CV of 8 wt% Pt/α-MoC\(_{(1-x)}\) in N\(_2\) saturated HClO\(_4\) at 100 mV/s prior to durability study (Black, ECSA ~ 36 m\(^2\)/g) and after a durability study (Red, ECSA is below instrument resolution). Durability study was conducted in O\(_2\) saturated HClO\(_4\) using an RDE setup rotating at 900 RPM with a sweep rate of 100 mV/sec from 1.3 – 0.6 V vs. RHE. A total of 5000 cycles were used in the study.

Appendix B. 2 CV of 8 wt% Pt/α-MoC\(_{(1-x)}\) in O\(_2\) saturated HClO\(_4\) at 5 mV/s at various rotation speeds after the durability study, described by Appendix B.1.
Appendix B. 3 Comparison of ORR activity before and after the durability study described by Appendix B.1.
Appendix C.1 Mo-N phase [48].
Appendix C.2 Mo-C phase diagram. [49].