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Multiple Phases of Molybdenum Carbide as Electrocatalysts for the Hydrogen Evolution Reaction**

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Abstract: *Molybdenum carbide has been proposed as a possible alternative to platinum for catalyzing the hydrogen evolution reaction (HER). Previous studies were limited to only one phase, β-Mo_2C with an Fe_2N structure. Here, four phases of Mo-C were synthesized and investigated for their electrocatalytic activity and stability for HER in acidic solution. All four phases were synthesized from a unique amine–metal oxide composite material including γ-MoC with a WC type structure which was stabilized for the first time as a phase pure nanomaterial. X-ray photoelectron spectroscopy (XPS) and valence band studies were also used for the first time on γ-MoC. γ-MoC exhibits the second highest HER activity among all four phases of molybdenum carbide, and is exceedingly stable in acidic solution.*

Hydrogen, as a clean renewable energy source, has become one of the promising alternatives to carbon-based fuels. Splitting water to produce hydrogen has attracted a great deal of attention recently.[1] To attain potent water splitting for a wide range of applications, both active and economical catalysts for the hydrogen evolution reaction are required.[1a,2] Although a few precious metals such as Pt, have exhibited high catalytic activity for HER, their excessive price and lack of abundance limit their application industrially. A possible replacement for Pt catalysts are molybdenum-based materials, such as molybdenum disulfide (MoS_2),[3] molybdenum boride (MoB),[4] molybdenum diselenide ($MoSe_2$),[5] and molybdenum carbide (Mo_2C),[4,6] which have shown promise for HER in both acidic and basic media. Molybdenum is much more abundant than precious metals and the United States is the largest producer of molybdenum.[7] Molybdenum carbide is one of the most investigated transition metal carbide systems because of its low cost, high melting point, good conductivity, and catalytic activity.[8] Recently, Liu et al. demonstrated porous molybdenum carbide nanowires that had increased catalytic activity toward HER compared with commercial Mo_2C.[6b] However, β-Mo_2C (Fe_2N structure) is the only phase of molybdenum carbide which has been studied for HER according to our knowledge.

Herein, we report the synthesis and catalytic testing of four phases of molybdenum carbide (α-MoC_{1-x}, β-Mo_2C, η-MoC, and γ-MoC) for HER, which is the first comparative electrochemical testing for multiple phases of molybdenum carbide. It is worth noting that β-Mo_2C, η-MoC, and γ-MoC have very similar hexagonal crystal structures but their stacking sequences are different. β-Mo_2C has an ABAB packing of the metal planes, while η-MoC and γ-MoC exhibit ABCABC and AAAA stacking sequence respectively. The cubic α-MoC_{1-x} is isostructural with NaCl which has an ABCABC stacking sequence. All the crystal information is listed in Table S1 in the Supporting Information. All four phases were synthesized from a unique amine–metal oxide composite material.[9] The synthesis details are listed in the Supporting Information. Briefly, the amine–metal oxide hybrid was precipitated from an aqueous solution of ammonium molybdate and 4-Cl-*o*-phenylenediamine (4Cl-oPDA) by adjusting the pH below 3. The hybrid was heated at 750 °C for 12 h to form α-MoC_{1-x} (Figure 1 a), 850 °C for 12 h to form β-Mo_2C (Figure 1 d), and 850 °C for 24 h to form γ-MoC (Figure 1 c), respectively. *p*-Phenylenediamine (pPDA) was used as the precursor to produce η-MoC (Figure 1 b) at 1050 °C with zero dwell time. $FeCl_3$ was mixed with the amine–metal oxide to help stabilize the γ-MoC upon reduction. η-MoC formation required NiI_2 in solution along with rapid ramping (24 °C min^{-1}) and cooling rates (50 °C min^{-1}) during the reduction process. X-ray diffraction patterns

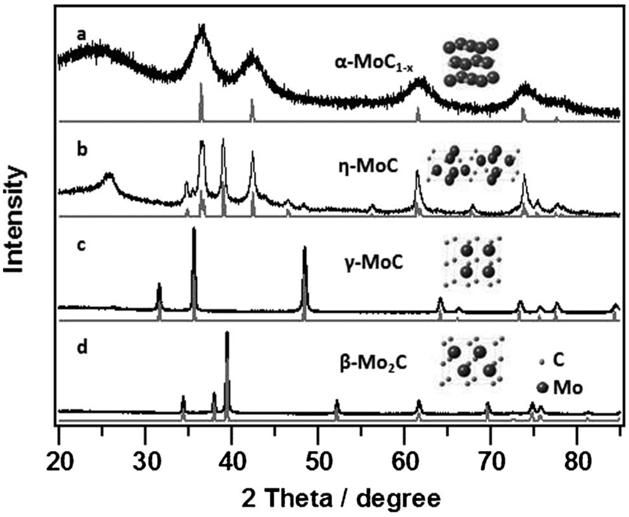

Figure 1. X-ray diffraction (XRD) patterns of a) α-MoC_{1-x} (JCPDS 01-089-2868), b) η-MoC (JCPDS 01-089-4305), c) γ-MoC (JCPDS 00-045-1015), and d) β-Mo_2C (JCPDS 00-011-0608). The insets show the corresponding crystal structures.

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(XRD) (Figure S1) shown both metallic iron and nickel impurities in the annealed samples. Therefore, to achieve clean phases of γ-MoC, excess hydrochloric acid was applied to dissolve all of the Ni and Fe compounds. The corresponding XRD patterns of clean final products are shown in Figure 1. Previous works have demonstrated that η-MoC could be formed at 1500 °C with a small amount of NiI_2 added to the solution with the other precursors.[9b] The latest data indicated that the formation temperature of η-MoC can be reduced by 450 °C to 1050 °C when more NiI_2 was added to the solution, which is the lowest temperature for η-MoC synthesis known thus far.[10] Both energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) data suggest that there are about 2 % Fe in γ-MoC and 5 % Ni in η-MoC samples after being washed by HCl (Figures S2–S4). Nowotny et al. concluded that 2 % Fe doping is necessary to stabilize γ-MoC phase in 1976, which is consistent with our results.[11] Outside of this article, there are very few references for γ-MoC and it has never been reported as a pure nanomaterial to date.[12]

Figure 2 a shows the electrocatalytic activity for all four phases of molybdenum carbide nanomaterials using a standard electrochemical configuration in 0.1 M $HClO_4$. The working electrode was prepared by depositing samples with a mass loading of 0.28 mg cm^{-2} onto a glassy carbon electrode (0.0707 cm^2). The HER activity for samples of Pt/carbon (10 wt %) and multiwall carbon nanotubes (MWCNTs) are also listed in Figure 2 a for comparison. Pt exhibits extremely high catalytic activity for HER, while there is no convincing HER activity observed from MWCNTs. Among all molybdenum carbides, β-Mo_2C exhibits very high HER activity only second to Pt, which confirmed the previous results.[4a,6b] γ-MoC shows similar activity to β-Mo_2C including a much higher current density and lower overpotential than α-MoC_{1-x} and η-MoC.

Figure 2 b shows Tafel plots [overpotential vs log (current density)] for both β-Mo_2C and γ-MoC. The β-Mo_2C electrode exhibits a Tafel slope of 120 mV/decade and an exchange current of 17.29 μA cm^{-2} ($\eta = 180$–220 mV). Comparatively, the Tafel analysis of γ-MoC shows an exchange current of 3.2 μA cm^{-2} and Tafel slope of 121.6 mV per decade ($\eta = 270$–310 mV). The Tafel slopes of ca. 120 mV per decade for β-Mo_2C and γ-MoC suggests their hydrogen evolution occurs through various reaction pathways.[6b,13]

To investigate the electronic structures of all four phases of molybdenum carbide, Mo 3d core level XPS spectra were collected (Figure 3). Mo 3d spectra are split into $3d_{5/2}$ and $3d_{3/2}$ peaks because of the spin–orbital coupling feature. XPS analyses for β-Mo_2C and MoS_2 have been widely studied, and are the references for determining the oxidation states of each phase of molybdenum carbide.[3c,4a,14] The peak fitting suggests that there are four oxidation states for Mo (Mo^0, Mo^{3+}, Mo^{4+}, and Mo^{6+}) on the surface of the carbides. Due to both Mo–Mo and Mo–C bonds in molybdenum carbides, the existence of a dominant Mo^0 peak along with small peaks of low oxidation states of Mo (Mo^{3+}) can be explained.[15] Previous studies indicated that the surface of molybdenum carbides can be contaminated with molybdenum oxides (MoO_2 and MoO_3) when they are exposed to the air.[4a,14b] α-MoC_{1-x}, β-Mo_2C, and γ-MoC were exposed to air for similar duration (55 to 60 days) while η-MoC was only exposed for 7 days. However, the quantitative analysis of XPS intensities for Mo^{6+} revealed the different degrees of surface contamination among the four phases. γ-MoC has the smallest amount of MoO_3 followed by β-Mo_2C, α-MoC_{1-x}, and η-MoC, which matches the order of stability from previous theoretical studies.[16] The XPS fitting data is listed in the Supporting Information (Table S2).

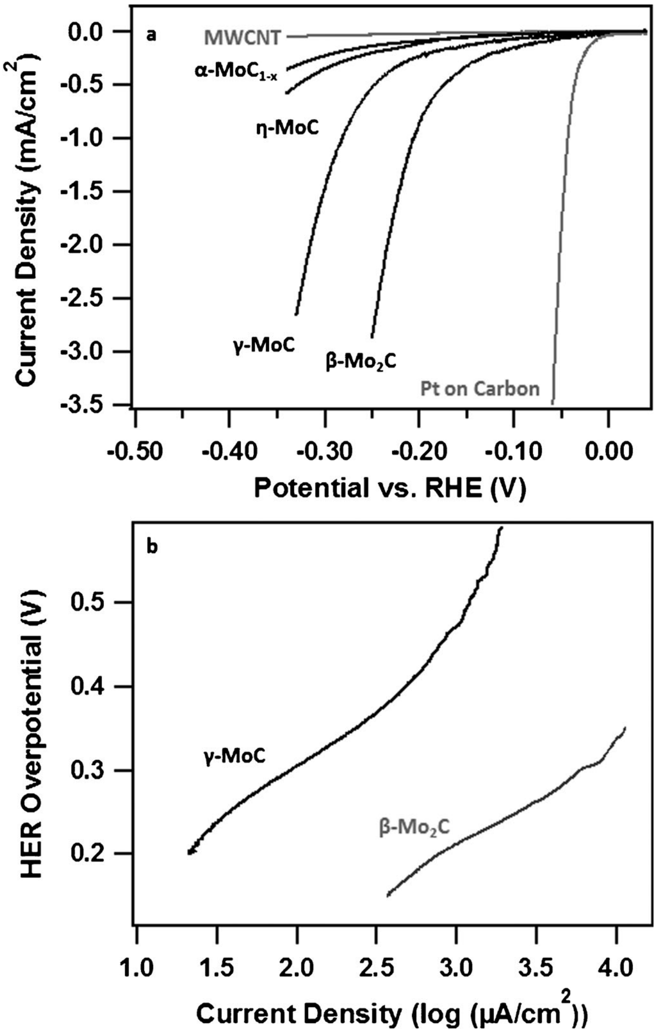

Figure 2. a) Polarization curves for four phases of molybdenum carbide, Pt on carbon support, and multiwall carbon nanotubes (MWCNTs) in 0.1 M $HClO_4$. b) The corresponding Tafel plots for γ-MoC and β-Mo_2C. The catalyst loading for all samples is 0.28 mg cm^{-2} and the scan rate is 2 mV s^{-1}.

The XPS valence bands for Pt, β-Mo_2C, and γ-MoC were also compared (Figure S5). The valence band shape of β-Mo_2C and γ-MoC are very similar to that of Pt, except β-Mo_2C has a slightly higher density around Fermi level than γ-MoC, which also makes β-Mo_2C less stable.[16a] γ-MoC is theoretically the most stable stoichiometric (1:1) phase, however most synthetic procedures will only result in the β-Mo_2C phase.[16] The observation of a more Pt-like Fermi level energy in β-Mo_2C and γ-MoC is a possible and necessary condition for high HER catalytic activity, however it is still not sufficient to completely explain the trends in activity.

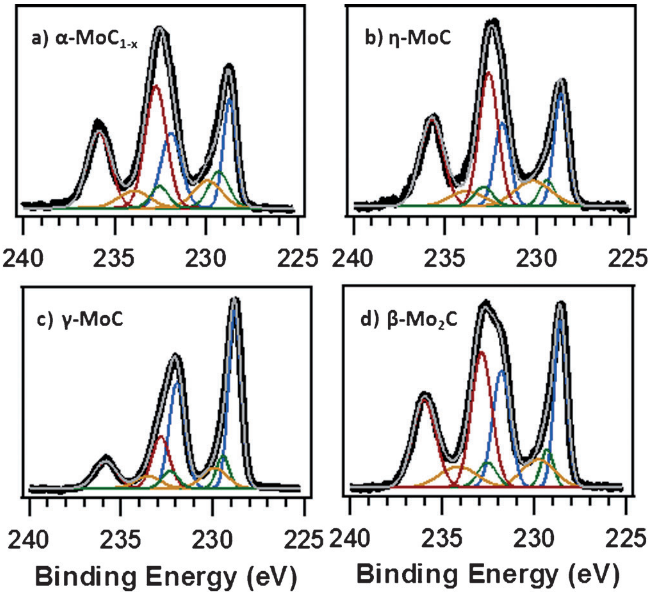

Figure 3. XPS Mo 3d spectra (without background, black) and the fitting peaks (gray) of a) α-MoC_{1-x}, b) η-MoC, c) γ-MoC, d) β-Mo_2C. Mo^0: blue, Mo^{3+}: green, Mo^{4+}: yellow, Mo^{6+}: red.

The durability of γ-MoC in acidic solution was evaluated by sweeping the γ-MoC catalyst for 1000 cycles (Figure 4a). After the 1000th cycle, the catalyst still performed as good as the initial cycle. Only a trivial current degradation was noticed in the final measurement. The long-term stability of γ-MoC catalyst was also examined by electrolysis at an anchored potential (Figure 4b, inset). The catalytic current densities fluctuated up and down due to the bubble formation at around −0.18, −0.75, and −1.95 $mA\,cm^{-2}$ over continuous 18 h at −240, −290 and −340 mV respectively. There was no significant currents degradation, thus, γ-MoC is stable under HER conditions, which supports the theoretical calculations that it is the most stable phase.[16]

Beyond the crystal and electronic structures, the morphology and size are another two possible factors that affect the catalytic activity for HER.[3e,6b] Figure 4c shows the transmission electron microscopy (TEM) images of γ-MoC particles with various particle sizes. No noticeable oxide coating on the surface of the carbide can be seen confirming the XPS results. Figure 4d shows the lattice fringes which measured 2.78 Å, consistent with the (001) plane of γ-MoC. The corresponding scanning electron microscopy (SEM) images of γ-MoC and β-Mo_2C are also listed in the Supporting Information (Figure S6). β-Mo_2C particles are nanospheres with ca. 120 nm diameter, while γ-MoC particles exhibited various morphologies and sizes. Small particles give higher surface area, which may enhance the catalytic activity for HER. Nevertheless, the size and shape control of γ-MoC particles still remains a challenge. The BET surface area of γ-MoC is $24.76 \pm 0.05\,m^2g^{-1}$, while β-$Mo_2C$ shows a BET surface area of $90.42 \pm 0.93\,m^2g^{-1}$. Small surface area could be the reason why γ-MoC shows lower activity for HER than β-Mo_2C. Future studies are underway to control the size and shape of γ-MoC and explore additional applications.

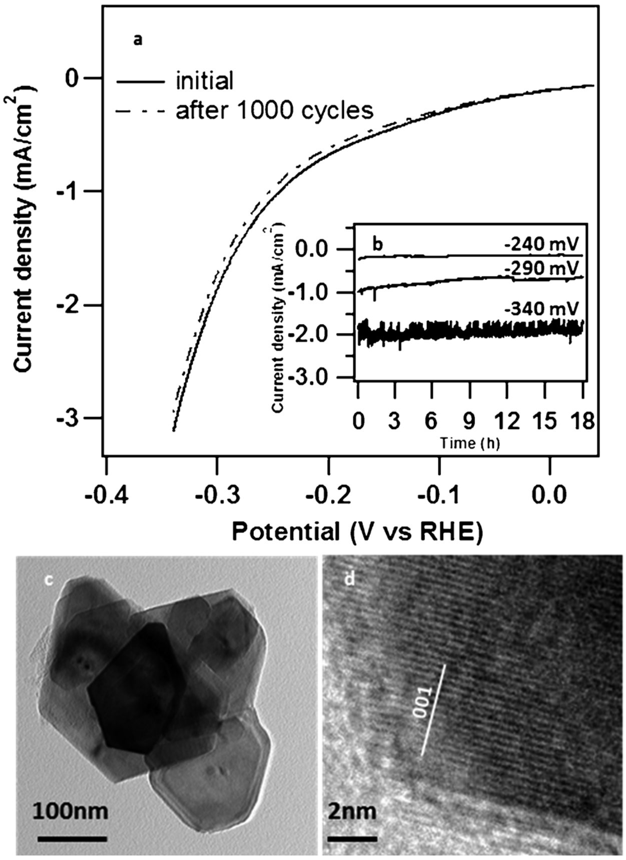

Figure 4. a) Stability of the γ-MoC with an initial polarization cure and after 1000 cycles in 0.1 M $HClO_4$ at scan rate of 50 $mV\,s^{-1}$. b) The inset shows the time-dependent catalytic current during electrolysis for γ-MoC in 0.1 M $HClO_4$ at −240 mV, at −290 mV, and at −340 mV. c) TEM image and d) HETEM image of γ-MoC.

In conclusion, four phases of molybdenum carbides have been synthesized and studied as catalysts for HER. Nanoparticles of γ-MoC have been stabilized for the first time as a clean phase and shown promise as a potential catalyst for HER. Based on both theoretical and experimental results, γ-MoC is the most stable phase among all four phases of molybdenum carbide. The size and shape control of γ-MoC particles still remains challenges, thus, γ-MoC has great potential to be an even better catalyst for HER. Additionally, the stabilization of phase pure nanoparticulate γ-MoC has opened the door for future studies and applications of molybdenum carbide.

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