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A Multi-Doped Electrocatalyst for Efficient Hydrazine Oxidation

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Dedicated to Professor Mordecai Rabinovitz on the occasion of his 85th birthday

Abstract: We report an efficient electrocatalyst for the oxidation of hydrazine, a promising fuel for fuel cells and an important analyte for health and environmental monitoring. To design this material, we emulated natural nitrogen-cycle enzymes, focusing on designing a cooperative, multi-doped active site. The catalytic oxidation occurs on Fe₂MoC nanoparticles and on edge-positioned nitrogen dopants, all well-dispersed on a hierarchically porous, graphitic carbon matrix that provides active site exposure to mass-transfer and charge flow. The new catalyst is the first carbide with HzOR activity. It operates at the most negative onset potentials reported for carbon-based HzOR catalysts at pH 14 (0.28 V vs. RHE), and has good-to-excellent activity at pH values down to 0. It shows high faradaic efficiency for oxidation to N₂ (3.6 e^{-}/N_2H_4), and is perfectly stable for at least 2000 cycles.

Electrocatalysis of hydrazine oxidation is an important challenge: hydrazine is a promising fuel for fuel cells^[1,2] and an important analyte for environmental and food monitoring.^[3] The hydrazine oxidation reaction (HzOR) is a multi-electron, multi-proton transformation. In alkaline solution, for example, it can occur according to the reaction: N₂H₄ + 4OH⁻ \rightarrow N₂ + 4H₂O + 4 e^- . Direct hydrazine fuel cells were first proposed in the 1960s,^[4] offering high theoretical electromotive force (1.56 V), zero carbon emissions, and easy fuel transportability. The recent advances in alkaline membrane technology restarted the search for more efficient and selective electrocatalysts, moving from scarce and costly elements (Pt, Pd, Au)^[5,6] to earth-abundant materials (Fe, Ni, Co).^[7–9] The latter, however, are easily covered by deactivating surface oxides. Thus, there is a strong need for active, stable, and earth-abundant electrocatalysts for the HzOR.

We now report an excellent HzOR electrocatalyst, discovered by emulating the cooperativity of enzymatic active sites. The biomimetic catalyst features multi-element catalytic sites dispersed on a mass- and charge-conducting scaffold, catalyzing the HzOR efficiently, selectively, and with high stability.

In the search for new HzOR electrocatalysts, we examined the engineering design principles employed in nature to drive redox catalysis in the nitrogen cycle. The active sites of hydrazineinvolving enzymes (e.g. hydrazine synthase and dehydrogenase, and nitrogenase) contain redox-active and earth-abundant elements such as Fe, Mo, V and Cu, and non-metals N, O and S.^[10] Importantly, several elements are intimately bound in these catalytic. In most synthetic HzOR catalysts, however, such multidoping is uncommon: most active sites possess 2–3 elements, as opposed to nature's 3–6. Moreover, even if several dopants are

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present, their separation in space prevents true cooperativity. For example, even in multi-doped particle/support HzOR catalysts,^[7] only reactants located near the base of each particle base can interact with both particle and support surfaces, unless the particles are very small.^[11,12]

In this work, we focused on emulating a key feature of nitrogen-cycle enzymes: having multiple elements doping a single catalytic site.^[13] The catalyst is composed of nanometric Fe₂MoC supported on N-doped, porous, graphitic carbon (Scheme 1). All heterodopants (Fe, Mo, N) participate in the catalysis, suggesting true cooperativity, and providing the first example of a carbide catalyst for the HzOR. The catalyst operates at low overpotentials with high faradaic efficiency, and is stable for thousands of cycles. By using carbon as a support,^[14–17] we could emulate other enzyme features such as nanometric active sites, high dispersion on a robust scaffold, and pathways for flow of reagents, products and charge to/from the catalytic sites.



Scheme 1. Designing a synthetic hydrazine oxidation electrocatalyst by emulating nitrogen-cycle enzymes, with a focus on multi-doped active sites. Left: part of the crystal structure of nitrogenase.^[18] Right: drawing of the synthetic Fe₂MoC@NC catalyst reported here, using the crystal structure of Fe₂MoC.^[19] Heterodopants common to both catalysts are nitrogen (blue), iron (orange), and molybdenum (cyan).

To design multi-doped catalytic sites, we simultaneously reduced Fe and Mo salts inside a hydrogen-bonded network of melamine and trimesic acid.^[20] Pyrolysis (800 °C / Ar) gave a composite material in which Fe₂MoC and FeO_x particles are evenly dispersed in a matrix of N-doped, porous, graphitic carbon ("Fe₂MoC@NC"). The oxides and amorphous phases were washed out by acid, leaving behind Fe₂MoC and N-doped carbon ("wash-Fe₂MoC@NC"). To compare to a metal-free catalyst, we pyrolyzed the melamine-trimesate network without Fe/Mo ("NC").

X-ray diffraction (XRD, Figure 1a) shows only graphite in NC, while the Fe₂MoC@NC composite also contains Fe₂MoC^[19] and Fe₃O₄ / Fe₂O₃.^[21] The oxide peaks disappear after washing. According to X-ray photoelectron spectroscopy (XPS; Tables S1–S4), Fe₂MoC@NC contains N (4.9 at%), O (5.5 %), Mo (1 %) and Fe (0.5 %); after washing, the relative N content rises to 7.5 at%. The deconvoluted N 1s spectrum (Figure 1d) reveals pyridinic (N_p), pyrrolic (N_{py}), graphitic (N_g), and oxidized (N_{ox}) nitrogen positions. Molybdenum exists in three oxidation states (Figure 1d,f): Mo⁸⁺ (δ = 0–3, carbide), Mo⁴⁺ and Mo⁶⁺.^[22] Iron is present as carbide (Fe⁸⁺, δ < 2) and oxide (Fe^{x+}, x = 2–3).^[23]

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High-resolution scanning electron microscopy (HRSEM) shows a macroporous, crumpled carbon covered by particle agglomerates (Figure 1g). Surface particles are removed by washing (Figure 1h), while back-scattered electrons reveal an abundance of smaller, well-dispersed nanoparticles near the surface (Figure 1i). According to high resolution transmission electron microscopy (HRTEM), the nanoparticles are 5 ± 2 nm in diameter, and are evenly distributed in a partially graphitic matrix. The particles and the matrix are identified by their interplanar distances (Figure 1j), as well as by elemental mapping of single particles in high-angle annular dark-field mode in scanning TEM mode (HAADF-STEM, Figure 1k-m). Fe and Mo are evenly distributed in the particle, at a ratio of 2:1 (Figure 1m). Nitrogen and oxygen are absent from the particles (confirming they are neither oxides nor nitrides) yet are evenly dispersed in the carbon matrix (Figure 1k). Overall, the three dopants - atomic N and nanoparticulate Fe₂MoC – are well dispersed in the material.

To understand the accessibility of catalytic sites to the flow of mass and electric charge, we studied the microstructure of the materials. The BET specific surface areas (SSAs) of Fe₂MoC@NC and wash-Fe₂MoC@NC are 230 and 223 m²/g. In contrast, the SSA of metal-free NC is only 89 m²/g. The N₂ sorption isotherms of Fe₂MoC@NC and wash-Fe₂MoC@NC (Figure 1b) are identical during initial adsorption (indicating similar micropore content) and different in the adsorption-desorption hysteresis region, testifying to different mesoporosity (Figure S1). Indeed, the mesopore volume rises from 137 to 205 mm³/g after washing (Table S5). Overall, metal doping introduces

microporosity (as metal ions oxidize the carbon) and mesoporosity (through self-templating), creating a hierarchical pore structure that exposes active sites to the flow of reagents and products.^[24-26]

The electrical wiring of the active sites to the external circuit is linked to the graphitic content of the carbon matrix. Multiple, continuous graphitic domains are seen by HRTEM (Figure 1j). Furthermore, XPS fitting of C 1s region shows that Fe₂MoC@NC contains a much higher sp²/sp³ ratio than NC (3.85 and 0.71, respectively). Raman spectroscopy confirm that the metals promote graphitization during pyrolysis (Figure 1c and S2). The disordered/graphitic peak intensity ratio (I_D/I_G) decreases from 1.30 (NC) to 1.01 (Fe₂MoC@NC), a value sufficient for excellent electrocatalysis.^[27]

The multi-doped catalysts show excellent HzOR activity, with an onset as low as 0.28 V vs. RHE for both Fe₂MoC@NC and wash-Fe₂MoC@NC (Figure 2a). This is the most negative onset potential reported so far for carbon-based HzOR catalysts at pH 14.^[17,28] This onset potential is only 300–500 mV more positive than electrocatalysts based on precious metals (Pt, Pd, Au); or on metals whose surface quickly oxidizes during HzOR (Ni, Co); or on unsupported particles (Table S6). The wash-Fe₂MoC@NC catalyst also shows excellent HzOR activity at lower pH values (Figure S3). At pH 13, an onset potential of 0.45 V vs. RHE is among the most negative values reported for non-precious, nonoxidizable, supported catalysts. At pH ~7 (phosphate buffer), the onset potential is 0.53 V vs. RHE, 140–230 mV more positive than



Figure 1. (a) Powder XRD pattern of Fe₂MoC@NC (red) and after washing (wash-Fe₂MoC@NC, blue), compared to metal-free, N-doped carbon (NC, black). (b) N₂ sorption isotherms at 77 K of the three materials. (c) Deconvoluted Raman spectrum of wash-Fe₂MoC@NC and NC. (d) Deconvoluted XPS of Fe₂MoC@NC in the regions of N 1s + Mo 3p, (e) Fe 2p, and (f) Mo 3d. Only the first peak of each multiplet is marked; 's' marks a satellite peak. (g) HRSEM of Fe₂MoC@NC, secondary electrons. (i) HRSEM, wash-Fe₂MoC@NC, back scattered electrons. (j) HRTEM of wash-Fe₂MoC@NC; interplanar distances marked for graphite and Fe₂MoC. (k) Elemental mapping of a single Fe₂MoC particle by STEM-HAADF, including (I) a combined elemental map for Fe and Mo, and (m) a line-scan across the particle.

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Figure 2. Voltammetry of electrocatalytic hydrazine oxidation. (a) Cyclic voltammetry (CV) on wash-Fe₂MoC@NC, Fe₂MoC@NC and NC catalysts (100 mM N₂H₄, 1 M KOH, scan rate 5 mV/s). The spikes occur when bubbles are released, unblocking the electrode surface. All other voltammograms are with wash-Fe₂MoC@NC: (b) Pure double-layer charging (no N₂H₄) at different scan rates, CV and total current densities at 0.216 V vs. RHE. (c) Full region CV (20 mM N₂H₄) at different scan rates, and plots of peak current density and peak potential vs. scan rate. (d) CV in different hydrazine concentrations, and peak current density vs. concentration. (e) Linear scan voltammetry (LSV) (10 mM N₂H₄, 1 M KOH) at different rotation speeds, analysed by a Koutecký-Levich plot at 0.65, 0.75 and 0.85 V vs. RHE. (f) Stability test, comparing the 1st and 2001st CVs (100 mM N₂H₄, 1 M KOH), and plotting current density at 0.5 V vs. cycle number.

the best electrocatalysts reported by Asefa *et al.*^[14,16] Finally, it is even active at pH 0 (0.5 M H₂SO₄); the onset potential of 0.76 V vs. RHE is still too positive to be useful, but nonetheless gives the first example of a HzOR electrocatalyst that works in strong acid while avoiding precious Pt, Pd or Au (Table S6).

The peak current density for HzOR was 20% higher on wash-Fe₂MoC@NC than on Fe₂MoC@NC, thanks to improved flow. Metal-free NC showed poor HzOR activity (onset potential 0.65 V vs. RHE), despite sufficient nitrogen doping, graphitization, and surface area (Table S5). A test with FeMoO₄ + Fe₃O₄ powders confirmed that oxide impurities do not contribute to HzOR activity (Figure S4). The advantage of the Fe₂MoC@NC composites over the controls suggests a powerful catalytic contribution from the carbides. To the best of our knowledge, this is the first example of carbides electrocatalyzing the HzOR

The exposure of active sites can be estimated from the catalysts' electrochemical surface areas (ECSA). The wash-Fe₂MoC@NC catalyst has the highest double-layer specific capacitance (40.5 mF/cm²), while Fe₂MoC@NC and NC have values of 17.4 and 21.5 mF/cm², respectively (Figure 2b and S5). These capacitances translate to ECSA values of 1012, 435, and 537 m²/gr, respectively.^[29] Thus, most of the micropores present in Fe₂MoC@NC (as detected by porosimetry, Figure 1b) are blocked by inorganic particles, and are exposed by washing.

To understand electrocatalysis on wash-Fe₂MoC@NC, we investigated the effects of scan rate (v), hydrazine concentration, and electrode rotation speed (ω) on the voltammetric waves. The peak current density (*j*_P) varies linearly with v^{1/2}, revealing that the oxidation peak is under complete diffusion control (Figure 2c). This eliminates the possibility for oxidation of electrode-bound species, such as the catalyst material itself. The identity of

hydrazine as the oxidized species is further corroborated by the linear dependence of peak current density on hydrazine concentration (Figure 2d). The peak potential varies linearly with log(v), proving that the oxidation process is irreversible (Figure 2c).^[30] This suggests complete oxidation to gaseous N₂, rather than to reversible intermediates. N₂ evolution is also suggested by the vigorous bubbling rising from the electrode during HzOR (Figure S7). No bubbling occurs at open circuit, suggesting that hydrazine decomposition is negligible. The faradaic efficiency of the oxidation was determined by linear sweep voltammetry on a disk electrode rotating at different rates using (Figure 2e). Koutecký-Levich analysis of the limiting currents reveals that 3.6 e⁻ are transferred (at 0.65 V vs. RHE) per N₂H₄ molecule during HzOR. This number is close to 4, meaning near-complete oxidation to N₂. At higher potentials, where the NC catalyst is active on its own, the value is very similar (3.5 e⁻ at 0.85 V vs. RHE), suggesting that the carbides contribute most of the activity. On the other hand, chemical decomposition (possibly promoted by the applied potential), could produce H_{2} ,^[8,31] the oxidation of which would lower the actual faradaic efficiency for HzOR.

The long-term stability of the catalyst was investigated by CV cycling (Figure 2f) and by chronoamperometry (Figure S6) in 100 mM hydrazine. The current drops initially, and then remains perfectly stable for 2000 cycles; the first and 2001st CVs are nearly identical (Figure 2f). Catalyst stability is crucial for practical applications.

To identify the dopants taking part in electrocatalysis, we studied the surface composition of wash-Fe₂MoC@NC by XPS, before and after the prolonged catalytic cycling. Catalysis strongly affects the nitrogen binding pattern: the $(N_p + N_{py}) / N_g$ ratio drops from 0.66 to 0.54 (Figure 3a,b). The pronounced change in edge

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nitrogen moieties (Np + Npy) testifies to their electrochemical activity.^[32] Furthermore, no new N 1s peak rises for a pyridonic group (N_p-C=O, ~399.7 eV),^[33] in contrast to N-doped carbon catalysing oxygen reduction.^[34] Both Fe and Mo are reduced by catalysis, according to XPS (Figure 3 and Table S3). For both metals, the carbide peaks are shifted to lower energies, testifying to reduction.^[22,23] For Fe, the oxide content further shifts from higher to lower oxidation states (Table S3). Similarly, the Mo⁶⁺ content drops to yield more Mo^{4+} and $Mo^{\delta+}$. Neither the loss of edge nitrogens or the reduction of metals can be attributed to XPS being an ex situ technique. If anything, transferring the catalyst to the XPS chamber would oxidize, rather than reduce, the material. Thus, the XPS study suggests that electrocatalytic reaction involves all doping elements: Fe and Mo in the Fe₂MoC particles, and edge nitrogen atoms. We hypothesize that the original Fe₂MoC particles are first reduced by hydrazine (corresponding to the initial high activity); the reduced catalytic sites then continue to electrooxidize hydrazine, transferring the electrons to the external circuit.



Figure 3. XPS study of the surface composition of wash-Fe2MoC@NC before (a,c,e) and after (b,d,f) 2000 CVs in 100 mM N₂H₄. The spectra show high resolution binding energies for (a,b) N 1s + Mo 3p, (c,d) Fe 2p and (e,f) Mo 3d.

In conclusion, we report the first carbide-based HzOR electrocatalyst, operating at low overpotentials over a wide pH range (onset potential 0.28 V vs. RHE at pH 14). This catalyst produces N₂ irreversibly, with a high faradaic efficiency (3.6 $e^ (N_2H_4)$, and is stable for at least 2000 cycles. These features are attained by emulating several enzyme features, focusing on cooperativity between multiple, intimately bound dopants at a single active site. The atomic (N_{pyridinic}) and nanoparticulate (Fe₂MoC) dopants nanoparticles are well-dispersed on a robust, hierarchically porous, and graphitic support, protecting the sites and assisting in mass- and charge-transfer. Based on this

discovery, we have started investigating the electrocatalytic mechanism of HzOR on this and other carbides by online mass spectroscopy and in situ surface characterization techniques. Furthermore, other enzyme properties may be emulated in the search for better nitrogen cycle electrocatalysts, such as selfhealing and selectivity for different amine types.

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