Pt Electrodes Enable the Formation of \([\text{superscript 4}]\)-O Centers in MOF-5 from Multiple Oxygen Sources

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Pt Electrodes Enable the Formation of $\mu_4$-O Centers in MOF-5 from Multiple Oxygen Sources

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ABSTRACT: The $\mu_4$-O$_2^-$ ions in the Zn$_4$(O$_2$C$^-$)$_6$ secondary building units of Zn$_4$(1,4-benzenedicarboxylate)$_3$ (MOF-5) electrodeposited under cathodic bias can be sourced from nitrate, water, and molecular oxygen when using platinum gauze as working electrodes. The use of Zn(ClO$_4$)$_2$•6H$_2$O, anhydrous Zn(NO$_3$)$_2$, or anhydrous Zn(CF$_3$SO$_3$)$_2$ as Zn$^{2+}$ sources under rigorous control of other sources of oxygen, including water and O$_2$, confirm that the source of the $\mu_4$-O$_2^-$ ions can be promiscuous. Although this finding reveals a relatively complicated manifold of electrochemical processes responsible for the crystallization of MOF-5 under cathodic bias, it further highlights the importance of hydroxide intermediates in the formation of the Zn$_4$(O$_2$C$^-$–R) secondary building units in this iconic material and is illustrative of the complicated crystallization mechanisms of metal-organic frameworks in general.

Electrode surfaces critically influence the observed potential of kinetically sluggish redox couples, such as the pH-changing reactions that are commonly used for electrochemically-induced crystallizations: water or oxoanion reduction. In addition to their electrochemical (i.e. kinetic) influence on the electrodeposition process, electrode surfaces also play key roles in the nucleation and growth of the electrodeposited materials. With this unique offering of controllable variables, electrodeposition becomes an attractive synthetic and mechanistic tool for studying the formation of various crystalline solids. We have been interested in using electrodeposition to control and study the formation of metal-organic frameworks (MOFs), whose synthesis is still largely empirical and relies on mechanisms of nucleation and growth that are still poorly understood.

We showed previously that electrochemical reduction of probases such as nitrate (Eqn. 1) on fluorine-doped tin oxide (FTO) leads to the deposition of a thin film of Zn$_4$(BDC)$_3$ (MOF-5; BDC = 1,4-benzenedicarboxylate; Figure 1). Other phases in the Zn-BDC system are also accessible by varying the applied potential, which ultimately affects the identity and activity of various solution species. Platinum electrodes are particularly effective for controlling either proton or nitrate reduction events. This allows the modulation of probe at a given potential with concurrent selective crystallization of pure phases and the formation of layered MOF heterostructures by simply dialing the applied potential. This unprecedented phase differentiation is important towards utilization of MOFs as functional materials and towards understanding fundamental aspects of solid-phase transformations involved in MOF crystallization. As the use of electrochemical techniques for MOF synthesis receives increasing attention, mechanistic investigations become critical in guiding future studies. In this work, we further examine the reactivity native to platinum electrodes and show that the source of the $\mu_4$-O$_2^-$ ions in MOF-5 is more promiscuous than previously anticipated.

$$\text{NO}_3^- + H_2O + 2e^- \rightarrow \text{NO}_2^- + 2OH^- \quad (1)$$

Figure 1. A portion of the crystal structure of MOF-5, highlighting a Zn$_4$(O$_2$C$^-$)$_6$ cluster. Blue, red, and grey sphere represent Zn, O, and C atoms, respectively. Hydrogen atoms are omitted for clarity.

Despite its iconic status in the field, or perhaps because of it, MOF-5 continues to challenge the fundamental understanding of MOFs. It was recently shown, for instance, that Zn$^{2+}$ ions dynamically bind solvent molecules and display fast exchange between 4-, 5- and 6-coordination in the as-synthesized material. One of the outstanding enigmas related to MOF-5’s secondary building unit (SBU) is the provenance of the $\mu_4$-O$_2^-$ that bridges the four zinc ions in Zn$_4$(O$_2$C$^-$–R). Some reports have speculated on the origin of these key bridging ions, surmising that they are products of acid-base reactions involving...
water,\textsuperscript{20} by analogy with studies on the formation of molecular basic zinc carboxylate species, \(\text{ZnO(O}_2\text{C–R)}\) (R = alkyl).\textsuperscript{21,22} A subsequent mechanistic study effected under anhydrous conditions suggested that \(\text{NO}_3\text{–}\) ions were instead the source of \(\mu_4\text{-O}^2\text{–}\) under solvothermal growth.\textsuperscript{23} Other reports also showed peroxydes facilitating the assembly of \(\text{Zn}_n\text{O(O}_2\text{C–h)}\) clusters in the presence of triethylamine at room temperature.\textsuperscript{24,25}

\[
\text{NO}_3\text{–} + \text{H}_2\text{BDC} + 2e^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + \text{BDC}^{2–} \quad (2)
\]

We showed previously that \(\text{NO}_3\text{–}\) can function as probase (Eqn. 2) and the sole source of \(\mu_4\text{-O}^2\text{–}\) in anhydrous \(\text{N,N-dimethylformamide (DMF)}\) when using either FTO or Pt as the working electrode (Figures 2 and S1).\textsuperscript{11,12} This led to an intriguing question: would MOF-5 form at all in the absence of nitrate? The relevance of this question stems from the fact that MOF-5 crystallization in the presence of nitrate is preceded by the formation of metastable layered zinc hydroxide phases such as \(\text{Zn}_n\text{(OH)}_3\text{(H}_2\text{O)}_2\text{(NO}_3\text{)}_2\). Because the nitrate anions in these intermediate phases are weakly bound and susceptible to topotactic exchange,\textsuperscript{12,26} we reasoned that MOF-5 may indeed be accessible in the absence of nitrate, from a combination of acid-base reactivity between \(\text{H}_2\text{BDC}\) and zinc hydroxides (Eqn. 3), and electrochemical generation of \(\text{HO}^–\) by water reduction, for instance (Eqn. 4).

\[
3\text{H}_2\text{BDC} + [\text{Zn}_4\text{(OH)}_8] \rightarrow \text{H}_2\text{O} + \text{MOF – 5} \quad (3)
\]

\[
\text{H}_2\text{O} + e^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^- \quad (4)
\]

We performed a series of experiments aimed at eliminating \(\text{NO}_3\text{–}\) from the deposition medium. First, we tested a deposition bath containing no nitrate, with \(\text{Zn(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O}\) as the source of \(\text{Zn}^{2+}\). Applying a potential of \(-1.50\text{ V}\) (all electrochemical potentials in this work are referenced to the Ag/Ag(\text{cryptand})\textsuperscript{+} couple, see Supporting Information) to a Pt gauze electrode in solutions of \(\text{H}_2\text{BDC}\), tetra-\text{n- butylammonium hexafluorophosphate (TBAPF}_6\text{)}\), and \(\text{Zn(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O}\) produced crystalline deposits with weak but well-resolved PXRD peaks corresponding to MOF-5 after 150 minutes of continuous electrolysis (Figures 3 and S3). In other words, under conditions where water is the sole source of oxygen atoms, MOF-5 still forms, albeit in lower quantity (Figure S7 and S9). Although perchlorate anions can, in principle, function as pro-bases in a similar manner to nitrate, cyclic voltammetry experiments of tetrabutylammonium perchlorate (TBAP) and \(\text{H}_2\text{BDC}\) solutions (i.e. solutions identical to the deposition bath safe for the presence of \(\text{Zn}^{2+}\)) confirmed that perchlorate is not reduced under these conditions on Pt cathodes (Figure S5 and S6).\textsuperscript{27} Because we have observed the formation of MOF-5 under cathodic electrolysis in the absence of nitrate, \(\text{H}_2\text{O}\) (and \(\text{HO}^-\)) must be able to act as the sole source for \(\mu_4\text{-O}^2\text{–}\).

Seeing that \(\text{H}_2\text{O}\) is itself a competent probase, we turned our attention to molecular oxygen, \(\text{O}_2\), as a potential probase. Under our experimental conditions, we found the \(\text{O}_2\) reduction potential at approximately \(-0.70\text{ V}\) (Figure 4), much more anodically shifted than the reduction of \(\text{Zn}^{2+}\) to \(\text{Zn}\) metal. Cyclic voltammetry of an \(\text{O}_2\)-saturated DMF-\text{anh} solution indicated one-electron reduction to the superoxide anion radical.\textsuperscript{28} The large peak-to-peak separation between this event and the oxidation event observed on the reverse potential scan is likely due to adsorption of superoxide onto the Pt electrode surface (Eqn. 5; \(\text{E}_{\text{pc}} = -1.19\text{ V}\), \(\text{E}_{\text{pa}} = -0.42\text{ V})\).\textsuperscript{29,30} In the presence of \(\text{H}_2\text{BDC}\), a new cathodic process is observed at \(-0.97\text{ V}\). This likely corresponds to \(\text{H}_2\) evolution from protons originating either from the carboxylic acid or from \(\text{O}_2\)-derived hydrogen peroxide.\textsuperscript{31} Notably, the formation of hydroxide from superoxide or peroxide should be thermodynamically favorable under our deposition potential (Eqn. 8 and 9).\textsuperscript{32}
Under these conditions, the O\textsubscript{2} reduction peak remains unshifted with E\textsubscript{p,c} = −1.19 V. The disappearance of the anodic peak at −0.42 V suggests that the relative concentration of stable reduced product is low in the now protic environment, possibly due a fast chemical step, such as the rapid disproportionation of superoxide to peroxide and O\textsubscript{2} (Eqns. 6 and 7).

\begin{align*}
O_2 + e^- & \leftrightarrow O_2^- \quad (5) \\
O_2^- + H^+ & \rightarrow HO_2 \quad (6) \\
2HO_2 & \rightarrow O_2 + H_2O_2 \quad (7) \\
HO_2 + H^+ + 2e^- & \rightarrow 2OH^- \quad (8) \\
H_2O_2 + 2e^- & \rightarrow 2OH^- \quad (9)
\end{align*}

Saturating a Zn(ClO\textsubscript{4})\textsubscript{2}•6H\textsubscript{2}O/DMF-anh deposition bath with O\textsubscript{2} before bulk electrolysis at −1.50 V led to the formation of MOF-5 in 30 minutes, whereas the control experiment under N\textsubscript{2} gas showed only zinc deposition (Figures 5 and S7) with. Moreover, MOF-5 formation under O\textsubscript{2} is independent of the Zn\textsuperscript{2+} source: replacing Zn(ClO\textsubscript{4})\textsubscript{2}•6H\textsubscript{2}O with anhydrous Zn(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}, which contain electrochemically inactive triflate anions, also led to competent formation of MOF-5 upon electrolysis at −1.50 V (Figure 6 and S11). Because O\textsubscript{2} is the only reactive oxygen species at this potential, it must serve as the sole source of \(\mu\text{-}O_2^-\) ions for the formation of MOF-5. It should be noted, however, that the mechanism for the formation of the Zn\textsubscript{2}O cluster in the presence of O\textsubscript{2} may yet be different than when the \(\mu\text{-}O_2^-\) ions come from nitrate or water. Indeed, O\textsubscript{2} reduction in the presence of metal cations is known to create peroxide species such as Zn(O\textsubscript{2}), which may undergo chemical transformations leading to alternative crystallization pathways compared to using either nitrate or water as the probase.\textsuperscript{29,30}

**Figure 4.** Cyclic voltammograms at 100 mV/s in DMF-anh (solvent background, black) of a saturated O\textsubscript{2} solution (red) and a solution of 15 mM H\textsubscript{2}BDC with saturated O\textsubscript{2} (blue) on a Pt electrode. The O\textsubscript{2}/O\textsubscript{2}\textsuperscript{−} couple (Eqn. 4) is observed at E\textsubscript{p,c} = −1.19 V, E\textsubscript{p,a} = −0.42 V.\textsuperscript{29,33} After the addition of H\textsubscript{2}BDC, the major reduction peak remained at −1.19 V. A weak and broad cathodic feature at approximately E\textsubscript{p,c} = −0.60 V was observed with decreasing peak current in each subsequent scans. The peak at E\textsubscript{p,c} = −0.97 V likely corresponds to H\textsubscript{2} evolution.

**Figure 5.** PXRD patterns of samples deposited in DMF-anh on Pt gauze electrodes at −1.50 V for 30 minutes (reagent concentrations [Zn(ClO\textsubscript{4})\textsubscript{2}•6H\textsubscript{2}O] = 75 mM, [H\textsubscript{2}BDC] = 25 mM). The working compartment was sparged with the indicated gas for 30 minutes before electrolysis and kept at a pressure slightly above 1 atm. throughout the deposition process. The PXRD pattern of Zn\textsubscript{2}(BDC)(OH)\textsubscript{2} was simulated with a preferential orientation along (001).\textsuperscript{34} The PXRD pattern of MOF-5 was simulated without additional parameters.\textsuperscript{34} See also Fig. S7.

**Figure 6.** PXRD patterns of a sample deposited in DMF-anh on Pt gauze electrodes at −1.50 V for 30 minutes (reagent concentrations: [Zn(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}] = 75 mM, [H\textsubscript{2}BDC] = 25 mM). The working compartment was assembled in a N\textsubscript{2} glovebox, sealed with parafilm, transferred outside, sparged with O\textsubscript{2} for 30 minutes before electrolysis, and kept under a pressure slightly above 1 atm. throughout the deposition process. PXRD patterns of MOF-5 and Zn\textsubscript{3}(BDC)(OH)\textsubscript{2}•4DMF are simulated.\textsuperscript{24,35} See also Fig. S11.

**Conclusions**

Using tunable variables in the process of cathodic electrodeposition, we were able to show that \(\mu\text{-}O_2^-\) in the Zn\textsubscript{2}O(O\textsubscript{2}C\textsuperscript{−})\textsubscript{6} SBU of MOF-5 can be accessed not just from nitrate, but also water and oxygen. On platinum, the well-
documented redox behaviors of both proton and oxygen reduction reactions were necessary to analyze the electrochemical behavior in the deposition solution. The relative crystallinity of the MOF obtained from reactions rigorously utilizing water or oxygen as the probe is lower than the crystallinity observed for material deposited from nitrate. This emphasizes the potential importance of previously identified layered zinc hydroxy-nitrates as intermediates during MOF-5 deposition under cathodic bias. Establishing the role of various probases, including O₂ as demonstrated here, will prove important in future exploits of cathodic electrodeposition, where varying other experimental parameters such as temperature and pressure may reveal additional aspects of nucleation and crystal growth in the canonic Zn-BDC system.

**Notes and references**

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† Supporting Information: available: chronoamperograms indicating deposition current traces, cyclic voltammograms of control experiments showing the stability of anions under electrolytic conditions, PXRD patterns of films obtained under different deposition times, hydration levels, applied potentials, and substrate concentrations.


(28) The saturation concentration of dissolved oxygen in DMF under 1 atm of O_2 is at 4.8 mM, a much lower concentration than the one of probase in solution. See the following references 19 and 20.


