Chemistry Europe European Chemical Societies Publishing

Electrochemical Oxidation of HMF via Hydrogen Atom Transfer and Hydride Transfer on NiOOH and the Impact of **NiOOH Composition**

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A great deal of attention has been directed toward studying the electrochemical oxidation of 5-hydroxymethylfurfural (HMF), a molecule that can be obtained from biomass-derived cellulose and hemicellulose, to 2,5-furandicarboxylic acid (FDCA), a molecule that can replace the petroleum-derived terephthalic acid in the production of widely used polymers such as polyethylene terephthalate. NiOOH is one of the best and most well studied electrocatalysts for achieving this transformation; however, the mechanism by which it does so is still poorly understood. This study quantitatively examines how two different dehydrogenation mechanisms on NiOOH impact the oxidation of HMF and its oxidation intermediates on the way to

Introduction

Currently, production of a wide variety of chemicals relies upon nonrenewable precursors derived from fossil fuels, which raises environmental and sustainability-related concerns.^[1,2] One method to address these concerns is to replace the fossil fuelderived precursors with biomass-derived ones, thereby opening up renewable and carbon-neutral pathways to access a variety of chemicals.^[3,4] One transformation in particular that has garnered a great deal of attention is the electrochemical oxidation of 5-hydroxymethylfurfural (HMF), which can be produced from biomass-derived cellulose and hemicellulose, to 2,5-furandicarboxylic acid (FDCA), a molecule most notable for being a possible replacement for the petroleum-derived terephthalic acid in the production of widely used polymers such as polyethylene terephthalate (PET).^[5,6] The electrochemical route for upgrading HMF to FDCA is particularly appealing since it can occur effectively at ambient temperatures and oxidation mechanism featuring chemical hydrogen atom transfer to Ni³⁺ sites while the second mechanism is a newly discovered potential-dependent (PD) oxidation mechanism involving electrochemically induced hydride transfer to Ni⁴⁺ sites. The composition of NiOOH was also tuned to shift the potential of the Ni(OH)₂/NiOOH redox couple and to investigate how this affects the rates of indirect and PD oxidation as well as intermediate accumulation during a constant potential electrolysis. The new insights gained by this study will allow for the rational design of more efficient electrochemical dehydrogenation catalysts.

FDCA. The first mechanism is a well-established indirect

pressure, does not require the addition of chemical oxidizing agents, can be catalyzed by inexpensive electrocatalysts (both homogeneous and heterogeneous), and can be driven by electricity produced from renewable sources.[5-9] Furthermore, HMF oxidation can be coupled with cathode reactions that produce valuable fuels and chemicals, further enhancing the economic appeal of the approach.^[10-12]

A variety of materials have been investigated as potential electrocatalysts for oxidation of HMF to FDCA, and NiOOHbased ones have emerged as among the most promising, able to convert HMF to FDCA with near quantitative yield and faradaic efficiency (FE).^[5,9,13-17] Despite these impressive results, however, there are still many questions remaining about the mechanism of this oxidation. Most works have assumed this reaction proceeds though the long-established indirect mechanism proposed by Fleischmann et al. for oxidation of alcohols and amines on NiOOH (and later extended to include aldehydes as they are oxidized after undergoing an initial hydration to form a 1,1-geminal diol) (Scheme 1).^[6,9,18-21] In this mechanism,

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cssc.202200675

$$OH^{-} + Ni(OH)_{2} \xrightarrow{-e} NiOOH + H_{2}O$$
(1)

(2)

$$(\text{RCH}_2\text{OH}_{\text{ads}} + \text{NiOOH} \xrightarrow{\text{HAT}} \text{RCHOH}_{\text{ads}} + \text{Ni(OH})_2 \quad (3)$$

 $\dot{RCHOH}_{ads} + 3NiOOH + H_2O \rightarrow \rightarrow RCOOH_{sol} + 3Ni(OH)_2$ (4)

Scheme 1. Literature mechanism proposed by Fleischmann et al. for the indirect oxidation of alcohols at NiOOH electrodes in alkaline aqueous media.^[19] Aldehyde oxidation is proposed to occur after an initial hydration to form the 1,1-geminal diol (an alcohol), after which it undergoes an equivalent oxidation mechanism to form the carboxylic acid.

This publication is part of a collection of invited contributions focusing on "Green Conversion of HMF". Please visit chemsuschem.org/collections to view all contributions.

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Ni(OH)₂ is first oxidized to NiOOH by the applied bias. This NiOOH then acts as a chemical oxidizing agent, reacting with alcohols through a non-electrochemical and rate-limiting hydrogen atom transfer (HAT) from the carbon at the α -position of the alcohol (or geminal diol in the case of aldehyde oxidation) to a Ni³⁺ site in the NiOOH, thereby reducing the NiOOH back to Ni(OH)₂.^[18,19] In such a mechanism, the applied bias does not directly drive the oxidation of HMF but instead is simply important for continuously regenerating the chemical oxidizing agent NiOOH, which is therefore needed only in a catalytic rather than a stochiometric amount.

In our previous work on the use of transition metal oxyhydroxides as electrocatalysts for HMF oxidation, we reported that in addition to the well-known indirect mechanism, there is also a second, potential-dependent oxidation mechanism enabled at potentials more positive than those needed for the Ni(OH)₂/NiOOH transition.^[9] Since this second mechanism should be different from the indirect mechanism, which involves the conversion of NiOOH to Ni(OH)₂, we speculated that in this second mechanism NiOOH may remain as NiOOH throughout the oxidation and referred to it as direct oxidation to give a contrast to indirect oxidation.^[9] We did not, however, closely probe this second mechanism in our earlier HMF oxidation study because HMF possesses both an alcohol and aldehyde functional group, which can complicate the mechanistic analysis, and therefore HMF is not the best model system to study for elucidating this second mechanism.

In order to investigate the second mechanism, we developed an electroanalytical technique that allowed us to deconvolute the rates of the two oxidation mechanisms and applied it to study the oxidation of a variety of simple alcohols and aldehydes first.^[22,23] The results revealed that our initial speculation that this second pathway involved oxidation on NiOOH with no change in the oxidation state of Ni³⁺ was incorrect. Instead, using a combination of experimental and computational results we showed that this second pathway is only active when Ni⁴⁺ is present and that it involves hydride transfer from the carbon at the α -position of the alcohol (or geminal diol) to those Ni⁴⁺ sites (Scheme 2).^[22,23] This hydride transfer is coupled with proton transfer from the alcohol group to a base in solution, which can occur either concurrently with

$2OH^{-} + Ni(OH)_2 \xrightarrow{-2e^{-}} NiO_2 + 2H_2O$	(1)
$OH^{-} + RCH_2OH \implies RCH_2O^{-} + H_2O$	(2)
$\text{RCH}_2\text{O}_{\text{sol}}$ \Longrightarrow $\text{RCH}_2\text{O}_{\text{ads}}$	(3)
RCH ₂ O ⁻ _{ads} + NiO ₂ <u>hydride</u> transfer RCHO _{sol} + Ni(OH)O ⁻	(4)
Ni(OH)O ⁻ + HO ⁻	(5)

Scheme 2. Hydride transfer mechanism we have previously proposed for oxidation of alcohols to aldehydes through the PD oxidation pathway.^[23] Aldehyde oxidation occurs though an equivalent mechanism as it exists in equilibrium with its hydrated form, the 1,1-geminal diol, a type of alcohol that can undergo the same oxidation mechanism to form the carboxylic acid.

or prior to (likely before adsorption in alkaline conditions) hydride transfer. Because this hydride transfer reduces the Ni⁴⁺ sites back to Ni²⁺, this pathway cannot be called a direct pathway. Another critical difference between indirect oxidation and this second pathway is the role the applied bias plays. For the second pathway, the application of a positive bias is necessary not only to generate the active Ni⁴⁺ sites but also to drive the hydrogenation reaction. As a result, the rate of oxidation through this pathway is potential-dependent and drops to zero as soon as bias is no longer applied even if Ni⁴⁺ remains. Consequently, we refer to this pathway as potential-dependent (PD) oxidation (Scheme 2).

From our studies investigating dehydrogenation mechanisms of simple alcohols and aldehydes, we established a general and comprehensive understanding of indirect and PD pathways and how they are affected by various factors.^[22,23] Our new understanding includes that aldehyde oxidation occurs preferentially through indirect oxidation while alcohol oxidation favors PD oxidation. Using this new understanding and the electroanalytical method we developed to deconvolute the rates of the indirect and PD oxidation, we are now well positioned to return to the more complicated case of HMF oxidation. Accordingly, the purpose of this study is two-fold. The first goal is to develop an accurate understanding of the mechanism(s) for oxidation of HMF on NiOOH as well as the various intermediates along the way to FDCA. This includes understanding whether these oxidations occur though the indirect or PD pathway, what steps tend to limit the reaction rate, and whether HMF tends to first undergo aldehyde oxidation to form 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) or alcohol oxidation to form 2,5-diformylfuran (DFF) (Scheme 3). The second goal is to use this understanding and our knowledge of the indirect and PD pathways to evaluate the effects of incorporating metal ions into NiOOH electrocatalysts to shift the potential of the Ni(OH)₂/NiOOH couple. Understanding the impact NiOOH composition has on the two dehydrogenation mechanisms of NiOOH will be highly valuable to future studies trying to rationally design next-generation catalysts for various electrochemical dehydrogenation reactions.

Results and Discussion

The NiOOH electrodes used in this study were prepared by electrodepositing a very thin $Ni(OH)_2$ film on a flat, 2D fluorine-



Scheme 3. Scheme depicting two possible routes for oxidation of HMF to FDCA. HMF can either undergo initial alcohol oxidation to form DFF or can instead undergo initial aldehyde oxidation to form HMFCA.



doped tin oxide (FTO) substrate. The Ni(OH)₂ film is thin enough that the scanning electron microscopy (SEM) images of the FTO substrate with and without this film look comparable (Figure S1). The use of thin films in this study minimizes the heterogeneity in the local environments of Ni sites as well as any impacts that the porosity or depth of the electrocatalyst could have on the transport or adsorption of the organic species within the electrocatalysts. This is critical to obtaining results that accurately reflect the intrinsic oxidation mechanisms of NiOOH.

Qualitative assessment through cyclic voltammetry

To begin, we collected cyclic voltammograms (CVs) in pH 13 solutions using a Ni(OH)₂ working electrode (WE) in the presence and absence of 5 mM solutions of HMF, HMFCA, DFF, and 5-formyl-2-furancarboxylic acid (FFCA) (Figure 1). We chose to use pH 13 for this study as we have previously shown HMF is unstable in pH 14 solutions,^[24] which would complicate mechanistic analysis. The CVs were collected in a rapidly stirred solution whose stirring speed was chosen such that further increasing the stirring speed no longer enhanced the oxidation current. This prevented depletion of the organic species (or hydroxide) around the electrode from having an effect on the current profiles associated with the indirect and PD pathways.

Rapidly stirring the solution has the same effect of preventing depletion of species around the electrode surface as using a rotating disc electrode while allowing us to use the same NiOOH electrode in the same setup for all experiments performed in this study (CVs, rate deconvolution analysis, constant potential electrolysis). The CVs obtained in a still solution are shown in Figure S2 for comparison.

All CVs were recorded by first sweeping the potential from open circuit in the positive direction and then returning to the initial potential. In CVs collected in the presence of an organic species, the indirect oxidation of the organic species appears as an increase in the Ni(OH)₂ oxidation peak during the forward scan and a decrease in the NiOOH reduction peak during the reverse scan.^[22,23] This is because when Ni(OH)₂ is oxidized to NiOOH during the forward scan, the concurrent indirect oxidation of organic species by NiOOH converts NiOOH back to Ni(OH)₂. As a result, more charge is passed oxidizing Ni(OH)₂ to NiOOH during the forward scan. During the reverse scan, since some of the NiOOH is reduced back to Ni(OH)₂ by the indirect oxidation of organic species, less charge is required to reduce NiOOH to Ni(OH)₂, diminishing the reduction peak.^[22,23] In the presence of each of the organic species tested here some degree of both enhancement in the Ni(OH)₂ oxidation peak and a diminishment in the NiOOH reduction peak are evident, suggesting that all are oxidized at least in part through the indirect pathway. Also, in the presence of all the organic species



Figure 1. CVs collected using a Ni(OH)₂ working electrode in pH 13 solutions with (red) and without (black) 5 mM solutions of (a) HMF, (b) HMFCA, (c) DFF, and (d) FFCA (scan rate: 10 mV s⁻¹). The solutions were rapidly stirred to eliminate the effect of mass-transport limitations.



the position of the Ni(OH)₂ oxidation peak has been shifted anodically, though in the case of HMF the shift is less pronounced. The most likely explanation for the delayed onset of Ni(OH)₂ oxidation is that HMF, HMFCA, DFF, and FDCA adsorb on the Ni²⁺ sites, which stabilizes Ni in the 2+ state and makes its oxidation difficult. This observation will be revisited in a discussion further below as it turned out to be important for understanding the oxidation mechanisms of HMFCA, DFF, and FDCA.

Unlike indirect oxidation, PD oxidation typically appears in CVs as a second oxidation feature occurring at more anodic potentials than the Ni(OH)₂/NiOOH redox couple. Additionally, as the name implies, this feature typically shows a clear potential dependence as, unlike indirect oxidation, its rate is driven by the applied bias and not by the oxidizing power of the NiOOH couple.^[22,23] We note that the species containing only an aldehyde (DFF, FFCA) do not show any clear indication of a PD oxidation feature, instead showing only the enhancement of the Ni(OH)₂ oxidation peak characteristic of indirect oxidation. Additionally, the cathodic peak corresponding to the reduction of NiOOH to Ni(OH)₂ is entirely absent from the reverse scan. This indicates that DFF and FFCA are oxidized predominantly though the indirect mechanism and that this process is fast enough to consume all the Ni³⁺ before it can be electrochemically reduced during the reverse scan. In contrast, for the species containing an alcohol (HMF, HMFCA), the current profiles are different. For HMFCA, in addition to the enhancement of the Ni(OH)₂ oxidation peak at around 0.55 V vs. Ag/AgCl indicative of indirect oxidation, there is a clear second feature that occurs at around 0.64 V vs. Ag/AgCl, well after the Ni(OH)₂ oxidation peak. Similarly, HMF also shows two features, though they do overlap. The first is a shoulder at around 0.5 V vs. Ag/AgCl, which corresponds to the position of Ni(OH)₂ oxidation and thus is related to indirect oxidation, while the second feature, attributable to PD oxidation, peaks at the more anodic potential of around 0.69 V vs. Ag/AgCl. Additionally, unlike with DFF and FFCA, CVs of HMF and HMFCA show a notable reductive wave corresponding to NiOOH reduction during the reverse scan, meaning the indirect process is not fast enough to fully consume Ni³⁺. Together, these results suggest HMF and HMFCA are primarily oxidized through the PD process. Finally, we note that as these CVs were obtained in rapidly stirred solutions, any decrease in oxidation current when the potential is swept in the positive direction is not due to the depletion of the organic species. Instead, it is evidence that the electrocatalyst becomes less active for oxidation of the organic species as the potential is swept to values closer to triggering the onset of the oxygen evolution reaction (OER). Using a combination of experimental and theoretical results, we have shown in a prior work that the most likely cause for this deactivation of NiOOH toward oxidation of alcohols and aldehydes at more anodic potential is an increase in the competition with hydroxide for adsorption on Ni^{4+.[23]} Moreover, in that work we showed that this competition affects aldehyde adsorption on Ni⁴⁺ more considerably than it does alcohol adsorption and therefore causes the current decay to initiate at less positive potentials for aldehyde oxidation than for alcohol oxidation.^[23]

Quantitative assessment through rate deconvolution

While the CVs discussed above can give a qualitative guide to which oxidation pathway is preferred, to achieve a quantitative measurement it is necessary to use the rate deconvolution procedure we developed to separate the rates of the two pathways. A detailed description of this procedure and the principles behind it can be found in our previous work,^[22] so only an overview will be provided here. In brief, the procedure is a method to first isolate and measure the rate of the chemical reaction between NiOOH and an organic species, a measurement that is equivalent to the rate of the indirect process. Then, assuming the potential being examined is one where only oxidation of the organic species is possible, we can note that the overall current (I_{tot}) will simply be the sum of the partial currents for PD (I_{PD}) and indirect (I_{ind}) oxidation [Eq. (1)]. Since I_{tot} can be measured easily, once I_{ind} is known Equation (1) can be used to calculate I_{PD}:

$$I_{\rm tot} = I_{\rm PD} + I_{\rm ind} \tag{1}$$

In order to isolate and measure l_{ind} , we perform a series of short, 3-step procedures (Figure S3). In the first step, a constant potential is applied at the Ni(OH)₂ WE in a solution containing the organic species and being stirred rapidly with the same speed used for the CV experiments. This ensures that the concentrations of solution species at the electrode surface do not change over time and thus are effectively "flooded". During this first, constant-potential step the NiOOH film is converted into the same state it would be in during a constant potential electrolysis at the chosen potential in the tested solution. In the second step the potential is no longer applied and the NiOOH electrode is instead left to sit in the rapidly stirred solution at open circuit for a specific length of time. During this step, neither oxidation of Ni(OH)₂ nor PD oxidation can occur since both require applied bias. NiOOH can, however, still react with the organic species as a chemical oxidizing agent like it does in the indirect pathway, oxidizing the organic species while being reduced back to Ni(OH)2. In the third step, a reducing potential is applied to rapidly convert the NiOOH that still remains after the second step back into Ni(OH)₂. The charge passed during this step represents how much of the NiOOH "reactant" generated by the bias applied in the first step remained after chemically reacting with the organic substrate in the second step with a reaction time equivalent to the time left at open circuit. By repeating this whole 3-step process for a variety of different times at open circuit in the second step, a data set can be obtained showing the disappearance of charge from the NiOOH film due to chemical reaction with the organic species as a function of time at open circuit. By examining whether (charge) vs. t, ln(charge) vs. t, or 1/(charge) vs. t plots give a good linear fit for the data, we can determine whether this reaction follows 0th, 1st, or 2nd order kinetics with respect to



charge in the NiOOH film and the observed rate constant for indirect oxidation ($k_{obs,ind}$) can be determined from the slope of the linear plot (Table S1). We note that this is an observed rate constant rather than a true rate constant (k_{ind}) because, as noted above, the rapid stir speed means the concentrations of solution species at the electrode surface are constant and can be incorporated into the rate constant according to Equation (2), where *a* and *b* are the reaction order with respect to the organic species and hydroxide, respectively:

$$k_{\text{obs,ind}} = k_{\text{ind}} \times [\text{organic species}]^a \times [\text{OH}^-]^b$$
 (2)

By using $k_{obs,ind}$ and the kinetics equations we can solve for the rate of the chemical reaction at 0 s at open circuit (when the NiOOH electrocatalyst is in the same state as it is in during a constant-potential electrolysis at the potential applied in step 1). This is a measure of the partial current for the indirect process (l_{ind}), which, along with the steady-state current observed in step 1 (l_{tot}), can be used to calculate l_{PD} using Equation (1). The rate deconvolution experiments described above were performed for 5 mm solutions of HMF, DFF, HMFCA, and FFCA at pH 13 and 1.52 V vs. the reversible hydrogen electrode (RHE). The deconvoluted currents are shown in Figure 2, while the kinetics plots used to obtain those currents are shown in Figure S4.

The quantitative rate deconvolution results shown in Figure 2 agree well with the qualitative picture given by CVs in stirred solutions. HMF and its oxidation products all have an indirect component to their current; however, for HMF and HMFCA the PD pathway dominates, representing 72 and 73% of the overall current, respectively. Conversely, for the species with only an aldehyde, the indirect process dominates instead, representing 67% of the current for DFF and 100% of the current for FFCA. The comparison between FFCA and DFF is also interesting in that DFF, which possesses 2 aldehyde groups, shows almost exactly double the indirect rate as FFCA, which has only one. Indeed, and perhaps unsurprisingly, the molecules with two active functional groups (HMF, DFF) are both substantially more reactive than those with only one (FFCA, HMFCA). This is likely because the presence of two reactive



Figure 2. Component of the current due to indirect (red) and PD (blue) oxidation of 5 mM HMF, HMFCA, DFF, or FFCA in a pH 13 solution at 0.55 V vs. Ag/AgCl.

functional groups increases the probability that a collision between the molecule and the NiOOH surface will result in adsorption that can subsequently lead to oxidation.

Constant-potential oxidation

To further examine the process of HMF oxidation, we also performed a constant-potential electrolysis at 0.55 V vs. Aq/ AgCl (1.52 V vs. RHE) in a pH 13 solution containing 5mm HMF and analyzed the changes in solution composition as the electrolysis proceeded (Figure 3). FFCA is the dominant product observed until more than half the stoichiometric charge is passed, indicating the relatively slow FFCA oxidation step does play an important role in limiting the rate of FDCA formation. Looking at this result, one may think that the application of a more positive bias is needed to expedite the oxidation of FFCA to FDCA. However, an important new insight we obtained from the rate deconvolution analysis is that at this pH and concentration FFCA oxidation occurs entirely through the indirect pathway and therefore is not expected to be enhanced by applying more positive potentials. In fact, our previous study showed that the rate of aldehyde oxidation can actually decrease when a more positive bias is applied and more of the Ni³⁺ is converted to Ni⁴⁺.^[23] This is because unlike the Ni³⁺ sites, the Ni⁴⁺ sites are active for OER and thus hydroxide ions will compete with aldehydes for adsorption on them. Because hydroxide adsorption tends to outcompete aldehyde adsorption,^[23] this can limit the current for aldehyde oxidation when increases to the applied potential increases the amount of Ni⁴⁺ sites and therefore limits the amount of aldehyde that is adsorbed on the NiOOH. Indeed, we confirmed that the steadystate current for FFCA oxidation actually decreases as the applied potential increases (Figure S5). This counterintuitive result that the fastest FFCA oxidation on NiOOH can be achieved at a less positive bias can be understood only when the two dehydrogenation mechanisms of aldehyde on NiOOH are recognized and comprehensively understood.



Figure 3. Change in concentration of HMF and its oxidation products over charge passed at 0.55 V vs. Ag/AgCl in a pH 13 solution containing 5 mM HMF.



Another interesting result shown in Figure 3 is that DFF accumulates to almost twice the extent as HMFCA (0.31 vs. 0.19mm) despite the fact that DFF is more reactive, which suggests that HMF is converted to FFCA predominantly through the DFF route with the HMFCA route occurring as a minor pathway under our conditions. We reasoned that the preference toward the DFF route could be because PD oxidation (which we showed in Figure 2 dominates for HMF oxidation at our condition) would selectively oxidize the alcohol in HMF over the aldehyde. This is suggested by our prior studies showing alcohols are primarily oxidized through the PD pathway while aldehydes are primarily oxidized though the indirect pathway.^[22,23] Our reasoning is further supported by the results we obtained by oxidizing HMF using NiOOH with no bias applied (meaning only the indirect pathway can occur). This experiment was carried out by repeatedly applying 0.55 V vs. Ag/AgCl to a Ni(OH)₂ film in a pH 13 KOH solution without any organic species, then moving the oxidized NiOOH electrode to a solution containing HMF and allowing it to chemically oxidize the HMF under open circuit condition. After this process was repeated 20 times the HMF solution was sampled and the products tested by HPLC.

The results of this experiment are shown in Figure S6 and reveal that when only the indirect oxidation pathway is allowed, the selectivity between HMFCA and DFF is reversed, with roughly twice as much HMFCA produced as DFF. This demonstrates that oxidation through the indirect pathway preferentially oxidizes the aldehyde to produce HMFCA, which in turn confirms that the greater amount of DFF observed in Figure 3 must be because the PD pathway preferentially oxidizes the alcohol in HMF to produce DFF. This finding means that HMF oxidation on NiOOH can occur through either the DFF route or the HMFCA route and that which one dominates will depend on the chosen oxidation conditions (i.e., the DFF route if PD oxidation is favored and the HMFCA route if indirect oxidation is favored). Our previous study showed that conditions such as a more positive potential, higher pH, and higher concentration of the organic species tend to promote PD oxidation and thus are likely to increase the preference toward the DFF route.^[23]

Comparison to prior literature

We note that most prior studies, which were performed without knowledge of the presence of two different oxidation pathways on NiOOH, have reported that HMF oxidation on NiOOH proceeds though the HMFCA route.^[14,21,25-31] While it is difficult to be certain without performing the rate deconvolution experiments, these studies were often conducted under conditions we would expect to favor PD oxidation as much as or more than those used in this study (0.55 V vs. Ag/AgCl in a pH 13 solution containing 5 mM HMF) where the PD pathway (and thus DFF formation) dominates. Therefore, we believe it is unlikely that the reason they all observed HMFCA instead of DFF is because they all were using conditions that heavily favored the indirect pathway. Instead, we think it is most likely because they used high-surface-area NiOOH often deposited on

three-dimensional, porous substrates such as Ni foam to maximize the surface area and the rate of HMF oxidation, which can distort the accumulation profile of the intermediates due to the reasons explained below.

For a high-surface-area, three-dimensional electrode, if a molecule is oxidized to one of the intermediates (HMFCA, DFF, FFCA) at a more interior site in the electrocatalyst and then desorbs, it would be almost surrounded by other catalyst sites. This would make it much more likely to reabsorb onto one of those sites and be further oxidized before it can make its way out into the bulk solution, as would be necessary for it to be detected using ex-situ analysis methods. While this is good when designing a fast and effective electrocatalyst, it is not ideal when analyzing the mechanism or attempting to ascertain what intermediates form. Moreover, we might expect this to be particularly problematic if the intermediates differ in activities for adsorption or oxidation. For example, DFF, which is more reactive than HMFCA, might more readily undergo further oxidation before making its way out of a three-dimensional catalyst's interior, meaning its amount will be more severely underestimated compared to HMFCA when using a thicker, porous catalyst. By contrast, the thin, flat electrodes used in our study do not have this issue, and so the intermediate profile we observed is more representative of what actually is produced during the reaction.

To test whether differences in the thickness of the Ni(OH)₂ electrode could substantially impact the detected intermediate profile, we also conducted an electrolysis of a pH 13 solution containing 5 mM HMF at 0.55 V vs. Ag/AgCl using a much thicker Ni(OH)₂ electrode. Our results show that simply increasing the deposition time from 45 s to 12 min to deposit a thicker Ni(OH)₂ electrode on the 2D flat FTO substrate (which is still significantly thinner than those deposited on 3D Ni foam substrates used in previous studies) significantly alters the accumulation of intermediates during the course of an electrolysis. As can be seen in Figure S7, the accumulation of DFF and HMFCA became negligible and even the accumulation of FFCA was diminished considerably, resulting in an almost linear increase of the terminal product FDCA over the coulombs passed. This result clearly demonstrates how the thickness of the film can alter the intermediate accumulation not by changing the actual oxidation mechanisms but rather by promoting the re-adsorption and further oxidation of intermediates before they escape the catalyst layer. This explains why prior studies using 3D electrodes could not detect the more reactive DFF intermediate during HMF oxidation and concluded that HMF oxidation occurs through the HMFCA route. This result also highlights the necessity of using a flat, thin electrocatalyst for an accurate mechanistic study.

Understanding 0th order behavior

For the simple alcohols and aldehydes we studied previously, a pseudo second order relationship between the indirect reaction rate and charge stored in the NiOOH film was observed (i.e., the best linear fit was obtained when 1/charge was plotted



against *t*).^[22,23] We note that this does not necessarily mean the reaction is truly "second order" with respect to charge stored in the NiOOH film. In fact, we expect that the true rate law is probably more complicated, and we do not give any chemical meaning to this "second order" relationship. Instead, we simply use this mathematical relationship as it accurately models the disappearance of charge from the NiOOH across the timeframe of interest, which allows us to determine $k_{obs.ind}$ and l_{ind} .

In this study, we found that HMF instead shows a first order relationship with charge stored in the NiOOH film (i.e., the best linear fit was obtained when ln(charge) was plotted against t) while for HMFCA, DFF, and FFCA the relationship is 0th order (i.e., the best linear fit was obtained when Q was plotted against t) (Figure S4). Again, we do not give any serious chemical meaning to the first order relationship observed for HMF and just use this relationship to obtain the best fitting of our experimental data to most accurately determine the indirect rate. The 0th order behavior of HMFCA, DFF, and FFCA, however, is bizarre in that it means the concentration of Ni³⁺ has no effect on the indirect rate of HMFCA, DFF, and FFCA oxidation. This would seem to be impossible because (at least according to how the indirect mechanism has traditionally been described) Ni³⁺ is not only a reactant consumed in the indirect reaction but also comprises the active sites where the organic species must first adsorb before undergoing further reaction (step 2 in Scheme 2).

To have a 0th order relationship it must be the case that the oxidized Ni sites are not involved in the rate-determining step. The only scenario that we believe is consistent with this is if DFF, HMFCA, and FFCA are able to adsorb on Ni²⁺ sites as well as on Ni³⁺ and Ni⁴⁺ sites and that the organic species adsorbed on Ni²⁺ sites can rapidly undergo HAT to adjacent oxidized sites in a step that is fast relative to the adsorption step. Since the slow, rate-determining adsorption step would then depend on the total number of Ni sites rather than on the number of oxidized Ni sites, a 0th order relationship to charge stored in the Ni film would result.

If the above explanation is correct, we would expect to see a deviation from 0th order behavior at some point as charge leaves the film as eventually the HAT step would no longer be fast relative to adsorption, since the HAT step will depend on the charge in the film. Similarly, if adsorption is truly the ratelimiting step and subsequent reaction of the adsorbed species is fast we would expect the indirect rate to increase as the concentration increases since the adsorption step is the one that has a direct kinetic dependence on the concentration of the unbound organic species (rather than the adsorbed species).

To test whether these predictions are accurate, we performed rate deconvolution experiments with time points collected up to almost full conversion of the film in a 10mm FFCA solution and compared those to the results from a 5 mM solution. As can be seen in Figure 4, the 0th order behavior holds well throughout the first 2 s of reactivity, corresponding to roughly 80% conversion of the NiOOH back to Ni(OH)₂. After this, however, the 0th order behavior breaks down and the same 1st order behavior seen for HMF emerges and describes the reaction well from 2 s onward to the final point collected at 3.5 s corresponding to around 99% conversion of the NiOOH. Moreover, when comparing the indirect current for 5 mm FFCA to that of 10mm FFCA, we can see the expected doubling of the rate, with the current increasing from 0.88 to 2.01 mA cm^{-2} . These results support our proposed mechanism that FFCA can adsorb on any Ni site, including ones in Ni(OH)₂ and then undergo a HAT step to adjacent oxidized sites that is rapid unless almost all the Ni sites are in the reduced Ni²⁺ state (which will not occur under applied bias unless substantially higher concentrations are used and the potential remains at 0.55 V vs. Ag/AgCl).

The ability of these molecules to adsorb on Ni(OH)₂ sites also provides an explanation for the delayed onset of the Ni(OH)₂/NiOOH conversion in the presence of the organic species mentioned when discussing Figure 1. Adsorption of these molecules on the Ni(OH)₂ would change the energetics of those sites, likely having a stabilizing effect. Moreover, oxidizing a Ni(OH)₂ site with a bound organic molecule may necessitate breaking bonds or interactions involving the organic molecule, further adding to the barrier. As such, we would expect adsorption of these molecules on Ni(OH)₂ to delay the onset of its oxidation, which is exactly what is observed. Moreover, this delay is much more substantial for the molecules which follow 0th order kinetics (HMFCA, DFF, and FFCA) with respect to



Figure 4. (a) Charge vs. time and (b) ln(charge) vs. time plots showing the consumption of positive charge stored in a NiOOH film for indirect oxidation of 10 mm FFCA in a rapidly stirred pH 13 solution at open-circuit condition. The NiOOH film used in this experiment was pre-oxidized at 0.55 V vs. Ag/AgCl in the FFCA solution.



charge in the NiOOH film rather than for HMF. This suggests HMF adsorbs less readily on Ni²⁺ sites and explains why the indirect oxidation of HMF has a different relationship with charge in the NiOOH film than does the oxidation of HMFCA, DFF, and FFCA. This also highlights that the ability to adsorb readily on Ni(OH)₂ and then undergo further oxidation is likely a property fairly unique to HMFCA, DFF, and FFCA rather than one shared more broadly by alcohols and aldehydes as none of the other organic species we tested have shown either a comparable shift in the Ni(OH)₂ oxidation peak nor 0th order kinetics with respect to charge stored in the NiOOH film.^[22,23] Finally, this ability to adsorb onto and react at Ni(OH)₂ sites also provides an explanation for the small amount of current observed in the presence of the organic species before the onset of Ni(OH)₂ oxidation that can be seen in Figure 1 and which has been reported previously.^[9] This current has previously been speculated to be due to oxidation of organic species on Ni(OH)2.^[9] Unlike both the indirect and PD mechanisms discussed above that involve the reduction of Ni sites as part of oxidizing the organic species, an oxidation at Ni(OH)₂ sites would likely be a direct electrochemical oxidation and involve no change in the Ni oxidation state. While the current for this process that occurs before the onset of Ni(OH)₂ oxidation is very low in all cases (perhaps due to the poor conductivity of Ni(OH)₂) it is much more pronounced for HMFCA, DFF, and FFCA than it is for HMF, further confirming that these molecules adsorb more readily on Ni(OH)₂ sites and that this current is due to oxidation occurring at Ni(OH)₂ sites.

Impact of NiOOH composition

There are various metal ions that are known to shift the potential of the Ni(OH)₂/NiOOH peak when incorporated into the Ni(OH)₂ structure.^[31-34] In this section, we investigated how such shifts of the Ni(OH)₂/NiOOH peak affect the indirect and PD oxidation rates and their contributions to the total anodic current. We chose to incorporate Co and Ga to shift the Ni(OH)₂/NiOOH peak cathodically and anodically, respectively. This was done by adding small amounts of Co(NO₃)₂ or Ga(NO₃)₃ to the deposition solutions (see the Experimental Section). Co was chosen because it has been one of the most common metals mixed with Ni in previous studies.^[29,31,32,35] Ga was chosen to shift the Ni(OH)₂/NiOOH peak anodically instead of the more commonly used Fe because, unlike Fe,[33,34] Ga does not significantly improve the performance of NiOOH for OER. Improved activity for OER could lower the faradaic efficiency for HMF oxidation and create potential complications in our rate deconvolution experiments.

The samples we prepared and investigated are summarized in Table 1. These films were prepared such that they all contain comparable absolute amounts of Ni regardless of the different percentage of Co and Ga present in each film. The film compositions were determined by dissolving these films in 1 vol% nitric acid and analyzing the resulting solutions by inductively coupled plasma-mass spectrometry (ICP-MS). We note that the amounts of Co and Ga incorporated and the

Table 1. NiOOH films with various compositions investigated in this study.					
Modification of the plating solution	Film composition	Ni content in film [nmol]	Co or Ga content in film [nmol]	Ni(OH) ₂ /NiOOH peak position [V vs. Ag/AgCl]	
2тм Со	NiOOH, 31 % Co	27	12	0.41	
1 mм Со	NiOOH, 19% Co	30	7	0.46	
no alteration	NiOOH	29	-	0.49	
0.5 mм Ga	NiOOH, 3.4% Ga	28	1	0.51	
1 mм Ga	NiOOH, 6.7 % Ga	28	2	0.56	

deposition conditions we used here were not chosen to achieve the best possible performance for HMF oxidation. Instead, they were chosen to provide a set of samples with clear differences in the position of the Ni(OH)₂ peak while maintaining the same morphology and thickness as the pristine NiOOH. This allows us to best identify the impact that shifts in the Ni(OH)₂/NiOOH couple have on indirect and PD oxidation. Therefore, the following data should not be used to judge the overall value of Co or Ga incorporation for improving HMF oxidation. The effect of the composition tuning on the Ni(OH)₂/NiOOH peak is shown in Figure 5 and is also summarized in Table 1.

The effects of the film composition on the indirect and PD oxidation pathways were also investigated through rate deconvolution analysis performed at 0.55 V vs. Ag/AgCl using 5 mM HMF solutions at pH 13. The deconvoluted currents and $k_{obs,ind}$ values are shown in Figure 6. For all films, the disappearance of charge due to indirect oxidation gave the best linear fit when ln(charge) was plotted against time (Figure S8). We note that the $k_{obs,ind}$ obtained from the slope of the ln(charge) vs. time plots is the overall observed rate constant for the indirect process as performed by the film (rather than only the Ni sites in the film). Since Co(OH)₂ can also be oxidized to CoOOH,



Figure 5. LSVs of NiOOH with various compositions taken in a pH 13 KOH solution (scan rate: 10 mV s^{-1}).





Figure 6. Plots displaying (a) the deconvoluted indirect and PD current and (b) $k_{obs,ind}$ when 0.55 V vs. Ag/AgCl is applied to a rapidly stirred pH 13 solution containing 5 mM HMF using NiOOH electrodes with various compositions.

which is capable of HMF oxidation, for the Co-containing films some of the current and contribution to $k_{obs,ind}$ may come from activity of Co sites. However, we expect the degree of HMF oxidation at Co³⁺ sites to be fairly small as CoOOH has previously been shown to be significantly less active toward HMF oxidation than NiOOH.^[9]

The results in Figure 6 reveal that there is a clear trend between activity toward indirect oxidation and the potential of the Ni(OH)₂/NiOOH couple. As the couple shifts anodically, there is an accompanying increase in the partial current for the indirect pathway, going from 0.18 mA cm⁻² for the NiOOH containing 31% Co up to 1.1 mA cm⁻² for the NiOOH containing 6.7% Ga. This results in an increase in the percentage of the current occurring through the indirect pathway as the potential of the Ni(OH)₂/NiOOH couple shifts anodically, increasing from a minimum of 23% for the NiOOH containing 31% Co to a maximum of 38% for the NiOOH containing 6.7% Ga. This increase in the indirect current is driven by the increase in $k_{obs,ind}$ as the Ni(OH)₂/NiOOH couple is shifted anodically, meaning individual Ni sites are more active toward indirect HMF oxidation. This trend is as expected and can be best explained using the diagrams shown in Figure 7.

The definition for overpotential (η) is the difference between the thermodynamic potential for a given reaction and the potential available to perform the given reaction. Since NiOOH serves as a chemical oxidant for indirect oxidation, the overpotential for indirect alcohol or aldehyde oxidation (shown as η_{ind} in Figure 7) is always the difference between the thermodynamic potential for alcohol or aldehyde oxidation $(E_{\text{org} \text{ ox.}})$ and the redox potential of Ni(OH)₂/NiOOH $(E_{\text{Ni(OH)}_2/\text{NiOOH}})$ regardless of the potential applied. Therefore, when the Ni- $(OH)_2$ /NiOOH couple shifts anodically, it increases η_{ind} and this change results in an increase in $k_{\rm obs,ind}$. The shift of the Ni(OH)₂/ NiOOH couple also has the effect of decreasing the overpotential for NiOOH generation (shown as η_{regen} in Figure 7), which is the difference between the applied potential ($E_{applied}$) and the redox potential of Ni(OH)₂/NiOOH. Under our conditions, however, the kinetics of the HAT step is more ratedetermining than those for regeneration of NOOH when determining the rate of HMF oxidation, so the anodic shift of



Figure 7. Scheme illustrating how shifting the potential of the Ni(OH)₂/ NiOOH couple affects the overpotential for indirect oxidation of an organic species, η_{ind} and the overpotential for regeneration of NiOOH from Ni(OH)₂, η_{regen} . E_{orgox} is the thermodynamic potential for oxidation of the organic species (e.g., alcohol or aldehyde), $E_{Ni(OH)_2/NiOOH}$ is the thermodynamic potential of the Ni(OH)₂/NiOOH redox couple, and $E_{applied}$ is the potential applied at the electrode.

the Ni(OH) $_2$ /NiOOH couple results in an overall increase in the oxidation current for indirect oxidation.

We note that the prediction that $\eta_{\rm ind}$ will affect $I_{\rm ind}$ is valid only when HAT is the rate-determining step for indirect oxidation. As mentioned above, unlike for HMF, the indirect oxidation of FFCA, HMFCA, and DFF were limited by the adsorption step. In such cases, anodically shifting the Ni(OH)₂/ NiOOH peak would not be expected to increase the rate of indirect oxidation since increasing the oxidizing power of NiOOH would only speed up steps that are already rapid. The effect of cathodically shifting the peak would depend on how much slower the HAT steps become with the less oxidizing NiOOH. If the HAT steps are still rapid relative to adsorption despite the decrease in the oxidizing power of the NiOOH, we would not expect to see any effect from the cathodic shift of the Ni(OH)₂/NiOOH peak. Conversely, if the decrease is enough that the HAT steps are no longer much faster than adsorption, we would expect that the indirect reaction would not follow Oth order kinetics with respect to charge in the film because the oxidized Ni sites would be involved in rate-affecting steps.



To illustrate this point, we performed rate deconvolution experiments comparing pristine, 19% Co-containing, and 6.7% Ga-containing NiOOH films for oxidation of 5mm FFCA in a pH 13 solution. The resulting charge vs. time plots along with the values of $k_{\text{obs.ind}}$ and l_{ind} are shown in Figure S9. As was expected, anodically shifting the Ni(OH)₂/NiOOH peak through Ga incorporation did not meaningfully change $k_{obs.ind}$ or l_{ind} . For the Co-containing films, FFCA oxidation also follows 0th order kinetics with respect to the charge in the NiOOH film, meaning FFCA adsorption is still rate determining. We also note that, with the Co-containing films, I_{ind} for FFCA oxidation is only 0.39 mA cm⁻², which is substantially lower than the I_{ind} of 0.88 mA cm $^{-2}$ for the pristine films and 0.98 mA cm $^{-2}$ for the Gacontaining films. Given that the 0th order behavior with respect to charge in the film is still observed for the Co-containing films, this lower I_{ind} cannot be explained by the decreased η_{ind} . Instead, it is most likely because the presence of Co has the additional effect of interfering with the adsorption of FFCA. Further evidence for this can be seen when comparing LSVs taken with pristine, Co-containing, and Ga-containing NiOOH films in solutions with and without 5 mm FFCA (Figure S10). As can be seen, while the LSVs taken with pristine and Gacontaining films show a significant anodic shift of the Ni(OH)₂/ NiOOH peak upon addition of FFCA (evidence of a strong interaction between FFCA and the Ni(OH)₂ in those films) no shift is observed with the Co-containing films. This supports that the addition of Co interferes with the ability of FFCA to interact with and adsorb on the electrocatalyst.

We now examine the effect of NiOOH composition tuning on the rate of PD oxidation. Ideally, PD oxidation, whose rate depends on the applied potential rather than the chemical potential of oxidized Ni, should not be directly affected by shifts of the Ni(OH)₂/NiOOH peak. Indeed, the Ga-containing samples in which the Ni(OH)₂/NiOOH peak has been shifted anodically show I_{PD} values comparable to those of pristine NiOOH (Figure 6a). On the other hand, I_{PD} was decreased by Co incorporation. Given that no change in I_{PD} resulted from the anodic shift induced by Ga incorporation, we do not think the decrease in I_{PD} caused by Co incorporation is due to the cathodic shift of the Ni(OH)₂/NiOOH peak. Instead, we believe that it is most likely due to the additional effect Co incorporation has of unfavorably affecting HMF adsorption on catalytic sites. This is related to our discussion above showing that Co incorporation weakened FFCA adsorption.

Electrolysis using NiOOH of various compositions

To further study how shifting the Ni(OH)₂/NiOOH peak affects the activity for HMF oxidation, we performed constant potential electrolysis at 0.55 V vs. Ag/AgCl of 5 mm HMF in pH 13 solutions using pristine, 31% Co-containing, and 6.7% Gacontaining films. The resulting *j*-*t* plots are shown in Figure S11, while the products detected by high-performance liquid chromatography (HPLC) at various values of charge passed are shown in Figure 8.

The data in Figure 8 shows there is very little difference between the electrolysis results using the pristine and the Gacontaining films. The current densities generated by these films during the electrolysis were also comparable (Figure S11). The overall similarity between these results is unsurprising based on the rate deconvolution data reported above; while the Ga incorporation did shift the preferred pathway to favor indirect oxidation of HMF a bit more (38% indirect vs. 28% indirect) the overall current density was similar. Moreover, as shown above, Ga incorporation would not have much effect on the conversion of FFCA to FDCA (which appears to be the slowest step) because the oxidation of FFCA is controlled by the adsorption step and not η_{ind} .

Incorporation of Co into the films did produce more substantial changes in the electrolysis results, though the overall intermediate profile is still similar. The biggest change is in the current density. This is as expected based on the rate deconvolution experiments which show the Co-containing films are less active for both HMF and FFCA oxidation, likely due primarily to weaker adsorption, though the lower oxidizing power of the Co-containing NiOOH also likely played a role in suppressing HMF oxidation through the indirect pathway. The changes to the intermediate profile, while still fairly minor, are more noticeable than the differences between the pristine and Ga-containing cases. DFF accumulates to roughly twice the level as it does in the pristine and Ga-containing cases, likely due to the shift toward PD oxidation (which favors DFF formation) induced by Co incorporation. Additionally, at earlier amounts of



Figure 8. Change in concentration of HMF and its oxidation products over charge passed at 0.55 V vs. Ag/AgCl in pH 13 solutions containing 5 mm HMF using Co-containing, pristine, and Ga-containing NiOOH.



charge passed more FFCA accumulates relative to the FDCA formed, likely due to the suppressed kinetics for FFCA oxidation causing more of the molecules to get "stuck" at this least reactive intermediate before eventually being oxidized to FDCA. Additionally, there is less FDCA formed after the stoichiometric amount of charge has been passed and more of the initial HMF has gone missing and is not found either as unreacted HMF or as any of the detectible oxidation products. This is because the less reactive Co-containing films took longer to pass the set charge and HMF and its oxidation intermediates, which are not completely stable in pH 13, degraded over time before being converted into FDCA.

Conclusion

In this study, we have provided a comprehensive mechanistic understanding of 5-hydroxymethylfurfural (HMF) oxidation on NiOOH using our rate deconvolution method. We showed that 2,5-diformylfuran (DFF) and 5-formyl-2-furancarboxylic acid (FFCA), which contain only an aldehyde group, are primarily oxidized through the indirect pathway, while 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), which contains only an alcohol, is oxidized primarily through the potential-dependent (PD) pathway. For HMF, which contains both an aldehyde and an alcohol, which oxidation pathway dominates (and thus which group tends to be oxidized first) depends on the oxidation conditions. Under the open-circuit condition, where only indirect oxidation is allowed, the aldehyde group was preferentially oxidized first, resulting in more formation of HMFCA than DFF. However, when 0.55 V vs. Ag/AgCl was applied and caused PD oxidation to be dominant, the alcohol group was instead preferentially oxidized first to form DFF. Moreover, the 0th order dependence with respect to charge in the NiOOH film observed for HMFCA, DFF, and FFCA oxidation allowed us to conclude that those molecules can adsorb on Ni²⁺ sites in addition to the oxidized Ni sites and can be oxidized through hydrogen atom transfer (HAT) to adjacent oxidized Ni sites, meaning the adsorption site and the site where HAT occurs need not be the same for these molecules. Also, for indirect oxidation of these molecules, the adsorption step appears to be rate limiting, with the subsequent HAT steps being fast unless the percentage of Ni sites in the oxidized state is very low.

We also examined the effect on HMF oxidation of shifting the Ni(OH)₂/NiOOH peak through composition tuning of NiOOH. The Ni(OH)₂/NiOOH peak position had a direct impact on the rate of indirect oxidation of HMF because it affected the overpotential for HAT, a step important for determining the rate of HMF oxidation. It did not, however, have much impact on the indirect oxidation of FFCA because for FFCA oxidation adsorption is the rate-determining step. Co incorporation does significantly decrease the rate of FFCA oxidation; however, this is not due to shifting the Ni(OH)₂/NiOOH peak position but rather by hindering FFCA adsorption. Anodically shifting the Ni(OH)₂/NiOOH peak through Ga incorporation did not have a noticeable impact on PD oxidation as the Ni(OH)₂/NiOOH peak position does not have a direct impact on the rate of PD oxidation. As with indirect oxidation of FFCA, Co incorporation did considerably decrease the rate of PD oxidation, but this was due to hindering adsorption and not because of the cathodic shift of the $Ni(OH)_2/NiOOH$ peak.

The results presented here reveal that the direct effect of shifting the potential of the Ni(OH)₂/NiOOH couple on the performance for HMF oxidation is modest. This insight suggests those seeking to make catalyst modifications to further improve the performance of NiOOH electrocatalysts toward HMF oxidation should focus on optimizing other catalyst properties (such as adsorption energy and morphology) rather than on tuning the potential of the Ni(OH)₂/NiOOH couple. However, for other organic species where indirect vs. PD oxidation can lead to different products, tuning the potential of the Ni(OH)₂/NiOOH couple could be an important tool for altering the selectivity of the reaction.

Experimental Section

Materials

The chemicals employed were all acquired from commercial sources and used without further purification. HMF (97%, Alfa Aesar), HMFCA (98%, Astra Tech), DFF (97%, Sigma Aldrich), FFCA (>98.0% TCl), FDCA (>98.0%, TCl), potassium hydroxide (\geq 85%, Sigma Aldrich), Ni(NO₃)₂·6H₂O (99%, Acros), KNO₃ (99%, Alfa Aesar), Ga(NO₃)₃ (99.9%, Alfa Aesar), Co(NO₃)₂ (98%, Sigma Aldrich), HNO₃, 70% (\geq 99.999%, Sigma Aldrich), Ni standard for ICP (1000±2 mgL⁻¹, Sigma Aldrich), Ga standard for ICP (1000±2 mgL⁻¹, Sigma Aldrich), Co standard for ICP (1000±2 mgL⁻¹, Sigma Aldrich). All solutions were prepared using deionized water (Barnstead Epure water purification system, resistivity > 18 MΩ cm).

Ni(OH)₂ electrode preparation

Amorphous α -Ni(OH)₂ films were prepared using an established technique featuring electrochemical nitrate reduction.^[36] This produces hydroxide, raising the local pH at the WE and causing Ni(OH)₂ to deposit on the WE to form a Ni(OH)₂ film. This process was controlled with a SP-200 potentiostat/EIS (BioLogic Science Instrument) and conducted with a 3-electrode setup in a single compartment glass cell. The WE was FTO, the counter electrode (CE) was Pt, and the reference electrode (RE) was Ag/AgCl (4 M KCl). The FTO WEs were prepared by cutting larger FTO plates into 2.5 cm×1 cm strips after which Cu tape was attached to the top to provide electrical contact. The FTO was then masked with electroplating tape (3 M Company) with a 0.5 cm² hole punched in it so that a well-defined conductive surface area was exposed. For the films that would be used in electrolysis, two 0.5 cm² holes were punched in the tape instead of one to increase the electrode surface area without changing the nature of the electrode. The Pt CE were prepared by sputter coating a 20 nm Ti adhesion layer followed by 100 nm of Pt onto clean glass slides. To prepare the thin and pristine Ni(OH)₂ films used for most experiments in this work a current density of -0.25 mA cm^{-2} was maintained for 45 s in an aqueous plating solution consisting of 10 mm Ni(NO₃)₂·6H₂O and 30 mm KNO₃. The thicker Ni(OH)₂ film used for one electrolysis was prepared using a larger FTO WE with 4 cm² exposed to the solution. The deposition solution was 50 mm Ni(NO₃)₂ and a current of -0.5 mA cm^{-2} was maintained for 6 min. The Ni(OH)₂ films containing Co and Ga were prepared by adding an amount of $Co(NO_3)_2$ (1 or 2 mm) or $Ga(NO_3)_3$ (0.5 or 1 mm) to the deposition

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solution used for the thin pristine Ni(OH)₂ deposition (10 mM Ni(NO₃)₂ and 30 mM KNO₃). The current density and deposition time were optimized for each deposition solution to give a uniform Ni(OH)₂ film with a comparable amount of Ni as in the pristine case and were as follows: 1 mM Co (-0.25 mA cm⁻², 54.5 s), 2 mM Co (-0.25 mA cm⁻², 57 s), 0.5 mM Ga (-1.2 mA cm⁻², 14 s), 1 mM Ga (-1.2 mA cm⁻², 18 s). After deposition, all of the Ni(OH)₂ films were rinsed with > 18 MΩ cm water and then dried with an air stream.

Electrochemical experiments

CVs and LSVs were performed using a 3-electrode setup in a glass single compartment. Ni(OH)₂ films were used as the WE, Ag/AgCl as the RE, and Pt as the CE. CVs and LSVs were performed by starting at open circuit and sweeping the potential first in the positive direction at a scan rate of 10 mV s⁻¹. For all CVs the potential was cycled at least twice, and the curves shown are from the second cycle. For the stirred CVs, the solution was rapidly stirred by a magnetic stir bar while the potential was being scanned.

Electrolysis was performed with the same 3-electrode setup described above, but in a glass divided cell rather than a single cell. The two compartments were separated by a glass frit, and each was filled with 14 mL of solution. The anolyte was a pH 13 solution of 5mm HMF unless specified otherwise while the catholyte was just a pH 13 KOH solution. The anode compartment was equipped with a stir bar and was rapidly stirred throughout the electrolysis. To allow the electrolysis to be completed more quickly despite using thin Ni(OH)₂ WEs that were only 0.5 cm² in surface area, multiple Ni(OH)₂ electrodes were immersed and used simultaneously. To do this, as mentioned above, when depositing the Ni(OH)₂ to be used for an electrolysis two 0.5 cm² holes were punched in the masking tape to allow two Ni(OH)₂ to be deposited onto the same FTO plate. For the electrolysis using pristine and Gacontaining films four of these FTO plates were arranged together (two plates back-to-back then one more on each side so the faces with the Ni(OH)₂ were all 90° apart). These were then joined together and brought into electrical contact with one another by wrapping more Cu tape around the Cu tape "handles" affixed to the FTO plates. This allowed all 4 FTO plates (for a total of eight 0.5 cm² Ni(OH)₂ electrodes) to be immersed and polarized simultaneously. For the Co-containing case, to allow the electrolysis to be completed in a comparable amount of time despite the lower current density, two of these four FTO plate arrangements were taped together side by side for a total of sixteen 0.5 cm² Cocontaining electrodes immersed in solution. In all cases, the Cu tape was well above the solution level so only the immersed Ni(OH)₂ electrodes could participate in HMF oxidation.

Electrolysis was performed at 0.55 V vs. Ag/AgCl unless specified otherwise and proceeded until the stoichiometric amount of charge was passed for full conversion of the HMF to FDCA (40.52C). The applied bias was paused after specified amounts of charge passed (generally, 5, 10, 15, 20, and 30C) so an aliquot (0.15 mL) could be drawn from the anolyte solution for analysis by HPLC, after which the potential was applied once more. The remaining charge to be passed was adjusted to account for the slightly lower solution volume after removal of the aliquots, so the true charge passed for each electrolysis was a bit less than 40.52C.

Product analysis

Product analysis for the aliquots drawn from the electrolysis solutions was achieved by HPLC performed using a Shimadzu Prominence-i LC-2030C 3D HPLC system equipped with an internal UV/Vis detector. The mobile phase was an aqueous solution of

0.1% sulfuric acid at a flow rate of 0.5 mLmin⁻¹ in isocratic mode. Ten microliters of the sample aliquots were injected into a 300 mm×7.8 mm ICSep ICE-Coregel 87H3 column (Transgenomic) and the column oven temperature was maintained at 65 °C. Product concentration was determined by comparing the peak position and intensity to those of standard solutions of known concentration. Retention times of 20, 23, 27, 32, and 39 min corresponded to FDCA, HMFCA, FFCA, HMF, and DFF, respectively. The UV/Vis signal whose intensity was used for quantification was analyzed at the λ_{max} for each compound with wavelength of 262, 258, 281, 283, and 288 nm corresponding to FDCA, HMFCA, FFCA, HMF, and DFF, respectively.

ICP-MS

The Ni and Co/Ga amount in our deposited films was analyzed by first dissolving the films in 10 mL solutions of 1 vol% nitric acid (70%, trace metal grade) in polypropylene centrifuge tubes. For each of the NiOOH conditions, 3 separate samples were prepared and analyzed by ICP and their results averaged to give the amount of Ni and Co/Ga in a film displayed in Table 1. Prior to being dissolved these films were used to conduct 2 CV cycles in a pH 13 solution to ensure they were in the same state films would be in prior to rate deconvolution analysis. The solutions were analyzed using a triple quadrupole inductively coupled plasma mass spectrometer (Agilent 8900 ICP-QQQ). For each sample, intensity data was collected in triplicate and averaged for ⁵⁹Co, ⁵⁸Ni, ⁶⁰Ni, ⁶⁹Ga, and ⁷¹Ga in the He gas mode. This intensity data was converted to concentrations by comparison with calibration curves collected just prior to sample measurement by analyzing freshly prepared standard solutions. For elements where more than one isotope was analyzed (Ni, Ga) the concentrations produced by both were averaged to give the concentration of the sample.

SEM

SEM images of the as-deposited thin $Ni(OH)_2$ films were obtained using a LEO Supra 55 VP (Zeiss) scanning electron microscope at an accelerating voltage of 5 kV.

Rate deconvolution procedure

Our three-step rate deconvolution procedure (Figure S3) has been described in detail elsewhere,^[22] so only a brief description will be provided here. The process was performed using a rapidly stirred, 30 mL aqueous solution containing the organic species in a sealed single-cell glass compartment with a 3-electrode setup. A thin Ni(OH)₂ film deposited according to the procedure outlined above was used as the WE, Ag/AgCl as the RE, and Pt mesh as the CE. Prior to its use in rate deconvolution experiments, each Ni(OH)₂ film was used to collect a CV in a pH 13 aqueous KOH solution (2 cycles with switching potentials of 0.9 and 0 V vs. Ag/AgCl). This was to confirm the Ni(OH)₂/NiOOH peak and water oxidation behavior of each film was consistent.

In the first step of the three-step procedure, a fixed potential (generally 0.55 V vs. Ag/AgCl) was applied to the WE in a rapidly stirred solution until the current reached a steady state value (typical 45 s). This converts the film into the steady-state condition it would be in during a potentiostatic electrolysis at the applied potential. Both the indirect and PD oxidation pathways are active during this step. In the second step, potential is no longer applied, and the film is left to sit in the stirred solution at open-circuit condition. During this time neither PD oxidation nor reoxidation of Ni(OH)₂ can occur since both require applied bias; however, the



indirect pathway can still occur as it proceeds through chemical (rather than electrochemical) HAT steps. This reduces a portion of the higher valent Ni sites generated during the first step back to Ni(OH)2. During the third step, the higher valent Ni sites still remaining after step 2 are rapidly reduced back to Ni(OH)₂ by sweeping the potential from open circuit to 0 V vs. Ag/AgCl at a scan rate of $1\,V\,s^{-1}$ and then holding the potential at $0\,V$ for 20 s. The magnitude of the charge passed during this third, reductive step corresponds to the amount of charge still stored in the film after some of it was used in step 2 to oxidize the organic species through the indirect pathway. Repeating this whole 3-step process with different times stirring at open circuit in step 2 allowed us to construct plots showing the disappearance of charge from the film as a function of time at open circuit. This was used to generate kinetics equations and determine the rate of charge loss from the NiOOH film at 0 s at open circuit, which corresponds to the rate of the indirect pathway under electrolysis conditions at the potential applied in step 1.

The specific kinetics equations used to determine l_{ind} from the rate deconvolution plots depends on the observed relationship between charge stored in the film and the rate of charge loss from the film (Table S1). For FFCA, HMFCA, and DFF, plots of charge vs. time were highly linear across the timeframe of interest, indicating oxidation of those species follows 0th order kinetics with respect to charge loss from the film across this time span. As such, the rate of charge loss from the film at time *t* can be described using a pseudo-0th order kinetics expression [Eq. (3)] where $k_{obs,ind}$ [Cs⁻¹] is the magnitude of the slope of the charge vs. time plot:

$$-\frac{\mathrm{d}Q_{\mathrm{film}}(t)}{\mathrm{d}t} = k_{\mathrm{obs,ind}} \tag{3}$$

When the NiOOH film is in the same state as it is in during a constant potential electrolysis (i.e., after 0 s at open circuit in the stirred solution after the initial constant potential step) the rate of charge loss from the film due to chemical oxidation will be equal to the rate of the indirect process during a constant potential electrolysis at the potential applied in step 1 [Eq. (4)]. For the 0th order case, because the rate of charge loss is independent of time and determined only by $k_{obs,ind}$ [C s⁻¹], l_{ind} [mA cm⁻²] can be obtained by simply multiplying $k_{obs,ind}$ by 1000 and dividing by the electrode area (0.5 cm²).

$$-\frac{\mathrm{d}Q_{\mathrm{film}}(t=0)}{\mathrm{d}t} = I_{\mathrm{ind}} \tag{4}$$

For HMF, while charge vs. time plots are not linear, ln(charge) vs. time plots are, which means the loss of charge due to chemical oxidation is best modeled as being 1st order in charge in the NiOOH films (Table S1). This means that for HMF, the rate of charge loss from the film can be described using a pseudo first order rate equation [Eq. (5)] instead of the pseudo 0th order rate equation shown in Equation (3). Here $k_{obs,ind}$ (s⁻¹) is obtained from the magnitude of the slope of the ln(charge) vs. time plots, and Q_t is the charge stored in the NiOOH film at time *t* as measured by the magnitude of charge that must be passed to reduce the film from the state it is in at time *t* to the Ni(OH)₂ resting state.

$$-\frac{\mathrm{d}Q_{\mathsf{film}}(t)}{\mathrm{d}t} = k_{\mathsf{obs,ind}} \times Q_{\mathsf{t}} \tag{5}$$

As shown in Equation (4), solving Equation (5) for t=0 will yield l_{ind} . This can be done as long as we known the charge stored in the film when t=0, Q_0 . The value of Q_0 can be found from the *y*-intercept of the ln(charge) vs. time plot since this will be equal to $ln(Q_0)$. In either case, once I_{ind} is known it can be compared to the steady-state current observed in step 1 of the rate deconvolution process (I_{tot}) to calculate the value of I_{PD} according to Equation (1).

When conducting the rate deconvolution analyses for a given condition (organic species, concentration, NiOOH composition) each data point in the kinetics plots (ln(charge) vs. time or charge vs. time) was obtained by averaging results from four different measurements obtained with four different Ni(OH)₂ films. When obtaining this data, each Ni(OH)₂ film was used to collect no more than four data points. This is because the rapid reduction in the third step of the rate deconvolution process can cause the films to gradually become deactivated upon repeated use for deconvolution trials (i.e., the amount of positive charge stored for a given condition can decrease for successive trials). Additionally, whenever a new Ni(OH)₂ film was used, the solution containing the organic species was also replaced with a fresh solution. Furthermore, we developed a procedure to monitor and correct for any differences in initial active Ni content between films as well as any slight film deactivation that occurs from repeated use. These procedures, which are described in detail in the Supporting Information, allowed us to adjust the data in such a way that any variations in active Ni sites from film to film or trial to trial were accounted for and did not interfere with the measurement.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Catalysis Science under Award DE-SC0020983.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: 2,5-furandicarboxylic acid · 5hydroxymethylfurfural · electrocatalysis · electrochemistry · NiOOH

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Manuscript received: April 3, 2022 Revised manuscript received: May 5, 2022 Accepted manuscript online: May 6, 2022 Version of record online: May 24, 2022