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# A Comparative Study of Nickel, Cobalt, and Iron Oxyhydroxide Anodes for the Electrochemical Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid

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### Abstract

2,5-furandicarboxylic acid (FDCA) has received increasing attention as a nearmarket platform chemical that can potentially replace terephthalic acid in the production of commercial and high-performance polymers, such as polyethylene terephthalate. FDCA can be obtained from the oxidation of 5-hydroxymethylfurfural (HMF), which is produced from the dehydration of C-6 monosaccharides obtained from cellulosic biomass. Recently, various heterogeneous Ni- and Co-based electrocatalysts were reported that can efficiently oxidize HMF to FDCA. The actual catalytically active species of these catalysts are most likely NiOOH and CoOOH or species related to NiOOH and CoOOH. However, the intrinsic catalytic properties of NiOOH and CoOOH for HMF oxidation have yet to be carefully and systematically investigated. In this study, we prepared thin and thick sets of NiOOH, CoOOH, and FeOOH films having comparable numbers of metal sites to systematically and methodically compare the intrinsic catalytic activity of these materials for HMF oxidation in a 0.1 M KOH (pH 13) solution. Our investigation revealed that they have distinctively different catalytic abilities for HMF oxidation. The use of extremely thin MOOH films containing limited numbers of catalytic centers allowed us to resolve anodic currents that were generated from HMF oxidation by multiple different oxidation pathways. By comparing the voltammetric results of thin and thick films, the effect of the film thickness on the current generated by different oxidation pathways could be observed. The thick set of MOOH films was also used to compare the performances of these films for constant potential HMF oxidation and product analysis. The work herein contributes to a better understanding of the mechanisms of HMF oxidation on Ni-, Co-, and Fe- containing heterogeneous electrocatalysts whose surfaces are covered by their hydroxide and oxyhydroxide phases.

**Keywords:** 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid, nickel oxyhydroxide, cobalt oxyhydroxide, iron oxyhydroxide, electrocatalyst, alcohol oxidation, electrochemical oxidation

## 1. Introduction

The valorization of cellulosic biomass into building-block chemicals and fuels has gained increasing attention as a potential carbon-neutral route toward achieving independence from fossil fuels.<sup>1-5</sup> Among the various useful molecules that can be obtained from biomass, 2,5-furandicarboxylic acid (FDCA) is a versatile near-market platform chemical with applications ranging from fine chemicals to pharmaceuticals to agrochemicals.<sup>6-11</sup> FDCA has also received particular attention as a promising replacement for terephthalic acid (TA) in the production of commercial and high-performance polymers, whose furan-containing analogues have been shown to exhibit superior physicochemical properties to those containing petroleum-derived TA.<sup>12-15</sup> FDCA can be obtained from the oxidation of 5-hydroxymethylfurfural (HMF), a product of the dehydration of C-6 monosaccharides, via the oxidation of both the alcohol and aldehyde groups to carboxylic acids (Figure 1).



Figure 1. Two possible pathways for HMF oxidation to FDCA.

Conventional methods used to oxidize HMF to FDCA typically include the use of high air or  $O_2$  pressures (3-20 bar), elevated temperatures (30-130 °C), and precious metal heterogeneous catalysts (Au, Pd, and Pt).<sup>7,10,16-21</sup> Recently, the electrochemical oxidation of HMF has received increasing attention due to its advantages of being environmentally benign, using water as the oxygen source, and proceeding at ambient temperatures and pressures without the need for chemical oxidizing agents.<sup>22-27</sup>

Electrochemical oxidation of HMF was investigated as early as 1991 using  $Ni(OH)_2/NiOOH$  covered Ni mesh, achieving an isolated yield of 71% and a Faradaic efficiency (FE) of 84% for FDCA production in pH 14.<sup>28</sup> More recently, Ni<sup>29</sup> or Ni-containing compounds such as Ni<sub>2</sub>P,<sup>30</sup> Ni<sub>3</sub>S<sub>2</sub>,<sup>31</sup>, and NiFe layered double hydroxides<sup>32</sup> have been shown to achieve high to near-quantitative FDCA yields and FEs in pH 14. In

addition, a recent report demonstrated an electrochemical FDCA production system based on a flow reactor with a Ni/NiOOH electrode which achieved an FDCA yield of 89% and a FE of 80% when using a highly concentrated HMF solution (~ 0.65 M) at pH 12.<sup>33</sup> Co-based compounds such as Co-P<sup>34</sup> and Co-metalloid alloys<sup>35</sup> have also been shown to achieve an FDCA yield and FE of > 90%.

The focus of most previous studies was to achieve high performances for HMF oxidation by using electrocatalysts deposited on high surface area 3D porous substrates (e.g. 3D Ni foam<sup>29-31</sup>, 3D Cu foam<sup>34</sup>, and carbon paper<sup>32</sup>). Also, many studies used catalysts that may not maintain their initial composition and structure under strongly anodic and alkaline conditions. In these studies, the actual catalytically active species may have been NiOOH and CoOOH or species related to NiOOH and CoOOH. Therefore, gaining in-depth understanding of the catalytic properties of NiOOH and CoOOH for HMF oxidation would be highly beneficial to better understand the properties of more complex, chemically unstable catalysts.

NiOOH has been reported to serve as a catalyst for alcohol oxidation through the conversion between Ni(OH)<sub>2</sub> and NiOOH; NiOOH is reduced to Ni(OH)<sub>2</sub> by oxidizing various aliphatic and aromatic alcohols (Eq. 1), and NiOOH is regenerated by the electrochemical oxidation of Ni(OH)<sub>2</sub> (Eq 2).<sup>36-37</sup> In this case, the anodic current obtained during alcohol oxidation is not due to direct oxidation of alcohol on NiOOH but rather due to the regeneration of NiOOH from Ni(OH)<sub>2</sub>, which is formed as a consequence of alcohol oxidation. This mechanism is referred to as indirect Ni(OH)<sub>2</sub>/NiOOH-mediated alcohol oxidation. The mechanism of CoOOH for alcohol oxidation is also reported to involve the conversion between Co(OH)<sub>2</sub> and CoOOH.<sup>38</sup>

NiOOH (s) + alcohol (aq) 
$$\rightarrow$$
 Ni(OH)<sub>2</sub> (s) + alcohol<sub>oxidized</sub> (aq) (1)

$$Ni(OH)_2(s) + OH^-(aq) \rightarrow NiOOH(s) + H_2O(l) + e^-$$
(2)

The purpose of the current study is to systematically investigate and compare the intrinsic catalytic properties of NiOOH, CoOOH, and FeOOH for HMF oxidation. Since MOOH (M = Ni, Co, and Fe) have often been investigated and compared as water oxidation catalysts, it would also be interesting and informative to compare their properties for HMF oxidation. For this purpose, NiOOH, CoOOH, and FeOOH films

were prepared as extremely thin, featureless films so that their intrinsic catalytic properties could be investigated without interferences caused by differences in morphology, surface area, and resistivity of these film. The use of extremely thin MOOH films containing limited numbers of catalytic sites allowed us to resolve anodic currents that were generated by HMF oxidation through previously unreported pathways for alcohol oxidation as well as the well-known M(OH)<sub>2</sub>/MOOH-mediated oxidation. The results discussed in this study will provide a better understanding of electrochemical HMF oxidation on MOOH electrodes, which may be useful for designing better MOOH-based catalysts for the electrochemical oxidation of other organic molecules.

## 2. Experimental Section

**Materials.** HMF (97%, Alfa Aesar), DFF (98%, TCI America), HMFCA (95%, Oxchem), FFCA (98%, TCI America), FDCA (97%, AstaTech Inc.), Ni(NO<sub>3</sub>)<sub>2</sub> • 6H<sub>2</sub>O (99%, Acros), Co(NO<sub>3</sub>)<sub>2</sub> • 6H<sub>2</sub>O (98%, Sigma-Aldrich), FeSO<sub>4</sub> • 7H<sub>2</sub>O (99%, Acros), KNO<sub>3</sub> (99%, Alfa Aesar), and KOH (85%, Sigma-Aldrich) were used without further purification. Deionized water (Barnstead E-pure water purification system, resistivity >18 MΩ cm) was used to prepare all solutions.

Electrodeposition of thin Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, and Fe(OH)<sub>2</sub> films on FTO. Thin Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, and Fe(OH)<sub>2</sub> electrodes were prepared via electrochemical nitrate reduction using an SP-200 potentiostat/EIS (BioLogic Science Instrument). A three-electrode setup consisting of an FTO working electrode (4 cm<sup>2</sup>), Pt counter electrode, and Ag/AgCl (4 M KCl) reference electrode was used. Pt counter electrodes were prepared by sputter coating a 20 nm Ti adhesion layer followed by 100 nm of Pt on pre-cleaned glass slides. Thin Ni(OH)<sub>2</sub> films were deposited from an aqueous plating solution containing 100 mM Co(NO<sub>3</sub>)<sub>2</sub> • 6H<sub>2</sub>O. Fe(OH)<sub>2</sub> films were prepared from an N<sub>2</sub>-purged solution containing 100 mM FeSO<sub>4</sub> • 7H<sub>2</sub>O and 200 mM KNO<sub>3</sub>. The pH of each solution was not adjusted prior to deposition. Thin Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, and Fe(OH)<sub>2</sub> films were

prepared potentiostatically by applying -0.9 V vs. Ag/AgCl and passing 5 mC cm<sup>-2</sup>. After deposition, the films were rinsed with deionized water and dried in air. The resulting films contained the same amount of electrochemically active metal ions, which was determined by comparing the charges necessary to oxidize the as-deposited thin M(OH)<sub>2</sub> films to MOOH films (Eq. 3).

$$M(OH)_2(s) + OH^-(aq) \rightarrow MOOH(s) + H_2O(l) + e^-$$
(3)

For this experiment, the oxidation of M(OH)<sub>2</sub> films was performed potentiostatically in a 0.1 M KOH solution using a three-electrode setup in an undivided cell at 1.45 V vs. RHE, which is below the onset for water oxidation for all materials, until the anodic current decayed to zero. Under this condition, the number of electrons required to complete the reaction equals the number of  $M^{2+}$  ions present in the M(OH)<sub>2</sub> film. The measured charge required to convert the as-deposited thin M(OH)<sub>2</sub> films was approximately 0.9 mC cm<sup>-2</sup> for all films, confirming that the as-deposited films contain the same amount of electrochemically active  $M^{2+}$  ions. By dividing the coulombs/cm<sup>2</sup> by the electric charge carried by a single electron, the number of metal sites/cm<sup>2</sup> could be easily calculated (Table S1). For Fe(OH)<sub>2</sub>, which spontaneously oxidizes to FeOOH over time under ambient conditions, special care was necessary; the electrochemical oxidation of Fe(OH)<sub>2</sub> was performed immediately after deposition of Fe(OH)<sub>2</sub> in an N<sub>2</sub>-purged 0.1 M KOH solution under an N<sub>2</sub> blanket. We note that typical electrical double layer capacitance measurements cannot be used to compare active metal sites present in M(OH)<sub>2</sub> films because of the insulating nature of these films.<sup>39</sup> The method described here, which we report for the first time, provides a simple yet accurate way to measure the active metal sites present in  $M(OH)_2$  films.

Electrodeposition of thick Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, and Fe(OH)<sub>2</sub> films on FTO. Thick Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, and Fe(OH)<sub>2</sub> electrodes were prepared using the same three-electrode setup used for the deposition of thin films. Thick Ni(OH)<sub>2</sub> films were deposited from an aqueous plating solution containing 10 mM Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 30 mM KNO<sub>3</sub>, and thick Co(OH)<sub>2</sub> films were deposited from a plating solution containing 10 mM Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 30 mM KNO<sub>3</sub>. Fe(OH)<sub>2</sub> films were prepared from an N<sub>2</sub>-purged

solution containing 10 mM FeSO<sub>4</sub>·7H<sub>2</sub>O and 50 mM KNO<sub>3</sub>. We note that all the plating solutions used to deposit thicker films commonly contained less metal ion precursors than those used to deposit thin films. This is because the use of more dilute solutions facilitated diffusion-limited growth of M(OH)<sub>2</sub>, resulting in the deposition of higher surface area films. The pH of each solution was not adjusted prior to deposition. Thick films were prepared galvanostatically by applying -0.25 mAcm<sup>-2</sup> for 12 min. After deposition, the films were rinsed with deionized water and dried in air. As with the thin M(OH)<sub>2</sub> films, the resulting as-deposited thick M(OH)<sub>2</sub> films contained the same amount of electrochemically active metal ions, which was confirmed using the same method described above. The charge necessary to convert the as-deposited thick M(OH)<sub>2</sub> films to MOOH was approximately 0.15 C cm<sup>-2</sup> for all films (Table S2).

**Characterization of prepared electrodes.** The surface morphology of each film was examined by scanning electron microscopy (SEM) using a LEO 1530 microscope with an accelerating voltage of 2 kV. Powder X-ray diffraction (XRD) (Bruker D8 Advanced PXRD, Ni- filtered Cu K $\alpha$  radiation,  $\lambda = 1.5418$  Å) was used to determine the crystallinity of the M(OH)<sub>2</sub> and MOOH films. UV-vis absorption spectra were measured using a Cary 5000 UV-vis-NIR spectrophotometer (Agilent) fitted with an integrating sphere attachment. In this setup, the electrode is located in the center of the integrating sphere, and its absorbance is calculated from the measurement of the light that is both reflected from and transmitted through the electrode.

## **Electrochemical experiments.**

Linear sweep voltammetry and cyclic voltammetry experiments were performed using a three-electrode setup in an undivided cell. M(OH)<sub>2</sub> or MOOH electrodes were used as working electrodes, while Ag/AgCl (4 M KCl) and Pt were used as reference and counter electrodes, respectively. A 0.1 M KOH (pH 13) solution was used as the electrolyte, and 5 mM HMF, DFF, HMFCA, or FFCA was added to the solution when necessary. We selected the use of a pH 13 solution even though a higher catalytic performance of alcohol oxidation is expected at pH 14<sup>40</sup> because the instability of HMF at pH 14 is known to result in undesirable humin formation, which makes this condition

undesirable for practical purposes.<sup>41</sup> Voltammetry experiments were conducted by sweeping the potential in the positive direction from the open circuit potential (OCP) at a scan rate of 5 mV s<sup>-1</sup> at room temperature and without stirring. Experiments for the constant potential oxidation of HMF were carried out using a three-electrode setup in an H-shaped divided glass cell with fritted glass as a divider. Prior to constant potential oxidation of HMF, freshly prepared thick Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, and FeOOH anodes were subjected to a single LSV in the positive direction (scan rate 5 mV s<sup>-1</sup>) to ensure complete oxidation of the film. The oxidized films were then used as working electrodes, while Ag/AgCl (4 M KCl) and Pt were used as reference and counter electrodes, respectively. The working electrode compartment consisted of 14 mL of a 0.1 M KOH solution containing 5 mM HMF, while the counter electrode compartment contained 14 mL of a 0.1 M KOH solution. The electrochemical oxidation was carried out at room temperature with stirring at various potentials. The reaction was stopped after 40.52 C were passed, which is the stoichiometric amount of coulombs necessary to convert the given amount of HMF to FDCA. Although electrode potentials recorded in this study were measured against an Ag/AgCl (4M KCl) reference electrode, all of the potentials in this work are presented against the reversible hydrogen electrode (RHE) for ease of comparison with other reports that use electrolytes with different pH conditions. The conversion between potentials versus Ag/AgCl to potentials versus RHE was performed using Eq. 4. The potentials used in this study were not corrected for uncompensated IR drop.

 $E(vs. RHE) = E(vs. Ag/AgCl) + 0.1976 V + 0.059 \times pH$  (4)

**Product Analysis.** After constant potential electrolyses, 150  $\mu$ L of solution were taken from the working electrode compartment and were analyzed using a Shimadzu Prominence-i LC-2030C 3D HPLC system equipped with an internal UV-Vis detector to calculate HMF conversion and oxidation product yields. An aqueous mobile phase composed of 0.1% sulfuric acid was used at a flow rate of 0.5 mL min<sup>-1</sup> in isocratic mode. 10  $\mu$ L sample aliquots were injected directly onto a 300 mm × 7.8 mm ICSep ICE-Coregel 87H3 column (Transgenomic), and the column oven temperature was maintained at 65 °C. The identification of the products and calculation of their concentrations were determined from calibration curves by applying standard solutions of known concentration. Retention times of 20, 23, 27, 32 and 39 min correlated to FDCA,

HMFCA, FFCA, HMF and DFF, respectively. Because each compound exhibits a different light absorption profile, detection wavelengths of 262, 258, 281, 283 and 288 nm were chosen as  $\lambda_{max}$  for FDCA, HMFCA, FFCA, HMF, and DFF, respectively.

The following equations were used to calculate HMF conversion, product yield, and FE for FDCA production where F represents Faraday's constant, 96485 C mol<sup>-1</sup>.

HMF conversion (%) = 
$$\frac{\text{mol of HMF consumed}}{\text{mol of initial HMF}} \times 100\%$$
 (5)

Product yield (%) = 
$$\frac{\text{mol of product formed}}{\text{mol of initial HMF}} \times 100\%$$
 (6)

FE for FDCA production (%) = 
$$\frac{\text{charge used for FDCA production}}{\text{total charge passed}} \times 100\%$$
 (7)

$$= \frac{\text{mol of FDCA formed x (6 x F)}}{\text{total charge passed}} \times 100\%$$

## 3. Results and discussion

The MOOH electrodes (M = Ni, Co, and Fe) used in this study were prepared from  $M(OH)_2$  films that were electrodeposited onto FTO substrates by nitrate reduction from plating solutions containing  $M^{2+}$  ions and nitrate ions.<sup>42</sup> Nitrate reduction increases the local pH at the working electrode (Eq. 8) and decreases the solubility of  $M^{2+}$  at the electrode surface. As a result,  $M^{2+}$  ions precipitate and are deposited as  $M(OH)_2$  films on the working electrode (Eq. 9). Fe(OH)<sub>2</sub> films are not stable under ambient conditions and spontaneously convert to FeOOH over time after deposition. The Co(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> films are stable at ambient conditions and were converted to CoOOH and NiOOH films by applying an anodic potential when required.

$$NO_3^{-}(aq) + H_2O(l) + 2e^{-} \rightarrow NO_2^{-}(aq) + 2OH^{-}(aq)$$
(8)

$$M^{2+}(aq) + 2OH^{-}(aq) \rightarrow M(OH)_{2}(s)$$
(9)

# Voltammetric study of the intrinsic catalytic activity of thin MOOH films for electrochemical HMF oxidation

The electrocatalytic properties of NiOOH, CoOOH, and FeOOH were first investigated using linear sweep voltammetry (LSV). The films used for these experiments were composed of extremely thin, featureless, and uniform MOOH films that possess comparable amounts of electrochemically active sites (Table S1). Since these extremely thin films conformally coated the FTO substrate, the rough nanoparticle morphologies shown in their SEM images (Figure 2a-c) are mainly of the underlying FTO substrate (Figure S1). The use of these films ensured that any differences in the measured catalytic current between the three materials were strictly due to the materials' intrinsic catalytic ability for HMF oxidation rather than influences stemming from disparities in surface morphologies or unequal electrochemically active sites in the films. Furthermore, the small current densities generated by these thin films gave better resolution of currents generated from different HMF oxidation mechanisms, which most likely could not be resolved by previous studies due to their use of high surface area Ni- and Co-containing catalysts.



Figure 2. SEM images of thin (a) NiOOH, (b) CoOOH, (c) FeOOH films used for voltametic studies.

The LSVs of a thin NiOOH film obtained in 0.1 M KOH (pH 13) is shown in **Figure 3a**. The first LSV was obtained by sweeping the potential from the OCP to the positive direction using an as-deposited Ni(OH)<sub>2</sub> film in the absence of HMF. Because there was no HMF in solution, any oxidation features observed during the first sweep must be due to the oxidation of the film and water. The oxidation peak centered at 1.43 V vs. RHE is due to the oxidation of Ni(OH)<sub>2</sub> to NiOOH, which is followed by the anodic

# current onset at 1.51 V for water oxidation (Figure 3a, black line). In order to confirm that the oxidation of $Ni(OH)_2$ to NiOOH was completed during the first LSV, a second LSV was obtained immediately after the first scan. The second LSV no longer showed the oxidation peak due to the oxidation of $Ni(OH)_2$ to NiOOH and showed only anodic current associated with water oxidation, confirming that the complete conversion of $Ni(OH)_2$ to NiOOH was achieved by the first LSV (Figure 3a, blue line).



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**Figure 3.** LSVs of thin (a) Ni(OH)<sub>2</sub>, (b) Co(OH)<sub>2</sub>, and (c) FeOOH films in a 0.1 M KOH solution (scan rate: 5 mV s<sup>-1</sup>). Three consecutive LSVs were obtained in the same solution; the first (black) and second (blue) LSVs were performed in the absence of HMF, while the third (red) was performed after the addition of 5 mM HMF (a1: Ni(OH)<sub>2</sub>/NiOOH-mediated indirect oxidation; a2: direct oxidation on MOOH; a3: direct oxidation on M(OH)<sub>2</sub>).

After the second LSV, 5 mM HMF was added to the solution and the OCP of the NiOOH electrode was allowed to equilibrate, which took less than 3 min. The change in OCP was due to electron transfer between the NiOOH electrode and HMF; NiOOH can oxidize HMF as a chemical oxidant while being reduced to Ni(OH)<sub>2</sub> under the open circuit condition. Therefore, the third LSV, obtained after establishing equilibrium between the electrode and the HMF solution, showed the reappearance of the oxidation peak corresponding to the oxidation of Ni(OH)<sub>2</sub> to NiOOH (Figure 3a, red line). Furthermore, since the NiOOH that was electrochemically regenerated during the third LSV could immediately participate in HMF oxidation and be reconverted to Ni(OH)<sub>2</sub> to NiOOH when HMF was present in the solution. As a result, the Ni(OH)<sub>2</sub>/NiOOH peak was larger in the third LSV than in the first LSV, and this difference could be directly related to the rate of the Ni(OH)<sub>2</sub>/NiOOH-mediated HMF oxidation.

Previously, the Ni(OH)<sub>2</sub>/NiOOH-mediated oxidation was reported to be the only mechanism for alcohol oxidation by NiOOH (denoted as a1 in Figure 3a).<sup>36</sup> The mechanism in the a1 region is the same as when NiOOH is used as a chemical oxidant under the open circuit condition. The rate determining step for the Ni(OH)<sub>2</sub>/NiOOH-mediated oxidation is known to be the extraction of a hydrogen radical at the alpha position of the alcohol, which converts NiOOH to Ni(OH)<sub>2</sub>.<sup>36</sup> The electrochemical regeneration of NiOOH from Ni(OH)<sub>2</sub> (Eq. 2) was reported to be fast.<sup>36</sup> However, in addition to the Ni(OH)<sub>2</sub>/NiOOH-mediated oxidation, our LSV shows two additional oxidation features related to HMF oxidation. One is the presence of oxidation current that appears after the Ni(OH)<sub>2</sub>/NiOOH peak but before the onset of water oxidation (denoted as a2 in Figure 3a). The new oxidation mechanism in the a2 region appears to be enabled only when a potential more positive than the redox potential for the Ni(OH)<sub>2</sub>/NiOOH conversion is applied to the NiOOH electrode. Most likely, this new mechanism achieves

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HMF oxidation on the NiOOH surface without involving the conversion of NiOOH to Ni(OH)<sub>2</sub> and will be referred to as direct oxidation of HMF in this study.

The third oxidation feature is the presence of oxidation current (denoted as a3 in Figure 3a) appearing before the Ni(OH)<sub>2</sub>/NiOOH oxidation peak. This means that HMF can be oxidized directly on the Ni(OH)<sub>2</sub> surface without involving the formation of NiOOH. The direct electrochemical oxidation of cysteine on a Ni(OH)<sub>2</sub> electrode at potentials well below the redox potential of the Ni(OH)<sub>2</sub>/NiOOH conversion has been previously reported.<sup>43</sup>

The LSVs of NiOOH obtained in the presence of 5 mM DFF, HMFCA, or FFCA instead of 5 mM HMF are shown in Figure S2a. They all commonly show three oxidation features (a1, a2, and a3). However, the anodic current densities generated in each region vary depending on the substrate type because the functional groups attached to the furan ring can affect the kinetics of the three different oxidation mechanisms to different degrees.

The three LSVs obtained in the same manner with a thin  $Co(OH)_2$  film are shown in Figure 3b. We note that before obtaining these LSVs, the as-deposited  $Co(OH)_2$  was pre-treated with cyclic voltammograms (CVs). This is because not all of the electrochemically active Co<sup>2+</sup> sites in the as-deposited Co(OH)<sub>2</sub> film can undergo reversible oxidation and reduction between Co(OH)<sub>2</sub> and CoOOH.<sup>44</sup> In other words, the Co(OH)<sub>2</sub>/CoOOH peak obtained from the anodic scan of the first CV of the as-deposited film, where all electrochemically active  $Co^{2+}$  ions are oxidized, is always larger than the Co(OH)<sub>2</sub>/CoOOH peak obtained from subsequent CVs where only the Co<sup>2+</sup> that can be reversibly oxidized and reduced are oxidized. Performing CVs until successive scans were identical ensured that only the Co ions that can undergo reversible conversion between Co(OH)<sub>2</sub> and CoOOH participated in the LSVs shown in Figure 3b. This way, any difference in the Co(OH)<sub>2</sub>/CoOOH peak obtained with and without HMF could be unambiguously attributed to the effect of HMF. The CVs used for the pretreatment of the as-deposited Co(OH)<sub>2</sub> film are shown in Figure S3a. The CV pretreatment revealed that only approximately 34% of the  $Co^{2+}$  sites in the Co(OH)<sub>2</sub> film are electrochemically reversible (Table S1). This means that the number of active Co sites in the Co(OH)<sub>2</sub> film after the CV treatment is only  $\sim 1/3$  of the active Ni sites in the Ni(OH)<sub>2</sub> film since all of

the as-deposited  $M(OH)_2$  films were prepared to have the same number of initial electrochemically active M sites.

The first LSV of  $Co(OH)_2$  in Figure 3b shows a peak for the  $Co(OH)_2/CoOOH$  conversion centered at 1.14 V vs. RHE. This peak was followed by anodic current for water oxidation, which has an onset at around 1.50 V vs. RHE. The second LSV that was obtained immediately after the first scan in the same solution no longer shows the oxidation current corresponding to the conversion of  $Co(OH)_2$  to CoOOH, suggesting that all of the Co<sup>2+</sup> ions that can be reversibly oxidized to Co<sup>3+</sup> were oxidized during the first LSV.

Before obtaining the third LSV, 5 mM HMF was added to the solution and the OCP of the CoOOH electrode was allowed to equilibrate. The third LSV showed a reappearance of the Co(OH)<sub>2</sub>/CoOOH peak (denoted as a1 in Figure 3b), suggesting that under the open circuit condition, CoOOH oxidized HMF by serving as a chemical oxidant and was reduced to  $Co(OH)_2$ . However, we note that the  $Co(OH)_2/CoOOH$  peak shown in the third LSV is smaller than the peak shown in the first LSV. This is different from the case of NiOOH where the Ni(OH)<sub>2</sub>/NiOOH peak was enhanced when HMF was present. The smaller Co(OH)<sub>2</sub>/CoOOH peak in the third scan compared to that in the first scan suggests two things. First, not all Co<sup>3+</sup> ions that can reversibly undergo electrochemical Co(OH)<sub>2</sub>/CoOOH conversion are catalytically active for chemical HMF oxidation and, as such, only a fraction of  $Co^{3+}$  in CoOOH was converted to  $Co(OH)_2$  by HMF oxidation under the open circuit condition. Second, the Co(OH)<sub>2</sub>/CoOOH-mediated HMF oxidation is not as fast as the Ni(OH)<sub>2</sub>/NiOOH-mediated HMF oxidation. Therefore, HMF in the solution cannot rapidly regenerate Co(OH)<sub>2</sub> (which would re-oxidize to CoOOH) during the time scale of the LSV scan. This results in a negligible amount of the current enhancement for the Co(OH)<sub>2</sub>/CoOOH peak during the LSV scan when HMF is present.

CoOOH also generated anodic current for HMF oxidation in the potential region between the  $Co(OH)_2/CoOOH$  peak and the onset of water oxidation (denoted as a2 in Figure 3b). As in the case of NiOOH, the a2 mechanism likely achieves HMF oxidation on the CoOOH surface without involving the conversion of CoOOH to Co(OH)\_2.

However, unlike  $Ni(OH)_2$ ,  $Co(OH)_2$  did not show any sign that it can directly oxidize HMF on the  $Co(OH)_2$  surface through the a3 mechanism.

We note that for both NiOOH and CoOOH, a slight current enhancement after the onset of water oxidation is observed when HMF was present, meaning that HMF oxidation can occur concurrently with water oxidation. Since the formation of Ni<sup>4+</sup> and Co<sup>4+</sup> is possible in this potential region,<sup>45-46</sup> we expect that HMF oxidation in this region can also be achieved through an additional mechanism that involves the formation of Ni<sup>4+</sup> or Co<sup>4+</sup> sites.

The LSVs of CoOOH obtained in the presence of 5 mM DFF, HMFCA, or FFCA instead of 5 mM HMF are shown in Figure S3b. They all commonly show anodic currents for the Co(OH)<sub>2</sub>/CoOOH conversion, meaning that CoOOH can oxidize DFF, HMFCA, and FFCA under the open circuit condition. However, none of them showed an enhancement for the Co(OH)<sub>2</sub>/CoOOH peak current, suggesting that their rates of Co(OH)<sub>2</sub>/CoOOH-mediated oxidation are also very slow. They also commonly showed anodic currents for their oxidation on the CoOOH surface through the a2 mechanism in the potential region between the Co(OH)<sub>2</sub>/CoOOH peak and the onset for water oxidation. Again, the current densities in the a1 and a2 regions varied depending on the substrate type because the functional groups attached to the furan ring affect the kinetics of the different oxidation mechanisms to different degrees.

The LSVs of FeOOH show no catalytic activities for HMF oxidation (Figure 3c). Since FeOOH remains as FeOOH under the open circuit condition, the first LSV shows only anodic current for water oxidation, as does the second LSV. When HMF was added to the solution, FeOOH could not serve as a chemical oxidant for HMF under the open circuit condition as the redox potential of the Fe(OH)<sub>2</sub>/FeOOH conversion is too low (approximately 0.24 V vs. RHE). As a result, the LSV obtained with HMF present in solution also did not show any anodic features related to the Fe(OH)<sub>2</sub>/FeOOH conversion. Furthermore, no sign of direct HMF oxidation on FeOOH was observed. This result indicates that although FeOOH is catalytic for water oxidation, it does not demonstrate any apparent catalytic ability for HMF oxidation. When the LSVs of FeOOH were obtained in the presence of 5 mM DFF, HMFCA, or FFCA instead of 5 mM HMF

(Figure S3c), a current enhancement before water oxidation was observed only with DFF, meaning that only the oxidation of DFF can occur before water oxidation on FeOOH.

#### **Electrochemical HMF Oxidation Using Thick MOOH films**

Due to their extremely low surface area, the thin MOOH films used for the voltammetric analysis could not be used to investigate the full conversion of HMF to FDCA because it took too long to pass the stoichiometric amount of charge required for the conversion. Extremely long electrolysis reaction times resulted in undesirable complications during product analysis, such as water evaporation affecting product concentrations, base-induced non-electrochemical humin formation, and crossover of intermediates to the counter electrode compartment, which made it difficult to assess the true intrinsic catalytic activity of each material during electrolysis.

Therefore, a set of thick MOOH films were prepared to perform constant potential HMF oxidation and analyze the product yields and FEs for FDCA production. While the morphologies of the thicker films varied depending on the material, the thickness of each film was controlled such that each film possessed comparable amounts of initially electrochemically active metal sites (Table S2). We also note that although the thick MOOH films are thicker and have higher surface areas than the thin films used in the previous section, they are still deposited on flat 2D FTO substrates and have limited surface areas compared to electrodes prepared using 3D porous substrates that have considerable thickness in the millimeter range.<sup>29-31,34</sup> Therefore, the performances that can be achieved by our flat, thick films cannot be as good as the catalysts that were deposited on 3D substrates. Our goal of using thicker films was not to achieve high performances, but rather to make thick enough samples with controlled electrochemically active sites to examine the effect of film thickness on the LSVs of these films for HMF oxidation and perform product analysis to accurately compare the performances of NiOOH, CoOOH, and FeOOH for FDCA production.

The morphologies of the thick NiOOH, CoOOH and FeOOH electrodes are shown in Figure 4, which are identical to those of as-deposited  $M(OH)_2$  films. These films were commonly composed of 2D plates or sheets that roughen the surface, creating porosities. The NiOOH film was composed of contoured nanoparticles, each of which

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was comprised of compactly packed nanoplates (Figure 4a). The CoOOH film was composed of 2D sheets with micron-level lateral dimensions that were vertically aligned against the substrate (Figure 4b). The morphology of the FeOOH was similar to that of NiOOH, but the average size of the individual nanoplates in each cluster was slightly larger, thereby increasing the size of each cluster. (Figure 4c). X-ray diffraction studies showed that all MOOH films are amorphous (Figure S4).



**Figure 4.** SEM images of thick (a) NiOOH, (b) CoOOH and (c) FeOOH films deposisted on FTO substrates. The insets in (a)-(c) show a higher magnification image.

Prior to using these films for constant potential HMF oxidation, LSVs of the thick NiOOH, CoOOH, and FeOOH films were obtained using the same procedures used to analyze the thin films. This allowed us to observe how the increase in the surface area and the presence of metal ions in more diverse structural environments affect the current generation in the different catalytic regimes.

The first LSV of the thick Ni(OH)<sub>2</sub> film shows a much broader Ni(OH)<sub>2</sub>/NiOOH peak than the thin Ni(OH)<sub>2</sub> film (Figure 5a, black line). This is because the thick, high surface area Ni(OH)<sub>2</sub> film contains Ni<sup>2+</sup> ions in diverse structural environments, and their structural environment directly affects their oxidation potential in Ni(OH)<sub>2</sub>. Consequently, a fraction of Ni<sup>2+</sup> ions in the thick Ni(OH)<sub>2</sub> film is either easier or more difficult to oxide than the Ni<sup>2+</sup> ions present in a thin, uniform Ni(OH)<sub>2</sub> film. As a result, the onset of Ni(OH)<sub>2</sub> oxidation was as early as 1.15 V, and the conversion of Ni(OH)<sub>2</sub> to NiOOH was not completed before water oxidation occurred. Nonetheless, the complete conversion of Ni(OH)<sub>2</sub> to NiOOH occurred during the first LSV, which was confirmed by the second LSV that no longer showed the Ni(OH)<sub>2</sub>/NiOOH peak (Figure 5a, blue line).



**Figure 5.** LSVs of thick (a) Ni(OH)<sub>2</sub>, (b) Co(OH)<sub>2</sub>, and (c) FeOOH films in a 0.1 M KOH solution. Three consecutive LSVs were obtained in the same solution: the first (black) and second (blue) LSVs were performed in the absence of HMF, while the third (red) was performed after the addition of 5 mM HMF (scan rate: 5 mV s<sup>-1</sup>).

The use of the thick films also allowed us to easily observe changes in the appearance of the electrodes as the oxidation states of the films changed (Figure 6). The as-deposited  $Ni(OH)_2$  was opaque white, but the NiOOH film obtained after the first LSV was opaque brown (Figure 6a,c). Judging by the appearances of the films, it was evident that not just the surface but rather the bulk of the thick films were oxidized, which is consistent with the ion channel structure that permeates throughout the bulk of the material.<sup>47</sup>

Immediately after the second LSV was completed, 5 mM HMF was added to the solution and the OCP was monitored. In the presence of HMF under open circuit conditions, the color of the NiOOH electrode gradually changed from opaque brown to opaque white over the course of 30 min as NiOOH was converted to Ni(OH)<sub>2</sub> as a result of oxidizing HMF (Figure 6c-d). After 30 min, the OCP had stabilized, suggesting that all NiOOH was converted to Ni(OH)<sub>2</sub>. The color of the resulting Ni(OH)<sub>2</sub> was identical to that of as-deposited Ni(OH)<sub>2</sub>, visually confirming the complete conversion of NiOOH to Ni(OH)<sub>2</sub> by Ni(OH)<sub>2</sub>/NiOOH mediated HMF oxidation. The corresponding UV-vis absorption spectra of these films can be found in Figure S5.

	As-dep	osited		After anodic	After soak in	
Electrode	at 0 h (M(OH) <sub>2</sub> ) After 2 h		After CV	sweep (MOOH)	HMF solution at OCP	
Ni(OH)₂ /NiOOH	a	b		C	d	
Co(OH)₂ /NiOOH	e	f	g	h		
Fe(OH)₂ /FeOOH	j	k			m	

**Figure 6.** Photographs showing changes in appearance of the thick films used in this study after various treatments.

A third LSV was obtained in the presence of HMF. As in the case of the thin film analysis, the Ni(OH)<sub>2</sub>/NiOOH peak reappeared and the size of the peak was greatly enhanced. Since the width and magnitude of the Ni(OH)<sub>2</sub>/NiOOH peak is so large, the oxidation currents caused by the a2 and a3 mechanisms could no longer be resolved from the oxidation current caused by the a1 mechanism. This result explains why the three different oxidation mechanisms found in our voltammetric analysis using extremely thin films could not be observed in previous studies.

Similar to the thin Co(OH)<sub>2</sub> film, the LSVs of the thick Co(OH)<sub>2</sub> film were obtained after pretreating them with CVs. Although the as-deposited thick Co(OH)<sub>2</sub> film showed a light blue color, the Co(OH)<sub>2</sub> film after the CV treatment changed to a red-black color due to the irreversibility of the Co<sup>2+</sup>/Co<sup>3+</sup> conversion during the first CV cycle, as previously explained (Figure 6e-g). Consistent with the thin Co(OH)<sub>2</sub> film, the CV pretreatment showed that only approximately 34% of the initially electrochemically active Co<sup>2+</sup> sites are electrochemically reversible (Figure S3b, Table S2). When this film was used for the first LSV it turned an opaque black due to the formation of CoOOH (Figure 6h). The second LSV, which no longer showed the Co(OH)<sub>2</sub>/CoOOH peak, confirmed the complete conversion of Co(OH)<sub>2</sub> to CoOOH during the first LSV. When CoOOH was immersed in the HMF-containing solution, the color of the CoOOH electrode slowly changed back to dark red over the course of 25 h (Figure 6i), which is the same color of the Co(OH)<sub>2</sub>/NiOOH, confirming the slow rate of HMF oxidation by the Co(OH)<sub>2</sub>/CoOOH conversion.

The LSV curve obtained in the presence of 5 mM HMF shows a  $Co(OH)_2/CoOOH$  peak that is comparable to that shown in the first LSV obtained with  $Co(OH)_2$  in the absence of HMF (Figure 5b). The fact that the  $Co(OH)_2/CoOOH$  peak in the first and third LSVs look comparable suggest in this thicker and higher surface area CoOOH film, the  $Co^{2+}/Co^{3+}$  ions that reversibly participate in the electrochemical  $Co(OH)_2/CoOOH$  conversion are all catalytically active for HMF oxidation under the open circuit condition. However, no catalytic enhancement of the  $Co(OH)_2/CoOOH$  peak was observed, which was expected given the slow rate of HMF oxidation by CoOOH under the open circuit condition. As in the case of the thin CoOOH, the thick CoOOH

showed enhanced anodic current for HMF oxidation owing to the direct HMF oxidation on the CoOOH surface at potentials between the  $Co(OH)_2/CoOOH$  peak and the onset of water oxidation.

As with the thin FeOOH film, the thick FeOOH film showed only water oxidation current during both the first and second scans (Figure 5c, black and blue lines). Also, unlike NiOOH and CoOOH, the FeOOH film showed no change in color after the addition of 5 mM HMF (Figure 6j-m) because FeOOH cannot serve as an oxidant for alcohol oxidation under the open circuit condition due to the very low potential of the Fe(OH)<sub>2</sub>/FeOOH couple. Consistent with the thin film study, the third LSV of FeOOH obtained with HMF did not show any additional oxidation features caused by direct HMF oxidation on FeOOH.

## Constant potential oxidation of HMF to FDCA using thick MOOH films

Constant potential oxidation of HMF was performed with thick NiOOH, CoOOH, and FeOOH films in a 0.1 M KOH solution containing 5 mM HMF at multiple potentials to compare the effect of potential on HMF oxidation. HMF conversion, product yields, and FE for FDCA production after passing the stoichiometric amount of change to convert HMF to FDCA for each case are summarized in Table 1. We note that at the stoichiometric amount of charge to convert HMF to FDCA, the yield for FDCA equals the FE for FDCA production. (For electrochemical reactions, the relationship between the yield and FE changes depending on the amount of charge passed relative to the stoichiometric charge required to complete the reaction. The detailed explanation, along with the performances of other Ni- and Co-containing electrocatalysts for HMF oxidation, can be found in Table S3.)

**Table 1.** Results of HMF oxidation using NiOOH, CoOOH, and FeOOH at various potentials after passing the stoichiometric amount of charge to convert HMF to FDCA.

Anode	Potential (V. vs. RHE)	Time (h)	HMF Conversion (%)	DFF (%)	HMFCA (%)	FFCA (%)	FDCA (%)	FE for FDCA (%)
NiOOH	1.47	4.7	99.8	0.03	1.31	1.79	96.0	96.0

	1.56	1.9	96.8	0.73	1.41	7.30	86.6	86.6
	1.62	1.1	88.0	1.67	3.44	12.5	69.9	69.9
	1.71	0.8	80.3	3.28	2.72	20.0	53.5	53.5
	1.56	22	95.5	0.56	13.6	30.8	35.1	35.1
СоООН	1.62	4.6	87.5	2.00	11.8	42.0	25.6	25.6
	1.71	1.7	48.8	5.51	7.30	26.3	6.02	6.02
FeOOH	1.71	2.3	16.0	3.64	2.74	4.30	1.59	1.59

The NiOOH electrode achieved the highest yield and FE for FDCA production (96.0%) at 1.47 V vs. RHE. As more positive potentials were used, water oxidation became a competing anodic reaction and FDCA yield and FE gradually decreased, with more HMF and HMF oxidation intermediates remaining in the solution at the end of the electrolysis. Judging from the LSV shown in Figure 3a where the mechanism a2 is turned on around ~1.45 V vs. RHE, we think that HMF oxidation at 1.47 V vs. RHE by the thick NiOOH film is mostly achieved by Ni(OH)<sub>2</sub>/NiOOH-mediated oxidation (a1). However, considering the heterogeneity of Ni sites present in the thick NiOOH films, it is possible that some Ni sites in the thick NiOOH film can oxidize HMF through mechanisms other than the Ni(OH)<sub>2</sub>/NiOOH-mediated oxidation at 1.47 V vs. RHE. We are currently developing electrochemical methods that can deconvolute the currents obtained during the constant potential HMF oxidation by the thick MOOH films into current by the a1 mechanism and that by the a2 mechanism.

The least positive potential that enabled CoOOH to generate an appreciable amount of current density for HMF oxidation was 1.56 V vs. RHE. Below this potential, extremely low levels of oxidation current were generated (Figure S6), and it was not possible to convert a meaningful amount of HMF before base-induced humin formation affected the product analysis. When HMF oxidation was performed at 1.56 V vs. RHE, the FDCA yield and FE were limited to 35.1% since water oxidation can also occur at this potential (Figure 5b). Since water oxidation by CoOOH involves the generation of  $Co^{4+}$  ions,<sup>46</sup> we think that HMF oxidation at 1.56 V vs. RHE may involve the formation of  $Co^{4+}$  ions in addition to oxidation through the a1 and a2 mechanisms. When HMF

oxidation was achieved at more positive potentials, as with NiOOH, the FDCA yield and FE decreased even further as water oxidation became an increasingly dominant reaction.

The results obtained for constant potential HMF oxidation with CoOOH suggests that although the LSV results show that CoOOH has the ability to oxidize HMF at a less positive potential than NiOOH due to the lower redox potential for the  $Co(OH)_2/CoOOH$  conversion, the slow kinetics of  $Co(OH)_2/CoOOH$ -mediated HMF oxidation along with the fact that not all  $Co^{3+}$  sites in CoOOH can be used for reversible electrochemical reactions, makes  $Co(OH)_2/CoOOH$ -mediated HMF oxidation less efficient than Ni(OH)\_2/NiOOH-mediated HMF oxidation. It appears that even the kinetics of direct oxidation of HMF on CoOOH are not fast enough to be used for constant potential HMF oxidation in the potential region where water oxidation does not occur. However, although CoOOH is inferior to NiOOH when prepared with comparable metal sites, this does not mean that CoOOH cannot achieve efficient HMF oxidation in high yield or FE. If CoOOH is prepared as an extremely high surface area electrode that contains a higher number of electrochemically reversible and catalytically active Co sites to enhance the current for HMF oxidation before water oxidation becomes dominant, CoOOH may also achieve HMF oxidation in a high yield and FE.

Using the FeOOH electrode, 1.71 V was the least positive potential that was able to generate comparable oxidation current to NiOOH and CoOOH. At this potential, water oxidation was already the dominant anodic reaction, and HMF conversion was low. Nonetheless, the formation of DFF, HMFA, FFCA and FDCA was detected, although their yields were not considerable (< 5%). This result suggests that although FeOOH has the ability to oxidize HMF to FDCA in the high potential region, the combination of a high overpotential requirement and the predominance of water oxidation will always make the FE for HMF oxidation extremely low.

## 4. Conclusion

We have comparatively investigated the catalytic activity of electrochemicallyprepared NiOOH, CoOOH, and FeOOH electrodes for the electrochemical oxidation of HMF to FDCA in a pH 13 solution. The use of thin films possessing essentially no

distinct surface morphologies and containing comparable metal sites enabled a systematic comparison of the intrinsic catalytic activity of each material. Also, the use of thin films containing a small number of uniform metal sites enabled us to observe evidence for the presence of multiple pathways of HMF oxidation that have not been previously observed for alcohol oxidation. Using thicker films, the effect of film thickness on the voltammetric responses of the MOOH films by different oxidation pathways could be examined, and the performances of the MOOH films for constant potential oxidation of HMF could be investigated. The result showed that NiOOH is the most efficient catalyst for electrochemical HMF oxidation, achieving up to 96.0% yield and FE for FDCA production at 1.47 V vs. RHE. Although CoOOH has the ability to initiate HMF oxidation at a lower potential than NiOOH due to the Co(OH)<sub>2</sub>/CoOOH conversion occurring at a less positive potential, the rate of Co(OH)<sub>2</sub>/CoOOH-mediated HMF oxidation was too slow to generate sufficient current density for constant potential HMF oxidation. When a more positive potential was applied to increase the rate of HMF oxidation through different oxidation mechanisms, water oxidation was also enabled, thereby lowering the FE for HMF oxidation. FeOOH did not exhibit any catalytic activity for HMF oxidation at potentials below the onset for water oxidation during both thin and thick film voltammetry experiments. However, the detection of trace amounts of FDCA during constant potential HMF oxidation performed at 1.71 V suggests that FeOOH also has the ability to oxidize HMF to FDCA, although it is not efficient. The results contained in this study provide a better understanding of MOOH as electrocatalysts for HMF oxidation, which can also be used as a foundation to design future studies for using MOOH for general alcohol oxidation.

### ASSOCIATED CONTENT

## **Supporting Information**.

The supporting information is available free of charge.

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SEM of bare FTO, comparison of active metal sites in MOOH films, performance comparison of Ni- and Co-containing electrocatalysts, XRD of M(OH)<sub>2</sub> and MOOH, UV-vis spectra of Ni(OH)<sub>2</sub> and NiOOH, additional LSVs of M(OH)<sub>2</sub> for the oxidation of DFF, HMFCA, and FFCA, CVs of thin and thick Co(OH)<sub>2</sub>, and J-t plot of CoOOH at 1.47 V vs. RHE (PDF)

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## Notes

The authors declare no competing financial interest.

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