

Improved Electrosynthesis of Biomass Derived Furanic Compounds via Nitroxyl Radical Redox Mediation

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Emily Carroll, Sarah L. Parker, Anna Fukushima, Sophie Downey, Delaney Miller, Zachary A. Nguyen, Dylan G. Boucher,* and Shelley D. Minteer*



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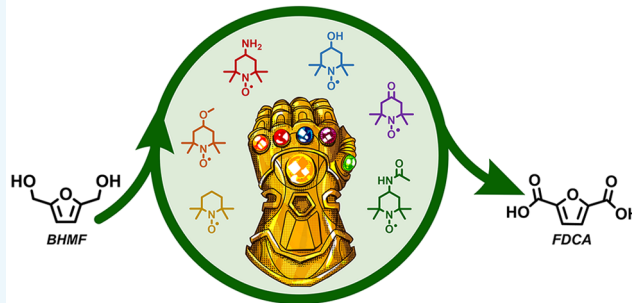


Supporting Information

ABSTRACT: Biomass is an abundantly available, underutilized feedstock for the production of bulk and fine chemicals, polymers, and sustainable and biodegradable plastics that are traditionally sourced from petrochemicals. Among potential feedstocks, 2,5-furan dicarboxylic acid (FDCA) stands out for its potential to be converted to higher-value polymeric materials such as polyethylene furandicarboxylate (PEF), a bio-based plastic alternative. In this study, the sustainable, electrocatalytic oxidation of stable furan molecule 2,5-bis(hydroxymethyl)furan (BHMF) to FDCA is investigated using a variety of TEMPO derivative electrocatalysts in a mediated electrosynthetic reaction. Three TEMPO catalysts (acetamido-TEMPO, methoxy-TEMPO, and TEMPO) facilitate full conversion to FDCA in basic conditions with >90% yield and >100% Faradaic efficiency. The remaining three TEMPO catalysts (hydroxy-TEMPO, oxo-TEMPO, and amino-TEMPO) all perform intermediate oxidation of BHMF in basic conditions but do not facilitate full conversion to FDCA. On the basis of pH studies completed on all TEMPO derivatives to assess their electrochemical reversibility and response to substrate, pH and reversibility play significant roles in the catalytic ability of each catalyst, which directly influences catalyst turnover and product formation. More broadly, this study also highlights the importance of an effective and rapid electroanalytical workflow in mediated electrosynthetic reactions, demonstrating how voltammetric catalyst screening can serve as a useful tool for predicting the reactivity and efficacy of a catalyst–substrate electrochemical system.

KEYWORDS: biomass, TEMPO, electrosynthesis, electrochemistry, oxidation, catalysis, plastic

Electrosynthesis: I Am Inevitable



INTRODUCTION

Global industrialization has escalated the demand for energy while simultaneously contributing to carbon emissions, global warming, and climate change. To avoid irreparable damage to the atmosphere and ecosystems on earth, there is an increasing urgency for large-scale decarbonization efforts, including: renewable energy generation, electrofuels, and fine chemical production derived independently from fossil fuel resources (e.g., coal, crude oil, natural gas). Green chemistry is a prominent effort focused on the sustainable production of chemicals to meet environmental goals. Over the last decade, organic electrosynthesis has emerged as a green approach for the synthesis of important molecules and chemical feedstocks. Organic electrosynthesis uses electricity to synthesize molecules via the oxidizing and/or reducing power from an electrode. Using electricity directly to carry out redox transformations allows the replacement of toxic oxidizing/reducing chemicals. Not only are electrons a cleaner reagent,

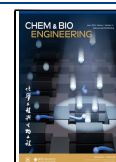
but they can be sourced from renewable “green” resources such as wind turbines, solar panels, and biomass. In particular, biomass has shown promise as a versatile and renewable feedstock and an alternative source for chemicals and energy derived from petroleum.¹ Biomass, derived from plant matter, is an abundantly available raw material from natural sources and industrial waste streams, which makes it an attractive source for carbon-neutral fuels and precursor chemicals. Presently, biomass is underutilized as a feedstock to produce both bulk and fine chemicals, polymers, and sustainable and

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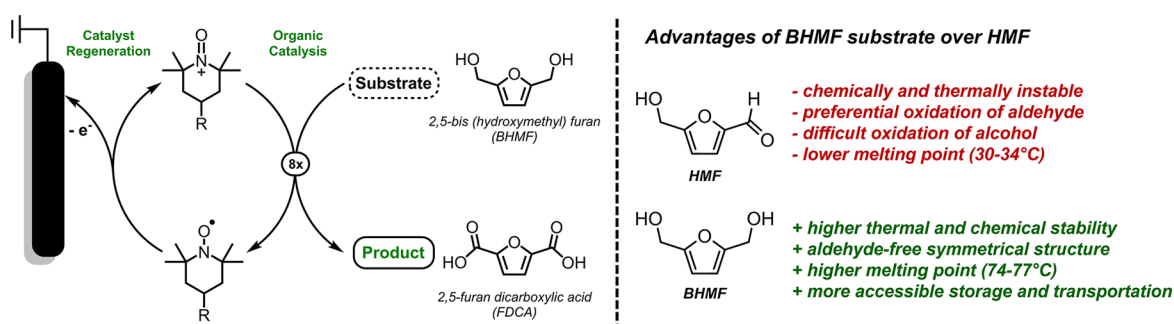


Figure 1. Catalytic scheme of mediated electrochemical oxidation of BHMF to FDCA. Oxidation of TEMPO catalyzes the eight electron oxidation where catalyst regeneration occurs at the electrode surface and homogeneous oxidation of substrate occurs in the bulk solution. Listed advantages of using BHMF as a substrate over HMF.

biodegradable plastics,² all traditionally produced from a dwindling fossil fuel supply.

The United States Department of Energy published a list of Top Value-Added Chemicals from Biomass to motivate and drive research in the field.³ Two molecules highlighted in this publication for their potential to be converted to higher-value chemicals are 5-hydroxymethylfurfural (HMF) and 2,5-furan dicarboxylic acid (FDCA). Several important transformations stem from the biomass-derived furan molecule HMF which is derived from C₆ sugars glucose and fructose.^{1,4} A key transformation of HMF is oxidation into the high value-added product FDCA. FDCA is one of the 12 building block chemicals highlighted from biomass upgrading because it is a precursor for polymeric materials including polyethylene furandicarboxylate (PEF), a bio-based alternative to petroleum-derived polyethylene terephthalate (PET) which is the most common plastic polymer material used in clothing, containers, plastic bottles, and manufacturing.^{5,6} While batch processing can accomplish the initial conversion of biomass-derived starch and cellulose to intermediate sugar platforms such as HMF, the conversion of these building blocks to secondary fine chemicals and polymerized materials remains challenging and experimentally complex. Traditional methods for the catalytic conversion of furan molecules rely on noble metal catalysts, organic solvents, and high temperatures and pressures.^{7–9} Alternatively, electrochemistry offers a streamlined approach to the synthesis of furan derivatives by eliminating the need for stoichiometric oxidizing reagents and harsh reaction conditions.^{10,11} Instead, an applied electric potential serves as thermodynamic driving force for catalysis at lower temperatures.

Such an approach was used by Choi and co-workers, where the electrochemical oxidation of HMF to FDCA was carried out using TEMPO as a homogenous catalyst.¹² Here, authors demonstrated a highly efficient electrocatalysis in pH 9.2 aqueous media under ambient conditions, with a $\geq 99\%$ yield of FDCA and a Faradaic efficiency of $\geq 93\%$. Additionally, a related electrocatalytic system was designed using an n-type BiVO₄ semiconductor as a photoanode where the overpotential required to initiate HMF oxidation was reduced significantly. Here, the photovoltage gained from the photo-generated holes in the BiVO₄ decreased the applied potential bias necessary for TEMPO oxidation. This study demonstrated that HMF transformations could be achieved at high yields and efficiencies without the need for precious-metal catalyst electrodes and stimulated interest in using organic mediators, specifically TEMPO, as homogeneous catalysts in biomass

valorization reactions. With this interest in TEMPO-mediated oxidation reactions, Choi and co-workers further investigated the electrocatalytic oxidation of HMF to FDCA using a less expensive TEMPO derivative, 4-acetamido-TEMPO (ACT), as an alternative catalyst.¹³ Here, authors show the advantage of TEMPO- and ACT-mediated electrooxidation that works efficiently in mildly basic conditions (pH 9–10) as compared to heterogeneous catalysts that require the use of more basic media. This is important because HMF becomes increasingly more unstable at high pH, polymerizing and forming insoluble polymer products. Chadderdon et al. accomplished the high efficiency paired electrochemical conversion of HMF to 2,5-bis(hydroxymethyl)furan (BHMF) and FDCA in a divided electrochemical cell.¹⁴ The hydrogenation of HMF to BHMF was catalyzed by carbon-supported Ag nanoparticles (Ag/C) and the homogeneous oxidation of HMF to FDCA was facilitated by 4-acetamido-TEMPO (ACT) at a carbon felt electrode. The paired cell achieved high yields of BHMF and FDCA (85% and 98%, respectively), demonstrating the utility of electrochemical conversions of biomass-derived furan molecules and once again revealing the effectiveness of TEMPO derivative catalysts. Recently, Zhu et al. proposed a new substrate alternative to HMF by studying the electrocatalytic production of FDCA from 2,5-bis(hydroxymethyl)furan (BHMF).¹⁵ BHMF is a reduced, more stable furan derivative of HMF that offers increased thermal and chemical stability compared to HMF, a molecule often subject to degradation at high pH and over time. In this study, CoOOH/Ni electrodes were fabricated and achieved complete BHMF conversion with 90.2% FDCA yield and 100% current efficiency when paired with H₂ evolution reaction at the cathode. Traditional thermal catalytic conversion of BHMF to FDCA has also been explored: Li et al. disclosed oxidation of BHMF to FDCA catalyzed by a carbon nanotube-supported Pd catalyst (Pd/CNT).¹⁶ The Pd/CNT catalyst demonstrated a maximum FDCA yield of 93.0% with a full conversion of BHMF after 60 min at 60 °C. This was compared to the traditional furan oxidation synthesis using HMF as a substrate, which only yielded 35.7% FDCA. Liu et al. also recently demonstrated selective production of FDCA from BHMF using porous nitrated carbon-supported bimetallic Au–Pd nanocatalysts that facilitated BHMF conversion of 100% and FDCA yield of 95.8% at 100 °C.¹⁷ The success of these thermal approaches for BHMF oxidation highlight a promising route to combining the efficiency of TEMPO mediated HMF electrochemical oxidation strategies with the thermal and pH

stability of BHMF demonstrated through heterogeneous catalysis.

Here, we use organic electrochemistry as an approach that combines the production demand of renewable, non-toxic, and recyclable polymeric plastics with the abundance of biomass feedstocks. Specifically, we focus on an intermediate reaction in this biomass upgrading process: the electrochemical oxidation of a reduced furan derivative, 2,5-bis(hydroxymethyl)furan (BHMF) to the polymeric precursor FDCA via mediated electrocatalysis (Figure 1). BHMF in this study serves as a model substrate for electrochemical oxidation of a wide variety of sugar-based substrates. In contrast to HMF, BHMF lacks the reactive aldehyde group present on HMF making it a more stable intermediate. HMF is notorious for its instability and is prone to quickly polymerize and participate in side reactions, such as the formation of humins.^{18–20} Selecting a more stable furan molecule, such as BHMF, could overcome certain industrial bottlenecks relating to storage and reaction stability. Utilizing a library of TEMPO redox mediators, we identify the key molecular parameters necessary for catalyzing selective alcohol oxidation. We demonstrate the complete electrochemical oxidation of BHMF to FDCA in near unity yields and high Faradaic efficiencies. These studies pave the way for BHMF as an alternative precursor to HMF for the electro-synthesis of FDCA and represent an opportunity for advancement in redox mediated commodity chemical production from biomass, an underutilized strategy in the present literature.

RESULTS AND DISCUSSION

Direct oxidation of BHMF at the electrode surface is not feasible due to the competing water oxidation reaction. This is demonstrated in Figure 2 which shows the cyclic voltammetric response of BHMF in borate buffer (pH 9.2, glassy carbon (GC) electrode, dashed green trace) where OER is observed at 1.2 V vs SCE. Aside from the onset of OER, no other electrochemical features are present in the BHMF voltammogram, indicating that it is not capable of being heterogeneously

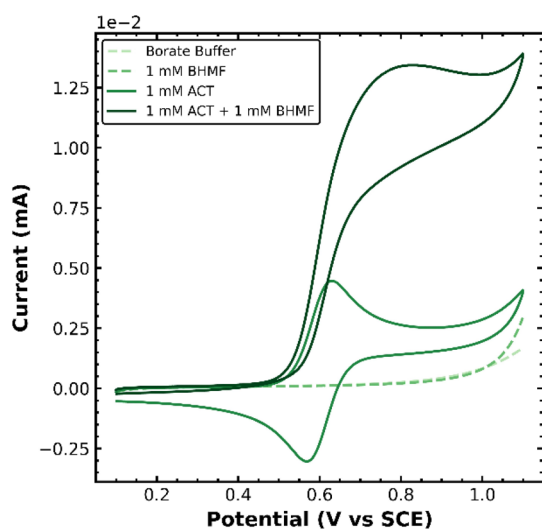


Figure 2. CVs showing electrochemical response of 1 mM BHMF substrate (dashed light green trace), 1 mM ACT (solid light green trace), and electrocatalytic response of 1 mM BHMF + 1 mM ACT (solid dark green trace). Scans taken at 10 mV/s in 0.5 M borate buffer (pH 9.2).

oxidized at the GC electrode surface in aqueous conditions. To enable electrocatalysis, an electrochemical mediator was chosen to facilitate homogeneous oxidation of BHMF and lower the overpotential required for the reaction. Nitroxyl radical-containing compounds, such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and its derivatives are widely utilized for their ability to electrocatalytically oxidize a wide range of alcohols under mild and environmentally benign conditions. The ability of TEMPO to serve as a catalyst for BHMF oxidation was examined using cyclic voltammetry (CV) where TEMPO derivatives were evaluated for catalytic activity in the absence and presence of BHMF. One TEMPO derivative, acetamido-TEMPO (ACT) is shown as a representation of classic electrocatalytic behavior (Figure 2, solid light green trace). The ACT electrochemical current response shows an ideal, reversible voltammogram centered at a redox potential of 0.60 V vs SCE and an anodic peak current of 4.47×10^{-3} mA. Once the substrate (BHMF) is introduced to a solution with catalyst (TEMPO) present, BHMF is oxidized by the electro-generated oxoammonium cation, (TEMPO⁺). This can be seen in the voltammogram in Figure 2 where catalytic behavior is observed in the voltammogram with BHMF and ACT present (solid dark green trace). With BHMF addition, there is an increase in the anodic current (peak current 1.34×10^{-2} mA, three-fold increase over the only TEMPO peak current) with an associated decrease in the cathodic return wave, indicative of homogeneous catalysis which returns the reduced form of TEMPO at the electrode surface.

Scan Rate Studies. To assess the ability of other TEMPO-based derivatives to act as competent oxidative mediators, their electrochemical reversibility needed to be evaluated at the basic pH necessary for FDCA conversion. Cyclic voltammetry (CV) scan rate studies were completed on six TEMPO derivatives to measure their redox potential and reversibility. Examined TEMPO derivatives were acetamido-TEMPO (ACT), methoxy-TEMPO (MT), TEMPO (T), hydroxy-TEMPO (HT), oxo-TEMPO (OT), and amino-TEMPO (AT). CVs were run in a 0.5 M borate buffer solution at pH 9.2 containing 1 mM of varying TEMPO catalysts and scan rates ranged from 10 mV/s to 1 V/s. Scan rate dependence of an electroactive molecule can give insight into the stability and reversibility of a molecule as well as the redox potential at which it is oxidized. Cyclic voltammograms for all six TEMPO catalysts are shown in Figure 3 at varying scan rates to demonstrate their electrochemical behavior. The oxidation potentials for each TEMPO derivative are as follows: ACT was 0.62 V, MT was 0.62 V, T was 0.53 V, HT was 0.62 V, OT was 0.715 V, and AT was 0.53 V. Three out of six catalysts, ACT (peak ratio of 0.90), MT (peak ratio of 0.87), and T (peak ratio of 0.97) display electrochemically reversible behavior in basic solvent conditions, as shown by equal magnitude anodic and cathodic peak currents. In addition, tight peak potential separation (ΔE_p) was observed for these catalysts (64 mV for ACT, MT, and T) indicating facile heterogeneous electron transfer. Finally, these three catalysts exhibited ideal linear relationship of the peak current (i_p) to square root scan rate as predicted by the Randles-Sevcik equation (see Supporting Information, SI, Figures S1–S2). This ideal voltammetric behavior indicates that these TEMPO species are stable and freely diffusing in solution. In contrast, the remaining three catalysts (HT, OT, AT), do not display electrochemically reversible behavior over all scan rates. HT and OT lose

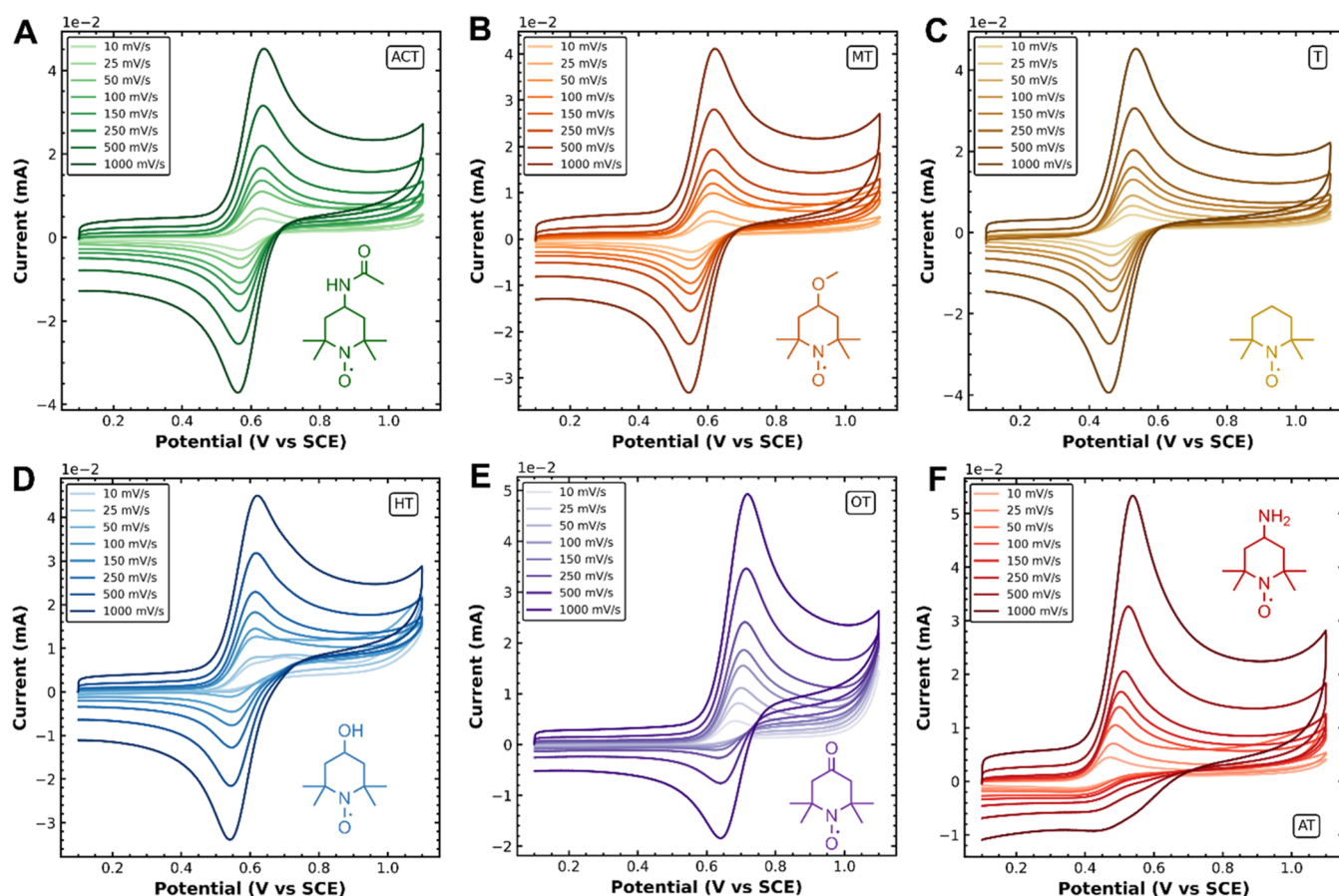


Figure 3. Cyclic voltammograms for a range of TEMPO derivatives with different structures (R groups) illustrating the relationship between the differences in R groups, oxidizing activity, and reversibility. (A) acetamido-TEMPO (ACT, green traces), (B) methoxy-TEMPO (MT, orange traces), (C) TEMPO (T, yellow traces), (D) hydroxy-TEMPO (HT, blue traces), (E) oxo-TEMPO (OT, purple traces), and (F) amino-TEMPO (AT, red traces). CVs obtained in a 0.5 M borate buffer solution (pH 9.2) containing 1 mM of varying TEMPO catalysts at scan rates 10 mV/s–1 V/s.

reversibility at lower scan rates demonstrated by a departure of cathodic/anodic peak current ratio from unity, while AT lacks reversibility over all scan rates. OT appears quasi-reversible above 250 mV/s scan rate where a reverse peak is still present as indicated by a peak ratio of 0.44 at 1000 mV/s. However, as scan rate decreases, the peak current ratio decreases to 0.32 and 0.24 at 500 and 250 mV/s, respectively. Below a scan rate of 250 mV/s, OT completely loses reversibility as indicated by peak ratios that range from 0.20 down to 0.17 at the slowest scan rate, 10 mV/s. Likewise, HT shows a similar trend of reversibility where HT is quasi-reversible above 100 mV/s scan rate as indicated by increasing peak ratios of 0.68, 0.74, 0.80, 0.83, and 0.84 at scan rates 100, 150, 250, 500, and 1000 mV/s, respectively. Below 100 mV/s, HT loses reversibility and the return peak, demonstrated by a significant decrease in peak current ratio to 0.42 at 50 mV/s and 0.24 at 10 mV/s. AT appears irreversible at all scan rates, and, as a result, the reverse peak current is difficult to reliably detect. The forward anodic peak current is consistent with the Randles-Sevcik linear relationship to square root scan rate. A complete list of peak current ratios for all catalysts can be found in [SI Table S1](#). This voltammetric behavior of HT, OT, and AT is consistent with an “EC” mechanism where an initial electrochemical step is followed by a chemical reaction, indicating the chemical decay of the catalytically active oxoammonium intermediate. This chemical decay of the oxidized intermediate prevents the

TEMPO species from being reduced back to its original state which results in the disappearance of the reverse peak and gives rise to peak current ratios <1.0.

The voltammetric scan rate data in [Figure 3](#) can be used to understand the reversibility of each catalyst and, in turn, predict the efficacy of the catalyst in an electrocatalytic reaction. CV can be a diagnostic technique and predictive model for the outcome of a subsequent bulk electrolysis experiment based on observations in mechanism and reversibility. Electrochemical reversibility indicates that a chemical species is capable of “turning over” or undergoing many redox cycles with no interfering chemical reactions nor other electrochemical events. An effective catalyst will continuously transfer electrons between the electrode and substrate without degradation or irreversible interference with the reaction of interest. For example, reversible catalysts ACT, MT, and T are predicted to experience high turnover and readily facilitate the oxidation of BHMf to FDCA. Quasi-reversible catalysts HT and OT are predicted to facilitate some BHMf oxidation, but due to competing chemical reactions in solution, may not perform as well as the reversible TEMPO catalysts. AT is predicted to facilitate minimal BHMf oxidation based on the irreversible CVs and the chemical reactions occurring in solution with the oxidized oxoammonium intermediate that outcompetes the turnover of AT back to its reduced state.

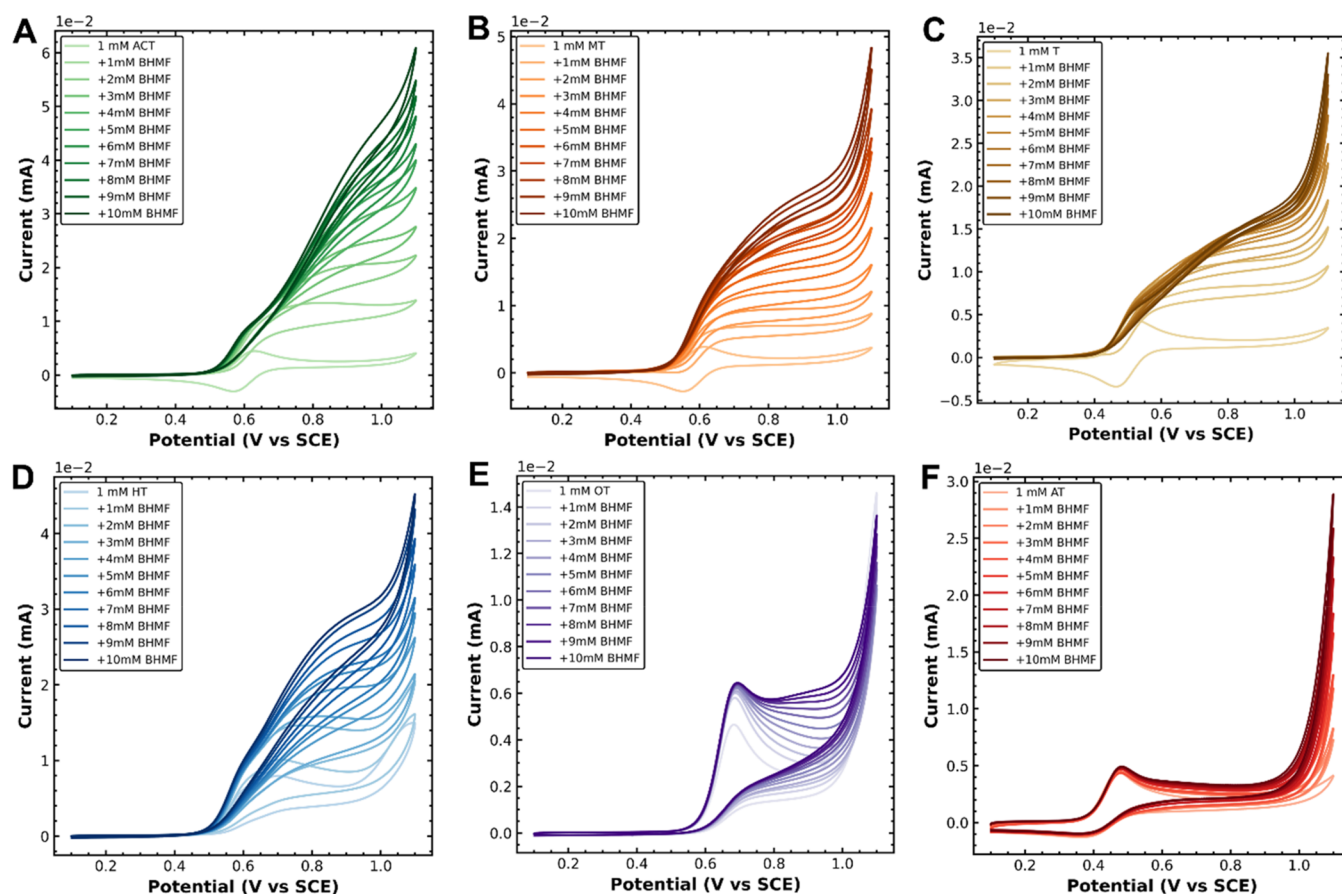


Figure 4. Cyclic voltammograms of (A) acetamido-TEMPO (ACT, green traces), (B) methoxy-TEMPO (MT, orange traces), (C) TEMPO (T, yellow traces), (D) hydroxy-TEMPO (HT, blue traces), (E) oxo-TEMPO (OT, purple traces), and (F) amino-TEMPO (AT, red traces) in the presence of increasing BHMf concentrations. CVs obtained in a 0.5 M borate buffer solution (pH 9.2) containing 1 mM of varying TEMPO catalysts at scan rate 10 mV/s.

Substrate Titrations. After the initial screening and assessment of the electrochemical reversibility of the TEMPO catalysts in basic conditions, the effect of adding substrate was examined. Briefly, BHMf substrate was added to a 1 mM solution of catalyst in 1 mM aliquots and the resulting voltammogram recorded. Figure 4 shows voltammograms of all six catalysts comparing the current responses with no substrate present to those with increasing substrate concentrations. Over the course of several additions of BHMf (1 mM to 10 mM), catalytic behavior was observed for ACT, MT, T, and HT TEMPO derivatives, as indicated by the increased forward current and decreased reverse current. At 10 mM BHMf and 10 mV/s, the observed peak currents were 5.48×10^{-2} mA for ACT, 2.81×10^{-2} mA for MT, 1.76×10^{-2} mA for T, and 3.07×10^{-2} mA for HT which represent a 12.3, 7.3, 4.1, and 5.0-fold increase in oxidative current over each catalyst peak current, respectively. In contrast, several TEMPO catalysts show little to no catalytic activity with substrate, such as OT and AT. In the OT CVs, there is a slight increase in anodic peak current with increasing substrate contributions as well as an increase in the current of the diffusional tail, but the irreversible voltammogram suggests that catalyst turnover is limited due to the competitive chemical step outlined previously. Similarly, the AT CVs show no catalytic behavior with hardly any changes in the voltammogram between substrate additions. The current is low, and the catalyst seems to support little to no catalysis of BHMf. Voltammetric

substrate titrations were completed at a range of scan rates from 10 mV/s to 1000 mV/s. A selection of faster scan CVs can be found in SI Figure S3. Specifically, the faster scan rate of 1000 mV/s in Figure S3 shows there is not a significant increase in the current with substrate titrations, indicating that at higher scan rates, the scanning time scale is faster than the chemical step between the TEMPO oxoammonium cation and BHMf.

The results of these experiments correlate with the predictions from the catalyst scan rate studies where reversible behavior was predicted to correspond to high turnover and catalysis ability in ACT, MT, and T whereas irreversible catalyst behavior was predicted to limit substrate catalysis and performance in OT and AT. In the substrate titrations, HT also showed catalytic behavior which validates the reversible behavior seen from HT at scan rates faster than 100 mV/s. From the voltammograms in Figure 4, it is clear that the catalysts that displayed reversible electrochemical behavior and catalytic responses with substrate (ACT, MT, and T) will effectively catalyze the oxidation of BHMf to FDCA in bulk electrolysis experiments. Catalysts that displayed reversible behavior over most scan rates and displayed catalytic responses with substrate (HT) are predicted to facilitate moderate oxidation of BHMf, perhaps to intermediate oxidized furan species. Conversely, OT and AT are hypothesized to not completely catalyze the BHMf oxidation reaction, as catalyst CVs demonstrate limited turnover capability and voltammetric

substrate titrations show minimal to no catalytic behavior when substrate is present.

Bulk Electrolysis. Voltammetry is a valuable technique to determine electrochemical reversibility as well as elucidate mechanism and kinetics. CV studies are quick, easy, and can provide valuable information about catalyst viability within a system before moving on to exhaustive electrolysis. Most electrosynthesis studies investigate the complete electrochemical conversion of substrate in solution through bulk electrolysis (chronopotentiometry and chronoamperometry) to exhaustively oxidize or reduce the species in solution. In this study, controlled potential electrolysis (CPE) experiments were conducted in an H-cell (glass frit separator) with a graphite rod working electrode and saturated calomel reference electrode (SCE) in the anode chamber, and a platinum mesh counter electrode in the cathode chamber. The mediated oxidation of BHMF occurs at the graphite rod anode while the platinum catalyzes hydrogen evolution reactions (HER) at the cathode. Experimental setup pictures are shown in SI Figure S4. In controlled potential coulometry, the working electrode is held at a specific potential, E (120 mV more positive than the oxidation potential of the mediator), and the system is continuously stirred so that the solution at the electrode interface is continuously refreshed. As BHMF in solution is oxidized and consumed, the bulk concentration is decreased and thus the oxidation current decreases exponentially. Eventually, the electrolysis finishes as the bulk concentration of BHMF is diminished and the current reaches background level. The total number of coulombs consumed in an electrolysis is used to determine the amount of substance electrolyzed. The charge (Q) passed during the experiment is given by the area under the $i-t$ curve and can be obtained by integrating the current with respect to time (eq 1).

$$Q(t) = \int_0^t i(t) dt \quad (1)$$

The charge can then be converted to the number of moles of species electrolyzed (N) using the following eq 2 where n is the number of electrons and F is Faraday's constant (96 485 C/mol).

$$Q = nFN \quad (2)$$

A representative $i-t$ trace for the electrolysis of BHMF catalyzed by ACT is shown in Figure 5 where current is measured over time and the total charge passed during electrolysis is represented by the shaded area under the curve. Each bulk electrolysis experiment was set up as follows. 10 mM BHMF substrate (5 mL, 5×10^{-5} mol) was prepared in borate buffer (pH 9.2) and added to the anode cell. Plain borate buffer (5 mL) was added to the cathode cell. A constant potential of +120 mV relative to the oxidation potential of each TEMPO catalyst was applied to the graphite working electrode in solution, and the current was allowed to baseline for ~15 min. Applied potential values for each catalyst are listed in SI Table S2. An initial spike in the current response is due to the charging of the electrode which decays to baseline quickly. At this point, the applied potential is not enough to directly oxidize BHMF (without catalyst) so no reaction occurs. 1 mM TEMPO catalyst is then injected into the anode chamber (100 μ L from a 50 mM stock solution) where an immediate current increase is observed due to the increase in concentration of electroactive species in solution. At this point, the TEMPO is able to continuously oxidize BHMF because the electrode is

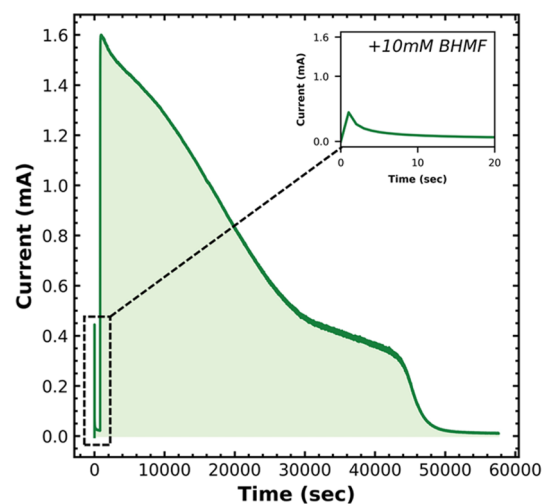


Figure 5. Bulk electrolysis $i-t$ trace for BHMF oxidation to FDCA, catalyzed by ACT. 10 mM BHMF, 1 mM ACT. Borate buffer pH 9.2.

poised at a potential positive enough to re-oxidize and “turnover” the TEMPO. An effective catalyst will continue to oxidize the substrate in solution until the substrate is completely consumed which is seen in the electrochemical response as a current decay. The electrolysis is complete when the current returns to baseline and no more substrate is present to be oxidized.

Bulk electrolysis experiments were conducted for each TEMPO catalyst in triplicate to assess how different TEMPO molecules are capable of oxidizing BHMF (individual bulk electrolysis traces for each catalyst available in SI Figure S5). Representative $i-t$ traces for each catalyst are shown in Figure 6 demonstrating the how the differences in electrochemical reversibility affects electrolysis. Catalysts ACT, MT, and T which all displayed electrochemically reversible behavior and catalytic responses with BHMF titrations also show similar $i-t$ traces lasting approximately 17 h (60 000 sec). The charge passed in these electrolyses fall within the same range of 36.0, 35.6, and 35.7 C of charge consumed using ACT, MT, and T, respectively (theoretical amount of charge passed for 5×10^{-5} mol BHMF was 38.6 C, see SI Equation S1). The electrolysis catalyzed by HT was also run for ~17 h but baselined much faster and only consumed 19.7 C of charge. OT baselined within 3 h and only passed 2.2 C of charge, supporting the hypothesis that this quasi-reversible catalyst that did not promote catalytic activity with substrate present is not capable of completely oxidizing BHMF. Generally, shorter $i-t$ trace times indicate that the catalyst does not turnover effectively and, as a result, only see partially oxidized products. For example, in bulk electrolysis experiments with irreversible catalysts (HT and OT), the current drops off rapidly, likely due to the complete use of the concentration of catalyst in solution. For these catalysts that have little-to-no turnover, the substrate is only oxidized with the amount of catalyst initially present which causes a quick reaction and a rapid decay of current. On the contrary, in experiments with reversible catalysts (ACT, MT, and T), the current decays slower as catalyst turnover continuously facilitates the conversion of BHMF to FDCA. The bulk electrolysis trace using AT is slightly different from the other TEMPO catalysts. After the AT is introduced to the anode chamber, the current spikes and initially decays similar to the other catalysts. However, the

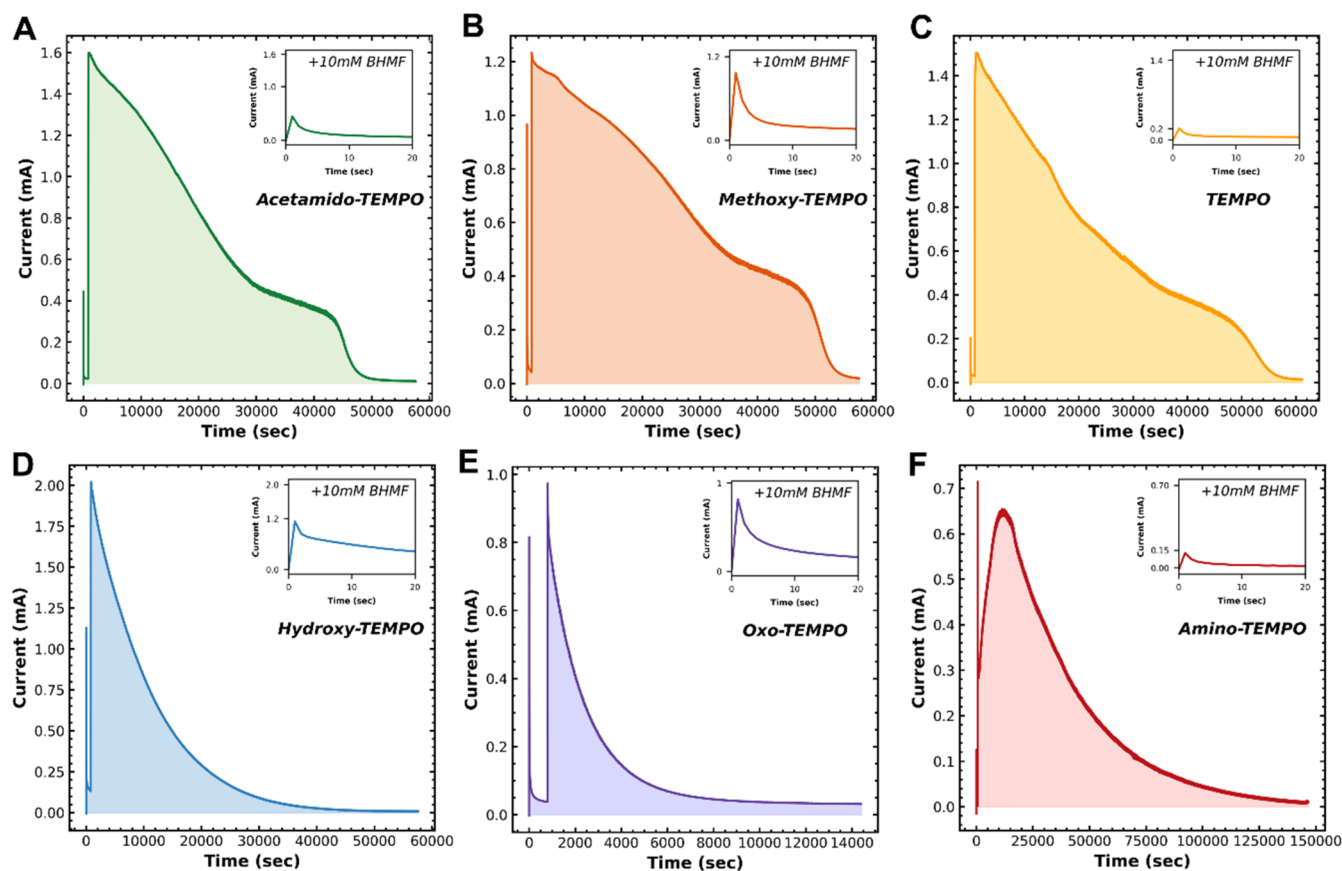


Figure 6. Bulk electrolysis traces for the oxidation of 10 mM BHMf catalyzed by 1 mM of various TEMPO catalysts in borate buffer solution (pH 9.2). (A) acetamido-TEMPO (ACT, green traces), (B) methoxy-TEMPO (MT, orange traces), (C) TEMPO (T, yellow traces), (D) hydroxy-TEMPO (HT, blue traces), (E) oxo-TEMPO (OT, purple traces), and (F) amino-TEMPO (AT, red traces).

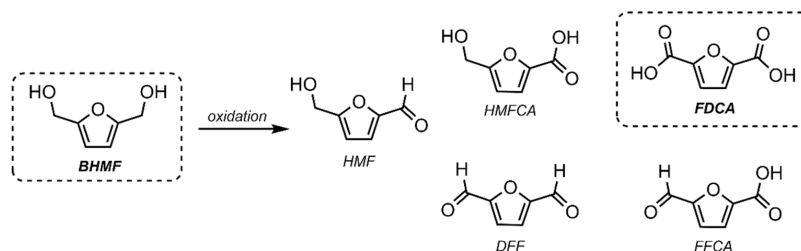


Figure 7. Oxidized products of BHMf highlighting the desired product, FDCA.

current starts to increase for 15 000 seconds before it peaks and returns to the expected exponential decay pattern and baselines after 42 h. This increase in current only occurs for the AT catalyst and is likely due to local pH fluctuations at the electrode surface upon addition with substrate. During this electrolysis, 27.9 C of charge was passed.

Product Analysis. The coulometry data obtained from the bulk electrolyses was paired with ultra high-performance liquid chromatography-mass spectrometry (UHPLC-MS) product analysis data to identify the oxidation products and calculate Faradaic efficiency of the BHMf oxidation reaction. All products extracted from the reaction chamber were separated and detected via LC-MS. Product yields were quantified based on a FDCA calibration curve developed via diode array detection (DAD) using commercial standards. Calibration data, linear fit equation, and LCMS information for BHMf and FDCA standards are found in *SI Figures S6–S12* and *SI Tables S3–S5*. On the basis of the MS results, ACT, MT, and

T catalyzed the complete oxidation of BHMf to FDCA, as evidenced by the presence of a characteristic FDCA mass spectrum from experimental bulk electrolysis samples. The Faradaic efficiency of this oxidation was $102.78 \pm 0.09\%$ with ACT, $106.7 \pm 0.1\%$ with MT, and $100.6 \pm 0.1\%$ with T. A sample calculation for Faradaic efficiency, including calculating the amount of moles electrolyzed during electrolysis, can be found in *SI Equations S2 and S3*. HT, OT, and AT all facilitated intermediate oxidation to a variety of semi-oxidized furan molecules with alcohol, aldehyde, and carboxylic acid functional groups (Figure 7), but did not oxidize completely to FDCA. These semi-oxidized furan molecules are HMF (hydroxymethylfurfural), DFF (2,5-diformylfuran), HMFCFA (5-hydroxymethyl-2-furancarboxylic acid), and FFCA (5-formyl-2-furancarboxylic acid). In the eight-electron oxidation of BHMf to FDCA, only a reversible catalyst is expected to facilitate the complete conversion while an irreversible catalyst with low turnover is expected to facilitate the primary

oxidations of the alcohol groups on BHMF, resulting in mixed, semi-oxidized products. A summary of the charge passed and Faradaic efficiency of each reaction is found in Table 1 and a complete description of intermediate oxidation products in HT, OT, and AT reactions with associated mass spectra can be found in SI Figures S13–S25 and Tables S6–S11.

Table 1. Yields for the Electrocatalytic Oxidation of BHMF to FDCA Catalyzed by Different TEMPO Catalysts^a

catalyst	charge passed (C)	bulk electrolysis yield (%)	HPLC yield (%)	Faradaic efficiency (%)
acetamido-TEMPO	36.0 ± 0.1	93.3 ± 0.4	95 ± 2	102.78 ± 0.09
methoxy-TEMPO	35.6 ± 0.3	92.2 ± 0.9	98 ± 3	106.7 ± 0.1
TEMPO	35.7 ± 0.8	92 ± 2	93.1 ± 0.2	100.6 ± 0.1
hydroxy-TEMPO	19.7 ± 0.1	intermediate oxidation		
oxo-TEMPO	2.2 ± 0.1	intermediate oxidation		
amino-TEMPO	27.9 ± 0.2	intermediate oxidation		

^aIncluded information: coulometry data, bulk electrolysis and HPLC yields, and Faradaic Efficiency (standard error included).

The results from the LC-MS product analysis indicate that the FDCA product is only detected from electrolyses that use ACT, MT, and T as catalysts. This outcome lines up precisely with the hypotheses made after the initial scan rate studies where the electrochemical reversibility of the catalyst was predicted to correlate with its effectiveness in a mediated electrocatalytic reaction. Additionally, further studies could focus on characterizing the state of the catalysts before and after bulk electrolysis experiments, leading to a deeper understanding of catalyst turnover and degradation. These

results emphasize the importance of voltammetry in electrocatalysis studies, especially those using a mediator as a catalyst. One set of voltammograms taken at a range of scan rates takes less than 30 min and an entire library of catalysts can be screened in 1 day. An informed and rational selection of a catalyst can save time and improve reaction yields with minimal upfront time commitment compared to running time-consuming bulk electrolysis experiments for catalyst selection and optimization.

pH Dependent Electrochemical Properties of TEMPO.

TEMPO catalyzed alcohol oxidation is a strongly pH dependent reaction, where superior catalytic activity of TEMPO and its derivatives is observed in basic conditions. In this reaction, TEMPO reacts with an alcohol substrate resulting in an overall 2-proton/2-electron oxidation (dehydrogenation) process where the activation and recycling of the catalyst is accomplished by oxidation at the electrode. The catalytic cycle for the oxidation of BHMF (Figure 8) features three electrochemically accessible TEMPO oxidation states: nitroxyl radical (T^\bullet), oxoammonium cation (T^+), and hydroxylamine (TH). The catalytically active oxoammonium species (T^+) is electrochemically generated by the one-electron oxidation of the inactive T^\bullet . The alcohol substrate (in this case BHMF) reacts with the catalytically active T^+ species and forms a TEMPO-alcohol intermediate complex. In basic conditions, a homogeneous two electron oxidation of the alcohol generates the corresponding aldehyde species and the reduced hydroxylamine TEMPO (TH). The active form of the catalyst (oxoammonium cation, T^+) is then electrochemically regenerated through a one proton coupled-two-electron oxidation of TH. A full explanation of the catalytic cycle is depicted in Figure 8 (adapted from Hickey et al).²¹ In acidic conditions, excess protons promote the disproportionation of the nitroxyl radical (T^\bullet) species to produce hydroxylamine (TH) and its protonated hydroxylammonium form (TH_2^+).²²

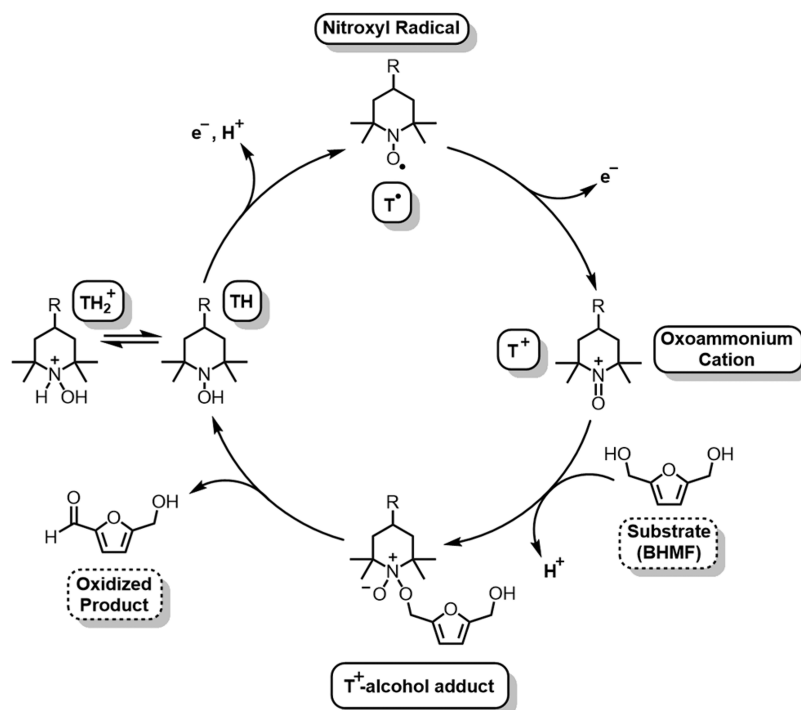


Figure 8. Catalytic cycle of TEMPO catalyzing an alcohol oxidation of BHMF.

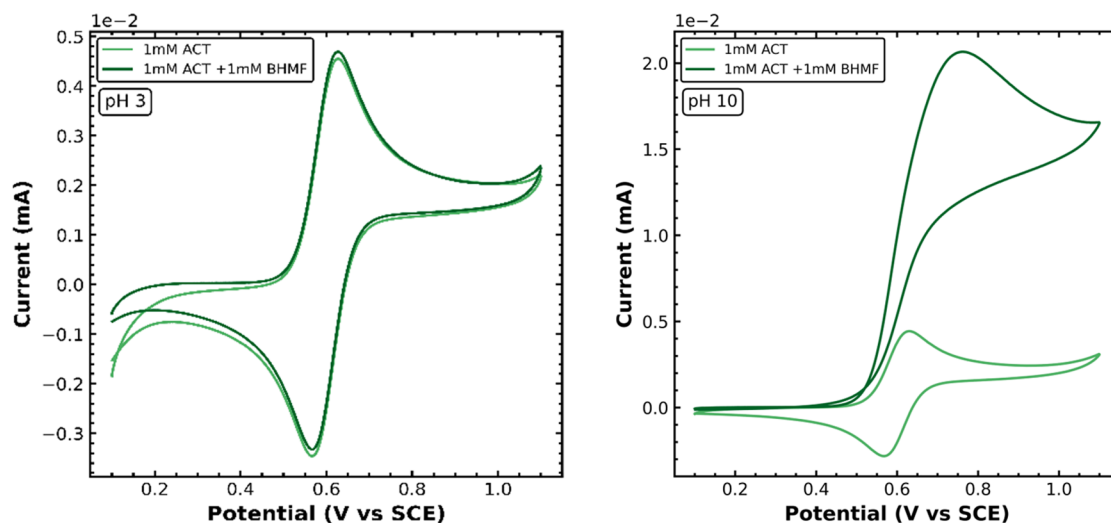


Figure 9. CVs showing the electrochemical response of 1 mM ACT (light green trace) and comparing the electrocatalytic response of 1 mM BHMf + 1 mM ACT (dark green trace) at pH 3 and pH 10. Scans taken at 10 mV/s in 0.5 M borate buffer.

These disproportionation reactions are fast under acidic conditions and ultimately lead to the inactivation of the T^+ species. Thus, the presence of base is necessary to facilitate the activation and regeneration of TEMPO catalyst. For more information, interested readers are directed toward studies by Bailey et al.²³ and Stahl^{24,25} investigating the mechanism of alcohol oxidation by oxoammonium cations. In this work, the redox-mediated oxidation of BHMf to FDCA was conducted in mildly basic (pH 9.2) electrolyte solution, conditions that have been shown to be well-suited for the electrochemical conversion of biomass-derived molecules such as HMF that are typically unstable in very acidic or basic environments.¹⁴

An investigation into the pH dependent electrochemical properties of TEMPO was conducted on all six TEMPO derivatives over a pH range of 3–10 to elucidate how changing solution pH affects catalyst reversibility and activity toward substrate oxidation. Voltammetry data was collected on each TEMPO species, evaluating pH dependence on scan rate and substrate additions. In the case of ACT, MT, and T, all three catalysts displayed electrochemically reversible voltammograms over the entire pH range (see SI Figure S31). The redox potentials of these species were also independent of pH. Though the electrochemical reversibility and oxidation potential are independent of pH, the electrocatalytic activity of TEMPO toward BHMf alcohol oxidation is still dependent on pH. To demonstrate this, a substrate addition of 1 mM BHMf was added to each catalyst solution immediately following the scan rate study (Figure 9). Cyclic voltammetry data taken with substrate in solution only shows catalytic behavior at pHs ≥ 8 for ACT, MT, and T. At solution conditions more acidic than pH 7, no catalytic behavior is observed, despite the TEMPO displaying perfectly reversible behavior (see SI Figures S26–S30). Thus, it is important to consider optimal solution conditions for catalyst and substrate.

Catalysts HT, OT, and AT have been labeled quasi- or irreversible thus far in this study and display interesting pH dependence. HT, OT, and AT all display electrochemically reversible voltammograms between pH 3–7 but start to lose reversibility in basic conditions around pH 8 and completely lack a reverse peak by pH 10 (see SI Figure S31). Upon addition of substrate, no catalytic behavior was observed in neutral or acidic conditions ($< \text{pH } 8$) and minimal catalytic

behavior was revealed in basic conditions ($\text{pH} \geq 8$), as described in previous sections. The redox potential of both HT and OT remain independent of pH and do not shift across the pH range. In contrast, the oxidation potential of AT does shift with changes in pH. At pH 3–6 the oxidation potential is 0.71 V vs SCE. At pH 7, the potential shifts negative to 0.67 V vs SCE and continues to shift negative as pH increases. At pH 8, 9, and 10 the observed oxidation potentials are 0.56, 0.49, and 0.45 V vs SCE, respectively. Cyclic voltammograms of AT across the pH range are shown in Figure 10, highlighting the

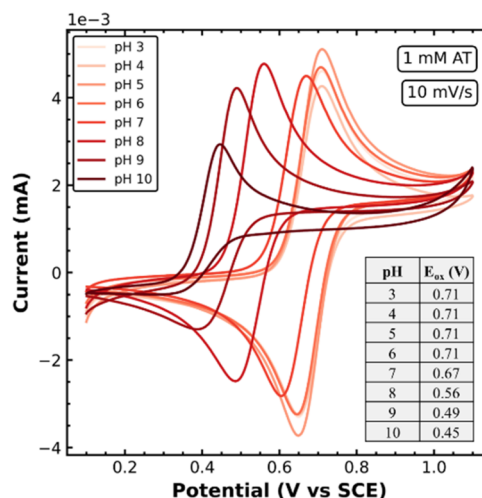


Figure 10. CVs comparing the electrochemical response of 1 mM AT over pH range 3–10. Scans taken at 10 mV/s in 0.5 M borate buffer. Oxidation potentials are reported as a function of pH.

shifting redox potentials. This pH dependent potential shift is consistent with literature reports that demonstrate the reversible oxidation potential of amino-TEMPO as strongly pH dependent.²⁴ This investigation into amino-TEMPO by Stahl and co-workers found that the primary amine substituent is what directs the pH sensitivity of amino-TEMPO's electrochemical behavior. Specifically, the amine protonation introduces an additional pK_a at each TEMPO oxidation state in the catalytic cycle (Figure 8) which drastically influences the

redox properties of the nitroxyl, therefore causing shifts in the redox potential.²⁴ Stahl and co-workers also observe that the AT oxidation is irreversible at high pH (consistent with data from this study) which they propose is a result of the oxidation of the amino group.

CONCLUSIONS

In summary, we have demonstrated the efficient and complete electrochemical conversion of BHMF to FDCA via TEMPO mediation. Specifically, we highlight the ability of reversible TEMPO derivatives (acetamido-TEMPO, methoxy-TEMPO, and TEMPO) which are highly electrochemically reversible in basic conditions to catalyze the complete oxidation of BHMF to FDCA, with quasi-reversible or irreversible derivatives (hydroxy-TEMPO, oxo-TEMPO, and amino-TEMPO) only accomplishing intermediate oxidation of BHMF. In addition to being an important electrochemical transformation of biomass derived substrates, these results emphasize the importance of an effective voltammetry workflow in catalysis studies for predicting reactivity and efficacy. The results of this model alcohol oxidation study confirm hypotheses based on quick and easy CV studies that can be completed in 1 day, supporting the argument that it is essential for an effective electrocatalysis or electrosynthesis study—especially a mediated study—to include voltammetry data. Compared to traditional methods for organic synthesis, electrosynthesis offers a more streamlined, economic, and environmentally friendly approach. However, using a redox mediator in a mediated electrosynthetic reaction can produce significant separation costs (in energy expenditure, time, and money).²⁶ For this reason, homogeneous mediated electrosynthetic reactions are most suitable for laboratory applications, as significant separation costs are present if a solution-based catalyst is used in a commercialized reaction. To address this concern, many commercialized electrosynthesis reactions use modified electrodes where the catalyst is immobilized or anchored to the electrode, eliminating the need for catalyst separation from the product. To further adapt this system for commercial scale, highest performing TEMPO catalysts would be immobilized on a carbon electrode, anchored through a linear polyethylenimine (L-PEI) polymer backbone in an effort to reduce separation costs and promote catalyst recovery and reuse in a scaled-up reaction.

EXPERIMENTAL METHODS

Materials/Chemicals. All chemicals were obtained from Sigma-Aldrich, except 2,5-bis(hydroxymethyl)furan (furan-2,5-diyldimethanol, 98%, Ambeed Inc.), 2,5-furandicarboxylic acid (>98.0%, TCI Chemicals), 4-amino-TEMPO (TCI Chemicals), and 4-acetamido-TEMPO (TCI Chemicals) and used with no further purification.

Electrochemical Measurements. All electrochemical measurements were performed at 25 ± 1 °C. Electrochemical characterization of the TEMPO catalysts was conducted using CH650E and CH611E potentiostats (CH Instruments). Voltammetry experiments were performed using a three-electrode electrochemical cell with a 0.07069 cm² glassy carbon working electrode (CH Instruments, CHI 104), saturated calomel reference electrode (SCE, CHI 150, CH Instruments), and a platinum mesh counter electrode. All potentials in this work refer to this SCE reference electrode. 0.5 M Borate buffer (pH 9.2 and pH 10) was used as the solvent supporting electrolyte for all experiments and prepared by dissolving 31 g boric acid +5 g NaOH pellets in 1 L water and adjusting to pH 9.2 or pH 10 using 10 M NaOH.

Electrochemical titration experiments were conducted to investigate catalytic behavior of the TEMPO catalysts. Cyclic voltammetry experiments were performed with a 1 mM solution of TEMPO-catalyst present in solution. 1–10 mM substrate (BHMF) additions were made, and voltammograms were recorded at 10, 25, 50, 100, 150, 250, 500, 1000 mV/s with the solution mixed thoroughly in between scans to refresh the concentration at the electrode surface. This was done by dissolving 1 mM TEMPO-catalyst in 5 mL of solution. Separately, a 5 mL stock solution of BHMF substrate was prepared with 100 mM substrate (64.1 mg BHMF) also containing 1 mM catalyst as to not alter catalyst concentration in the experimental cell. A 50 μ L aliquot of substrate stock solution was injected into the experimental cell and mixed thoroughly for every 1 mM substrate addition. (Tip: prepare a 1 mM, 10 mL catalyst solution and split for use in experimental cell and substrate stock solution.)

Controlled potential bulk electrolysis experiments were performed on a Biologic VSP potentiostat by applying an anodic overpotential (η) of 120 mV for each TEMPO catalyst based on the oxidation peak of the CV. Experiments were conducted in a divided H-cell with a glass frit divider using a graphite rod working electrode (2.5 cm immersed, 0.4 cm diameter), saturated calomel reference electrode (SCE, CHI 150, CH Instruments), and a platinum mesh counter electrode. The anode chamber was stirred at 500 rpm. The anode chamber contained 4.9 mL of 10 mM substrate (BHMF) and the cathode chamber contained 5 mL buffer solution. The current was allowed to baseline initially with substrate in solution. An aqueous solution of catalyst (100 μ L of 50 mM stock solution) was injected into the anode cell after baseline current was maintained. The final concentration of catalyst and substrate in the anode chamber was 1 mM and 10 mM, respectively. The experiment ran until baseline current was achieved (between 4–40 h).

Product Analysis. LC-MS product separation and analysis was completed by extracting the contents of the anode reaction chamber and diluting the experimental samples to 10, 25, and 50 μ M based on starting material concentrations in water (Optima[®] LC/MS suitable for UHPLC-UV, Fisher Chemical). UHPLC-MS was performed to confirm the formation of FDCA. Ex-situ product analysis was done using an Agilent 1290 Infinity II, diode array detector, and iQ Mass Selective Detector with a Poroshell 120 EC-C18, 2.1 \times 50 mm column. The mobile phase was water (18 Ω Milli-Q) (99.95%) and methanol (Optima LC/MS Grade) (0.05%) with 0.1% by volume formic acid additive at a flow of 0.400 mL/min with a column temperature of 40° C. The diode array detector was set to 265 nm for the detection of FDCA and 220 nm for BHMF. The mass range was 100–200 *m/z*, positive fragmentation, capillary voltage 3.5 kV, gas flow 11.0 L/min, nebulizer pressure 30 psi, gas temperature 350° C, fragmentor voltage 85 V. Individual molecules were detected using diode array detection (DAD) and Mass Spectrometry (MS). Product identification was made based off mass-to-charge (*m/z*) ratios from the mass spectrometer while product quantification was calculated using the DAD detector. For product quantification, DAD signal intensities were compared to a calibration curve and used to calculate the amount of moles of product present in the experimental sample to compare to the original amount of moles of starting substrate. Method development by ZN.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/cbe.4c00034>.

Additional voltammetry and electrochemical analysis for all TEMPO compounds, photographs of experimental bulk electrolysis setup, and LCMS data and spectra (PDF)

AUTHOR INFORMATION

Corresponding Authors

Shelley D. Minteer – Department of Chemistry, University of Utah, Utah 84112, United States; Kummer Institute Center for Resource Sustainability, Missouri University of Science and Technology, Rolla, Missouri 65409, United States;

orcid.org/0000-0002-5788-2249;

Email: shelley.minteer@mst.edu

Dylan G. Boucher – Department of Chemistry, University of Utah, Utah 84112, United States; Email: dylan.boucher@utah.edu

Authors

Emily Carroll – Department of Chemistry, University of Utah, Utah 84112, United States; orcid.org/0000-0003-1660-0687

Sarah L. Parker – Department of Chemistry, University of Utah, Utah 84112, United States

Anna Fukushima – Department of Chemistry, University of Utah, Utah 84112, United States

Sophie Downey – Department of Chemistry, University of Utah, Utah 84112, United States

Delaney Miller – Department of Chemistry, University of Utah, Utah 84112, United States

Zachary A. Nguyen – Department of Chemistry, University of Utah, Utah 84112, United States

Complete contact information is available at:

<https://pubs.acs.org/10.1021/cbe.4c00034>

Notes

The authors declare no competing financial interest.

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