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# TEMPO-Modified Linear Poly(ethylenimine) for Immobilization-**Enhanced Electrocatalytic Oxidation of Alcohols**

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# **Supporting Information**

ABSTRACT: We demonstrate a method to simultaneously immobilize the oxidation catalyst, TEMPO, while dramatically enhancing its electrocatalytic activity toward several biologically available alcohols. TEMPO is covalently immobilized onto linear poly(ethylenimine), which is then cross-linked onto the surface of a glassy carbon electrode to form a hydrogel through which substrates can readily diffuse. The TEMPO-LPEI electrode is used as an anode capable of generating currents from 0.41  $\pm$  0.06 mA cm<sup>-2</sup> in the presence of 250 mM sucrose to 8.20  $\pm$  0.04 mA cm<sup>-2</sup> in the presence of 2 M methanol and  $33.4 \pm 9.4$  mA cm<sup>-2</sup> in the presence of 500 mM formate under neutral pH and at 25 °C. The newly described anode is combined with an enzymatic biocathode to construct a hybrid biofuel cell to produce  $0.38 \pm 0.04$  mA cm<sup>-2</sup> while using 2 M methanol as a fuel source.



# 1. INTRODUCTION

Biologically available sugars and short-chain alcohols are seen as attractive potential fuel sources because they have high energy density and low toxicity. Recently, there has been great interest in the development of catalytic cascades that can facilitate multiple oxidative steps to increase the amount of energy extracted per molecule of fuel (energy density) at the anode of a fuel cell.<sup>1-4</sup> Organic alcohol-containing fuels can be electrochemically oxidized by transition metal catalysts to generate current densities in the range of milliamperes per square centimeter;<sup>5</sup> however, these catalysts often require alkaline conditions with elevated temperature and pressure to achieve high rates of oxidation (current density) and are rarely capable of deep oxidation. Therefore, there remains a significant need to develop environmentally friendly oxidation catalysts that are capable of facilitating multiple oxidative steps and are suitable for use in a fuel cell.

As a promising alternative to precious metals, TEMPO is a simple, organic oxidation catalyst capable of oxidizing a wide range of alcohols and aldehydes at room temperature and under mild aqueous conditions.<sup>6</sup> TEMPO has previously been shown to electrochemically oxidize primary and, to a lesser extent, secondary alcohols to the corresponding aldehydes and ketones.<sup>7–9</sup> The mechanism of TEMPO proceeds through an initial electrochemical oxidation step from a stable nitroxyl radical to the catalytically active oxoammonium salt; subsequent oxidation of the substrate results in a hydroxylamine, which is oxidized to the nitroxyl radical, completing the catalytic cycle.

For practical application in a fuel cell, it is desirable to immobilize TEMPO to prevent cross-contamination at the cathode, simplify the diffusional kinetics, and allow for reusability of the catalyst. TEMPO derivatives have been heterogenized onto a polymer matrix at an electrode interface;<sup>4,10</sup> however, previous studies have demonstrated that the immobilization of TEMPO results in a significant decrease in catalytic activity as a result of diffusional restrictions caused by the immobilizing matrix.<sup>11-13</sup> Previously, redox-active hydrogels based on either poly(vinylpyridine) (PVP) or poly-(ethylenimine) (PEI) have been used to entrap enzymatic catalysts because their ability to swell allows for rapid substrate diffusion throughout the gel matrix.<sup>14–16</sup> In such systems, polymers are doped or modified with redox moieties to facilitate rapid electron transfer to the active site of an oxidoreductase enzyme. We sought to modify this construct to allow for the redox mediator to also act as the catalyst. In addition, we have recently demonstrated the enhancement in electrocatalytic activity of TEMPO toward a simple bioavailable alcohol by the presence of a covalently linked basic amine functionality.<sup>17</sup> On the basis of this discovery, we envisioned using an amine-containing polymer to simultaneously enhance the catalytic rate of a relatively unreactive TEMPO species and act as an anchor for immobilization onto an electrode surface.

Herein, we demonstrate a TEMPO-modified linear poly-(ethylenimine) (TEMPO-LPEI) anode material that can be

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cross-linked onto the surface of a carbon electrode to electrocatalytically oxidize a wide range of saccharides and short chain alcohols under neutral aqueous conditions at room temperature. The catalytic activity of TEMPO-LPEI is compared with that of an analogous nonimmobilized TEMPO derivative to reveal a dramatic increase in the catalytic current density as a result of immobilization. In addition, we demonstrate how this immobilized organic oxidation catalyst can be combined with a previously reported enzymatic biocathode<sup>18</sup> to operate as a hybrid biofuel cell.

# 2. EXPERIMENTAL SECTION

**2.1. Chemicals and Solutions.** All chemicals were purchased from Sigma-Aldrich unless otherwise specified. Catalytic pH profile experiments and fuel cell experiments were performed using 200 mM phosphate/citrate buffer solutions at variable pH for the pH profiles and pH 5.0 for the fuel cell experiments, both at 25 °C. All other electrochemical experiments were performed using a 150 mM phosphate buffer at pH 7.0 and 25 °C.

**2.2. Scanning Electron Microscopy.** Samples were imaged by a FEI Quanta 600 FEG scanning electron microscope with true environmental (water vapor ambient) mode. The vapor pressure was controlled to be 0.24-0.31 Torr. The accelerating voltage was 15 kV with spot size 3.0 and dwell time 10  $\mu$ s. Both secondary and back-scattered electron images were captured.

**2.3. Electrochemistry.** Electrochemical experiments were performed using a CH Instruments 611C potentiostat. Cyclic voltammetry (CV) and constant potential amperometry experiments were performed with a standard three-electrode cell with a SCE reference electrode, a Pt mesh counter electrode, and a 3 mm glassy carbon electrode. Glassy carbon electrodes were polished with successive 1 and 0.5  $\mu$ m alumina slurries and rinsed with 18 M $\Omega$  water prior to use.

2.4. TEMPO-LPEI Electrode Film Preparation. Immobilized TEMPO-LPEI electrode films were prepared by dissolving the TEMPO-modified polymer into 0.05 M HCl (10 mg/mL). The polymer solution (80  $\mu$ L) was then combined with 2.5 M glutaraldehyde (0.25  $\mu$ L), and the mixture was stirred using a vortex generator for 10 s. For MWCNT-infused films, the polymer solution (80  $\mu$ L) was combined with carboxylated MWCNTs and stirred using a vortex generator for 15 s; to that mixture was added 2.5 M glutaraldehyde (0.25  $\mu$ L), which was then sonicated for 1 min and then stirred using a vortex generator for 20 s. For both film formulations, the electrode film solution mixture  $(3 \ \mu L)$  was coated onto the surface of a polished 3 mm glassy carbon electrode using a pipet tip to evenly distribute the solution across the electrode. The electrode films were allowed to cure under ambient conditions for 12 h prior to use.

**2.5.** Homogeneous 4-Methoxy-TEMPO Electrochemistry. Homogeneous TEMPO electrochemical characterization was done by performing CVs on a 2.5 mM solution of 4methoxy-TEMPO at 10 mV s<sup>-1</sup> at 25 °C in the absence and presence of substrate using 150 mM phosphate buffer, pH 7.0 and 25 °C. Catalytic pH profiles were generated by determining the catalytic current density ( $j_{max}$ ) in the absence and presence of 1 M glycerol at various values of pH using a 200 mM phosphate/citrate buffer at 25 °C.

**2.6. Electrochemistry of Cross-Linked Films of TEMPO-LPEI.** All films were electrochemically equilibrated prior to use by running CV scans in the absence of substrate to allow for stable and quasi-reversible redox peaks; 20 scans at 50 mV s<sup>-1</sup> from 0.0 to 0.8 V vs SCE. Electrochemical characterization of cross-linked TEMPO-LPEI films was performed using constant potential amperometry. Substrate kinetics were determined by measuring the change in current at a fixed potential of 0.8 V vs SCE while injecting various aliquots of substrate using a 150 mM phosphate buffer at pH 7.0 and 25 °C. Catalytic pH profiles were determined by monitoring the change in current at a fixed potential of 0.8 V vs SCE with the injection of various aliquots of 5 M glycerol (pre-equilibrated to the desired pH) using 200 mM phosphate/citrate buffer at 25 °C and various pHs.

**2.7. Hybrid Biofuel Cell Characterization.** Fuel cells consisted of a MWCNT-containing TEMPO-LPEI film on a 3 mm glassy carbon electrode (as described above) and a laccase biocathode. Electrochemical experiments were performed using a standard three-electrode cell with the reference and counter electrode connected to the TEMPO-LPEI anode and the working electrode connected to the laccase biocathode. Current and power density curves were generated using linear sweep voltammetry at 1 mV s<sup>-1</sup> in the absence and presence of 2 M methanol using stirred 200 mM phosphate/citrate buffer at pH 5.0 and 25 °C with ambient O<sub>2</sub> concentration.

#### 3. RESULTS AND DISCUSSION

**3.1. Synthesis and Characterization.** TEMPO was immobilized onto linear poly(ethylenimine) via a glycidyl linkage. Hydroxy-TEMPO (1) was combined with epichlor-ohydrin in the presence of a phase transfer catalyst and NaOH to produce 4-glycidyl-TEMPO (2), which was subsequently treated with LPEI overnight at room temperature to yield the desired TEMPO-LPEI polymer (3) (Scheme 1). Initially,

Scheme 1. Synthesis of TEMPO-LPEI (3) Where 4-hydroxy-TEMPO (1) Is Reacted with Epichlorohydrin To Form 4-Glycidyl-TEMPO, Which Subsequently Is Reacted with Linear Poly(ethylenimine) To Result in 27% Substitution of the Polymer Backbone



TEMPO-LPEI was cross-linked with glutaraldehyde onto the surface of a glassy carbon electrode; however, the resulting film proved to be physically unstable in  $H_2O$  and could be observed delaminating from the electrode. This problem was addressed by the addition of carboxylated multiwalled carbon nanotubes (COOH-MWCNTs) into the films to enhance structural rigidity and improve active surface area. SEM micrographs are shown in Figure 1 of the TEMPO-LPEI films with and without MWCNTs before and after being probed by cyclic



Figure 1. SEM micrographs of cross-linked TEMPO-LPEI films without MWCNTs (1) and with carboxylated MWCNTs (2) prior to use (a) and after multiple CVs (b).

voltammetry. In the absence of MWCNTs, the cross-linked films undergo rapid delamination that corresponds to the loss in electrochemical signal. However, films containing MWCNTs appear to exhibit swelling, but remain adhered to the electrode surface and maintain their electrochemical signal. This indicates that the incorporation of the MWCNTs adds a degree of structural rigidity, which in turn results in an enhanced electrochemical stability.

After synthesizing the TEMPO-modified polymer, we sought to determine how the electrocatalytic characteristics of the immobilized TEMPO compared with that of an analogous homogeneous TEMPO derivative. The catalytic activity of both the TEMPO-LPEI films and 4-methoxy-TEMPO (homogeneous catalyst) were determined with a combination of slow scan rate cyclic voltammetry and constant potential amperometry. Representative catalytic CVs of TEMPO-OMe and TEMPO-LPEI in the absence and presence of glycerol are shown in Figure 2. The reversible oxidation and reduction peaks correspond to the nitroxyl radical species and oxoammonium salt being oxidized and reduced, respectively. In the presence of substrate, the oxoammonium salt is chemically converted into the hydroxylamine while producing the oxidized substrate; the hydroxylamine is then electrochemically oxidized back to the nitroxyl radical and subsequently to the active oxoammonium salt. Electrocatalysis in the CV is thus observed as an increase in the peak oxidative current density, with a corresponding decrease in the peak reductive current density, and the catalytic current density  $(j_{max})$  is defined by the difference between the peak oxidation current in the presence of saturating substrate concentrations and the oxidative current in the absence of substrate. Because of the swelling and shrinking of the TEMPO-LPEI hydrogel film, it is exceptionally difficult to determine the exact concentration of TEMPO within any given film. Thus, a concentration of homogeneous methoxy-TEMPO was selected to result in a comparable capacitance-corrected peak anodic current  $(i_{pa})$  to that of the immobilized TEMPO species.

**3.2. Electrocatalytic Activity Comparison.** The catalytic activity of both catalysts was determined for a variety of



**Figure 2.** Comparative CVs of 2.5 mM 4-methoxy-TEMPO (A) and a cross-linked film of TEMPO-LPEI (B) in the absence (dashed) and presence (solid) of 1 M glycerol. CVs were performed using a 150 mM phosphate buffer at 10 mV s<sup>-1</sup>, pH 7.0, and 25 °C.

biofuels, including methanol, glycerol, and sucrose; the resulting calibration curves are shown in Figure 3. Values of  $j_{\text{max}}$  for TEMPO-LPEI were between 2× and 50× higher than that of the homogeneous TEMPO analogue for all of the substrates examined, while reaching  $j_{max}$  values as high as 8.20  $\pm$ 0.04 mA cm  $^{-2}$  in methanol compared with 0.72  $\pm$  0.06 mA  $cm^{-2}$  for the homogeneous catalyst. The largest increase in  $j_{max}$ between the immobilized and homogeneous catalysts is observed in the presence of isopropyl alcohol. Where the homogeneous methoxy-TEMPO is virtually unreactive toward the simple secondary alcohol, TEMPO-LPEI is able to generate  $3.5 \pm 0.9$  mA cm<sup>-2</sup> in the presence of 5 M isopropyl alcohol in 150 mM phosphate buffer at pH 7 and 25  $^\circ$ C. This result runs counter to previous reports and conventional wisdom, which indicates that immobilization of a TEMPO catalyst will necessarily result in decreased activity due to diffusional restrictions induced by immobilization.<sup>11</sup> Evidence from our previous work suggests that the presence of a covalently linked amine can enhance the rate of electrocatalytic alcohol oxidation by TEMPO.<sup>17</sup> Although the exact nature of this rate enhancement is still under investigation, our present results indicate that the localized abundance of amines from the LPEI backbone may be inducing a similar effect. Such a result is not trivial because it implies that any TEMPO catalyst could be immobilized in a polyamine network to enhance the catalytic rate while simultaneously localizing the electrochemical catalysis. A further discussion on the possibility of self-reactivity between the TEMPO catalyst and the polyamine backbone as **ACS Catalysis** 



Figure 3. Electrocatalytic calibration curves of cross-linked TEMPO-LPEI films ( $\bullet$ ) and in situ 2.5 mM 4-methoxy-TEMPO ( $\bigcirc$ ) for methanol, ethanol, isopropyl alcohol, glycerol, fructose, and sucrose. Concentration profiles were determined using 150 mM phosphate buffer at pH 7.0 and 25 °C.

well as overall film stability can be found in the Supporting Information.

It should be noted that the kinetics of the catalytic reaction are altered upon immobilization onto a PEI hydrogel. Because of the complex nature of substrate diffusion through hydrogel films, all kinetic parameters presented here refer to apparent values that do not necessarily correspond to the absolute kinetics of the immobilized TEMPO catalyst but, rather, the observed combination of diffusional and kinetic effects experienced by the catalyst within the hydrogel matrix. A complete list of kinetic parameters as well as a preliminary product analysis is provided in the Supporting Information (Table S1 and Scheme S1). The apparent Michaelis-Menten constant  $(K_m^*)$  for TEMPO-LPEI is approximately double that of the homogeneous methoxy-TEMPO catalyst for all of the substrates examined. In addition, the magnitude of catalytic current densities for TEMPO-LPEI appears to be dependent on the relative size of the substrate. These combined results indicate that the immobilized TEMPO catalyst is, in fact, limited by diffusion, but to a significantly lesser extent than previously studied methods for TEMPO immobilization.<sup>11</sup> This is likely a result of the hydrogel nature of cross-linked LPEI films, which allows for dramatic swelling of the polymer film upon electrochemical oxidation of TEMPO and subsequently facilitates rapid diffusion of the substrate through the polymer network.

In addition to enhanced catalytic activity and rapid diffusion, LPEI provides a localized buffer region to facilitate TEMPO catalytic activity under mildly acidic conditions.<sup>19,20</sup> A comparative pH profile shown in Figure 4 for the catalytic activity of each catalyst toward 1 M glycerol highlights the expanded pH range of TEMPO-LPEI films compared with homogeneous methoxy-TEMPO. This characteristic allows for much more mild reaction conditions than those required for many transition metal electrooxidation catalysts, and thus,



**Figure 4.** Comparative pH profile of cross-linked TEMPO-LPEI films ( $\bullet$ ) and homogeneous 2.5 mM 4-methoxy-TEMPO ( $\bigcirc$ ). Profiles were determined using 200 mM phosphate/citrate buffer with 1 M glycerol at variable pH and at 25 °C.

TEMPO-LPEI films are more compatible with a wide range of biological catalysts that can be used to facilitate deeper biofuel oxidation.

**3.3. Reaction Cascade for the Complete Oxidation of Methanol.** To determine the feasibility of using TEMPO-LPEI films to catalyze multiple oxidations for a single fuel source, our focus shifted toward methanol as a simplified substrate for which the pathways to complete oxidation are limited, with the predominant oxidation pathway going through formaldehyde and formate intermediates prior to formation of  $CO_2$ . The catalytic current densities of TEMPO-LPEI films with each intermediate, methanol, formaldehyde, and formate were determined using constant potential amperometry and confirmed using cyclic voltammetry. Reaction profiles for formaldehyde and formate are provided in the Supporting Information (Figure S3) and representative voltammograms are



Figure 5. Representative cyclic voltammograms of MWCNT-infused TEMPO-LPEI films in the absence (black) and presence (blue) of 400 mM formaldehyde (A) and 500 mM sodium formate (B). Experiments were performed on 3 mm glassy carbon electrodes using 150 mM phosphate buffer at 10 mV s<sup>-1</sup>, pH 7.0, and 25 °C.

(described above),  $4.8 \pm 0.4 \text{ mA cm}^{-2}$  in formaldehyde, and  $33.4 \pm 9.4$  mA cm<sup>-2</sup> in a solution of formate at pH 7.0 and 25 °C. These results indicate that a catalytic oxidative cascade of methanol with TEMPO-LPEI should be limited by the oxidation of formaldehyde, which could be the result of equilibrium between formaldehyde and its corresponding monohydrate under aqueous conditions. The equilibrium between formaldehyde and formaldehyde monohydrate lies heavily in favor of the monohydrate, which is the form that is active toward oxidation by TEMPO; however, the small amount of the substrate in the nonhydrated form could be responsible for the relatively lower reactivity when compared with that of methanol. The extraordinary catalytic current density generated by TEMPO-LPEI in the presence of formate is largely attributed to the formation of  $CO_2$  gas, which both allows for the rapid diffusion of products away from the electrode surface and subsequently skews the catalytic equilibrium to favor continued oxidation. The successful oxidation of each intermediate of the methanol oxidation cascade indicates that TEMPO-LPEI films are capable of the complete oxidation of methanol under low temperature conditions and at neutral pH.

**3.4. TEMPO-LPEI Films in a Hybrid Fuel Cell.** The expanded pH range of TEMPO-LPEI allowed us to consider the possibility of coupling our new anodic material with an enzymatic biocathode to construct a compartmentless hybrid

enzymatic/organic catalyst biofuel cell. Such enzymatic cathodes are not catalytically active under basic conditions but are capable of reducing  $O_2$  under mild acidic conditions at room temperature. A previously reported biocathode was selected that utilizes the direct electron transfer of a laccase enzyme that can generate nonlimiting current densities under the desired conditions.<sup>18</sup> Methanol was chosen as a fuel source for the hybrid biofuel cell for the high catalytic current densities achieved by the TEMPO-LPEI anode. A representative power curve is shown in Figure 6. The maximum current density for



**Figure 6.** Current density (black) and power density curves (blue) for a fuel cell consisting of a cross-linked TEMPO-LPEI anode and a DET laccase cathode. Curves were generated using 200 mM phosphate/ citrate buffer with 2 M methanol at pH 5.0 and 25  $^{\circ}$ C. The corresponding controls were run in the absence of methanol and are shown as dashed lines.

the resulting fuel cell was 378 ± 39  $\mu$ A cm<sup>-2</sup>, with a maximum power density of 8 ± 1  $\mu$ W cm<sup>-2</sup> using a solution of 2 M methanol at pH 5.0 and 25 °C. The lack of a diffusion-limited region of the current density curve suggests that the hybrid fuel cell is presently limited by the low overall cell potential ( $E_{cell}$ ), which is largely due to the relatively high oxidation potential of the TEMPO-LPEI anode material. Despite a low overall cell potential, these results provide an initial proof of concept for the use of TEMPO derivatives as organic electrocatalysts in the context of a fuel cell.

## 4. CONCLUSION

We have demonstrated a method of covalent immobilization of 4-glycidyl-TEMPO onto a LPEI backbone, which, when crosslinked onto a carbon electrode, can result in a dramatic enhancement in the catalytic current density (as high as 8.20 mA cm<sup>-2</sup>) when compared with an analogous homogeneous TEMPO catalyst. It is currently thought that the enhanced activity is derived from the cationic nature of the polymer backbone; however, the exact nature of the rate enhancement is currently being investigated. This new electrocatalytic material was shown to oxidize several bioavailable alcohols as well as several short-chain alcohols under neutral aqueous conditions at 25 °C. Such a broad substrate range allows for the possibility of utilizing an immobilized TEMPO catalyst to facilitate a wide range of oxidative cascades. TEMPO-LPEI was coupled with a DET laccase cathode to construct a hybrid enzymatic/organic catalyst biofuel cell capable of generating 378  $\mu \rm A~cm^{-2}$  in a 2 M aqueous methanol solution at pH 5.0 and 25 °C. Although the fuel cell is limited by a low cell potential, it provides a proof of concept demonstrating the possibility of using an immobilized

TEMPO species as the anodic catalyst in a fuel cell operating at near neutral pH. Furthermore, ongoing research is focused on the development of TEMPO catalysts that can operate at lower oxidation potentials while maintaining high catalytic activity under mild aqueous conditions.

# ASSOCIATED CONTENT

# **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01668.

Experimental procedures, synthesis and characterization of TEMPO-LPEI, preliminary product analysis, electrochemical film stability analysis, and substrate kinetics (PDF)

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#### Notes

The authors declare no competing financial interest.

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