Ionic Liquid Stabilized TEMPO Catalysis for Alcohol Oxidation

*Min Li[†], Kevin Klunder[†], Emmy Blumenthal[†], Matthew B. Prater[†], Jack Lee[†], John E. Matthiesen[‡], Shelley D. Minteer[†]**

† Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, UT, 84112, United States. ‡ 2265 S State St, Salt Lake City, UT, 84115, United States.

*Corresponding Author: Shelley D. Minteer

Email Address: minteer@chem.utah.edu

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ABSTRACT

N-oxyl reagents, particularly 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), have been extensively used for alcohol oxidations. While TEMPO-mediated oxidations are kinetically and thermodynamically favorable in high pH electrolytes, base-induced degradation often results in significant loss of catalytic activity. Herein, we demonstrated enhanced alkaline stability of

TEMPO derivative in ionic liquids (ILs). By incorporating TEMPO in imidazole-anchored IL, no loss of current was observed at pH 10.0 after 2.0 h during the oxidation of butanol and glycerol, while TEMPO in polycaprolactone (PCL), a patternable binder material, degraded 58.5%, and 67.1%, respectively. The stability enhancement was further demonstrated by analyzing the conversion of glycerol in an 800 μL electrochemical cell using bulk chemical analysis techniques. Successive cycles of glycerol oxidation indicated 14-fold stability enhancement by applying IL in TEMPO electrode composite in comparison to PCL. The strategy demonstrated here provides an opportunity to prepare catalytic systems with enhanced stability. Further, this method provides the ability to convert what are typically homogeneous catalysts to heterogeneous systems.

INTRODUCTION

Among catalysts developed for alcohol oxidations, N-oxyl compounds, such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), have enjoyed widespread applications due to their remarkably low-cost, high activity, and metal-free nature.[1] The oxidized oxoammonium species ($TEMPO^+$) are required for alcohol oxidation and are generated from the chemical or electrochemical oxidation of TEMPO. The use of chemical oxidants (e.g., NaOCl,[2] or NOx/O_2[3]), however, produce undesired byproducts and often requires a co-catalyst (e.g., n-Bu_4NBr[4,5] or pyridine hydrobromide[6]) to generate active oxoammonium cation *in situ*. Alternatively, the electrochemical generation of $TEMPO^+$ by one-electron oxidation of TEMPO is simple, clean, and versatile.[7] The electrons replace traditional oxidants, thus circumventing byproduct formation. Moreover, electrochemical analysis renders it possible to directly and easily observe catalysis, which is otherwise not attainable *via* traditional thermal synthesis. Further, the

activation of alcohol oxidations by external potential gives rise to reactions operated under mild conditions (*e.g.,* ambient temperature and pressure). Thus, the potential degradation of thermally unstable alcohols can be significantly prevented. While many TEMPO-based electrochemical synthetic strategies utilize homogeneous catalysts,[8] the use of heterogeneous catalysts is highly advantageous as it does not require removal from the final product.[9] Finally, catalyst fouling can severely decrease catalyst activity (in the order of graphite felt > glassy carbon > graphite due to increased surface area). Thus, developing a stable surface-immobilized catalyst is critical for repeated syntheses.

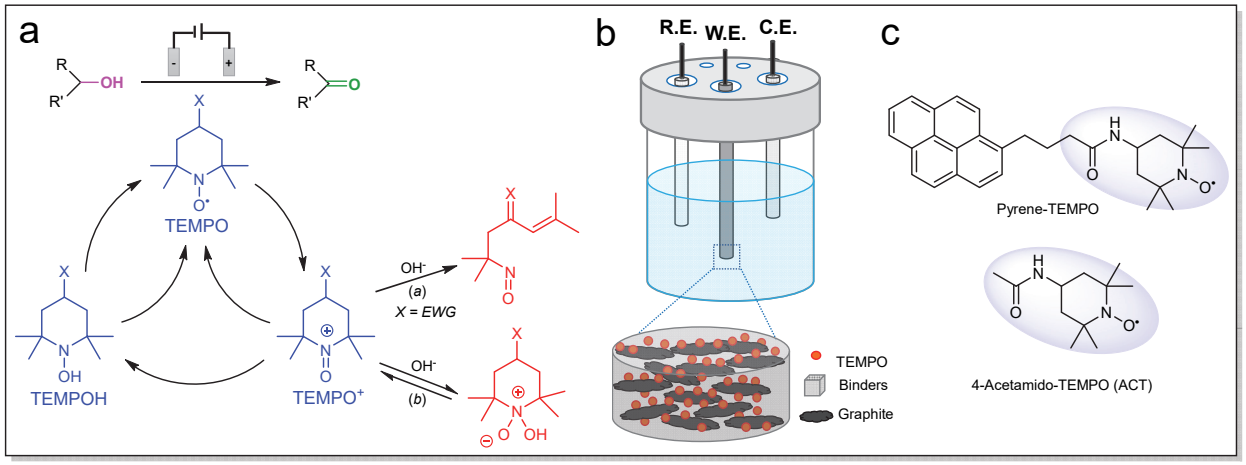
Regardless of the advancements made in TEMPO-mediated studies, the use of TEMPO in electrochemical oxidations still encounters challenges. In particular, the performance of TEMPO and its derivatives in catalysis and synthetic oxidations are well documented, but examples of their stability are rare.[8,10] In TEMPO-mediated reactions, oxidations are mainly performed in alkaline conditions as high pH electrolyte alleviates both kinetic and thermodynamic limitations[11] (*e.g.,* comproportionation of $TEMPO^+$ with TEMPOH, and oxidation of the corresponding hydroxylamine to TEMPO). However, oxoammonium species are susceptible to base-induced degradation, which results from the elimination reaction that cleaves C-N bond and consequently ring-opening of the oxoammonium (pathway (a) in **Scheme 1a**).[12] This is especially problematic for electron-deficient aminoxyls. In many instances, this catalyst degradation process has challenged the use of high pH electrolytes for long-term electrosynthesis. For instance, F. Geneste *et al*. reported the attachment of TEMPO *via* an amide link to a graphite felt electrode. Though the catalytic stability was improved after immobilization in comparison to TEMPO in solution, the current-voltage response decreased to 50% after 50 scans at pH 10.3.[13] Another example is the immobilization of TEMPO in a Nafion film for

carbohydrate oxidation at pH 10.[14] The catalyst was active, but the activity of TEMPO decreased dramatically. Aside from the ring opening-associated degradation, $TEMPO^+$ may also form a zwitterionic adduct (TEMP(OH)O) at high pH values (pathway (b) in (**Scheme 1a**).[9,15,16] The formation of this TEMP(OH)O from $TEMPO^+$ is an equilibrium process and favors TEMP(OH)O when increasing base concentration.[8] As a result, the base-promoted decomposition and the formation of the inert zwitterion compete with the base-promoted formation of TEMPO/$TEMPO^+$, resulting in the loss of reactive $TEMPO^+$ for further alcohol oxidation. Recently, Cardiel *et al.* evaluated the stability of 4-acetamido-TEMPO (ACT) at pH 12. Almost a quarter of ACT was degraded after 30 min.[17] Consequently, the development of catalyst systems that enable preserving TEMPO catalytic activity at high pH values remains an important challenge.

The advent of room-temperature ionic liquids (RTILs) as the solvent or in an electrode composite has opened up many new opportunities for the improvement of catalyst performance.[18,19] The ionic nature of RTILs, wide electrochemical window and good solubility for both organic and inorganic molecules, provide various advantages in electro-synthesis. RTILs are a 'designer' solvent in which their physicochemical and electrochemical properties (e.g., thermal stability[20] and electrochemical stability[21,22]) can be tuned *via* cations or/and anions. RTILs have thus resulted in an exciting class of catalytic systems with properties not attainable with traditional organic solvents. For example, TEMPO in RTILs[23-26] or TEMPO-derived ionic liquids (ILs)[27,28] have shown to be capable of recovery and reuse without any significant loss of catalytic activity. A multilayered covalently supported ionic liquid phase (mlc-SILP) system has given a new dimension to IL-based catalysis.[29-31] In mlc-SILP, bisvinylimidazolium salt is oligomerized with thiol-anchored solid (e.g., silica), resulting in the covalent addition of

multilayered IL on silica. The resultant mlc-SILP combines the benefits of both homogeneous and heterogeneous catalysts. RTILs, therefore, hold great promise in developing effective catalytic systems.

In this paper, we present efforts in extending the high alkaline chemical stability of RTILs to enhance the catalytic activity of TEMPO derivatives under alkaline conditions. To achieve this, a hydrophobic TEMPO was homogeneously mixed in RTILs with graphite being added to improve the conductivity of the composite. The resultant carbon ionic liquid electrodes (CILEs) (**scheme 1b**) are employed as a part of the biphasic system (electrode phase and electrolyte phase) – reactant moves to the boundary of the CILE, reacts, and is then released back into the solution. Consequently, the strategy demonstrated here addresses the issue of base-induced TEMPO degradation and also converts what are typically homogeneous catalysts to heterogeneous systems. A key point is that the use of TEMPO in alcohol oxidations has been extensively demonstrated.[8,10] What distinguishes the approach reported here from existing strategies is that CILEs enhance the TEMPO catalytic stability by simply tuning its microenvironment. This feature, when combined with highly active TEMPO derivatives, will facilitate alcohol conversions, particularly for primary aliphatic alcohols.



Scheme 1. (a) Simplified mechanism for TEMPO-mediated alcohol oxidation under basic condition. Adapted from ref [8]. Compounds engaged in the catalytic cycle are labeled in blue, and two possible TEMPO degradation pathways are highlighted in red. **(b)** Schematic description of the electrode composites studied in this work. Binders are RTILs. PCL as a binder was also studied as a comparison. A hydrophobic TEMPO is required to form the composite. **(c)** Chemical structure of pyrene-TEMPO, and the analog of 4-acetamido-TEMPO used in the present work.

EXPERIMENTAL SECTION

Materials. 1-methylimidazole (>99.0%, TCI), 1-methylpyrrolidine (>99%, TCI), 1-bromobutane (>98%, TCI), 1-bromohexane (>98%, TCI), 1-bromodecane (>98%, TCI), potassium hexafluorophosphate (>95.0%, TCI), and lithium bistrifliimide (>98%, TCI) were purchased from Fisher Scientific (Thermo Fisher Scientific, Inc., Waltham, MA). Trihexyltetradecylphosphonium chloride (≥95.0%), methyltrioctylammonium bromide (97%), 1-butyl-3-methyllimidazolium tetrafluoroborate (≥98%), isoquinoline (97%), 1-pyrenebutyric acid (97%), 4-amino-TEMPO (97%), N,N'-dicyclohexylcarbodiimide (DCC, 99%), and 4-dimethylamino pyridine (4-DMAP,≥99%) were purchased from Sigma-Aldrich, Inc. (St. Louis, MO). Pyrene-TEMPO was prepared according to a literature procedure.[25] Details of the preparation of RTILs are shown in the Supporting Information.

Electrochemical Methods. The details of the preparation of CILEs and PTPEs are described in the Supporting Information. All electrochemical experiments were performed with CH Instruments 611C and 660E potentiostats (CH Instruments, Inc., Austin, TX). Cyclic voltammetry (CV) and constant potential amperometry experiments were conducted with a

standard three-electrode cell using SCE as a reference electrode, and carbon as a counter electrode. pH 10 0.1 M carbonate buffer was used as the electrolyte, and 55.5 mM alcohols were applied in all experiments, unless otherwise indicated.

Electrochemical Cell Fabrication. An 800 μL electrochemical cell was designed and fabricated for the detection of analytes. The working and counter electrodes were made from a 0.125″ poly(methylmethacrylate) (PMMA) sheet (*Acrylic Mega Store in Amazon*). A 0.250″ PMMA sheet (*Mifflin*) was used for other interface layers. A PLS6.150D Laser-Cutter tool (*Universal Laser Systems*) was configured with an Epilog Zing (30 Watt, *Epilog Laser*) CO_2 laser to cut and raster (ablate) the materials. The materials were then patterned and cut into several rectangular pieces that were stacked compressed together using machine screws and nuts to form a watertight cell. Laser-cutting and rastering details are described in the Supporting Information.

Glycerol Conversion. To quantitatively analyze glycerol conversion and C_3 products, reaction mixtures were analyzed on a Waters H-Class UPLC fitted with an Aminex HPX-87H column connected in series with photodiode array (PDA) and QDa detectors. A 10 uL sample was injected into the column at 0.6 mL/min flow rate using 0.1% formic acid mobile phase at room temperature (~23 °C). The quantity of analytes in the samples was obtained by analysis of exact masses $(M+H)^+$ or $(M+Na)^+$.

RESULTS AND DISCUSSION

High pH electrolytes promote TEMPO-mediated oxidations, while the degradation of TEMPO is also favorable in base.[8] Ionic Liquids (ILs), however, possess good alkaline chemical stability and TEMPO solubility.[33,34] This gives us an opportunity to design electrode composites in which ILs are used as on part of a biphasic system (electrode phase and buffer phase) preventing

TEMPO from being decomposed (**Scheme 1b**). First, a TEMPO-based composite with IL 1-decyl-3-methylimidazolium bistriflimide (C_{10}mimNTf_2) was developed. Another composite electrode system composed of polycaprolactone (PCL) as binder[35] (PTPEs) was prepared as a comparison due to its low melting point, low cost, and good solubility in organic solvents.[35] Pyrene-TEMPO[32] (**Scheme 1c**) was chosen as the TEMPO moiety for use in both composite electrodes, because of its hydrophobicity and ability to pi-pi stack to carbon surfaces. In this work, we do not seek to prepare new TEMPO derivatives, but rather develop an electrode platform in which RTILs actively performed in the catalytical system. Thus, our strategy below could be used for other nitroxyl radicals that have been designed.

Catalytic Activity of CILEs Towards Different Alcohol Substrates. Before evaluating the catalytic stability of CILEs, the catalytic activity of the electrode composites towards different alcohols were initially investigated. As the TEMPO to IL ratio also plays an important role in catalytic performance, the amount of IL, and graphite/TEMPO ratio were first optimized (**Figure S1**). The optimum ratio of TEMPO to IL was found to be 0.48:5 (mg : μL). The optimized ratio resulted in the largest current density observed at 0.9 V vs. SCE during the oxidation of 1-butanol using cyclic voltammetry.

With the optimized ratio, the TEMPO-mediated oxidation of CILEs in a series of alcohol substrates was studied (**Figure 1**). The increased anodic peak shows the onset potential of each substrate during the TEMPO-mediated oxidations.[36] Another critical feature observed is the variances among the anodic current of different alcohols. Specifically, the anodic current of primary alcohols is considerably higher than that of secondary alcohols, likely the result of the lower pKa of primary alcohols and small steric hindrance.[37,38] In addition, electron-rich substrates (e.g., benzylic alcohols) exhibit larger anodic currents than aliphatic alcohols.[39,40]

The differences in the oxidation reactivities of alcohols highlight the need for maintaining the stability of TEMPO-based composites, particularly for substrates with low oxidation rates. For example, the pyrene-TEMPO used in this work has a current density of 8.3 mA/cm^2 (at 0.8 V vs. SCE) for benzyl alcohol. However, 1-butanol has a density that is nearly 50% lower. In the case of glycerol, although it possesses two primary alcohols, the reaction rate was surprisingly comparable to 1-butanol. Due to the low activity of these aliphatic alcohols, it is not only important to develop catalysts that are active, but also highly stable.

In the following work, glycerol is highlighted as a case study considering it is a biomass-derived aliphatic alcohol. 1-butanol was included as another model substrate for evaluation of CILEs due to its structural similarity to glycerol, but only one primary alcohol is present. Here we are interested in examining whether the CILEs developed would improve the oxidation stability of aliphatic alcohols, and further, whether the ILs utilized, coupled with the fundamental understanding of their properties, would allow flexibility and control in the catalytic system.

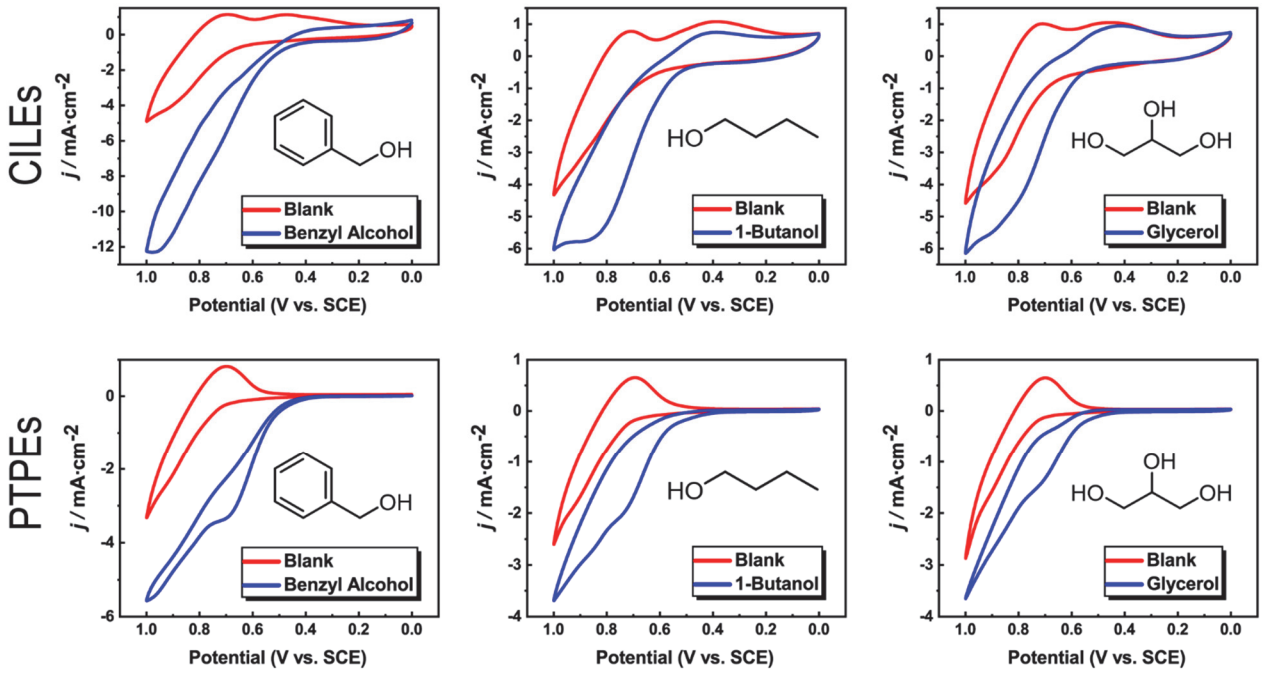


Figure 1. Representative cyclic voltammograms (5 mV s^{-1}) of various alcohols in 0.1 M carbonate buffer (pH 10) using two-electrode composites CILEs (top), and PTPEs (bottom), respectively.

Catalytic Stability of TEMPO-Based Electrode Composites in ILs. Considering TEMPO-mediated oxidation is pH sensitive and can induce degradation, amperometry using CILEs and PTPEs were performed at a pH range of pH 9.0 to pH 12.0. **Figure 2** shows the amperometric results of the different electrode platforms with electrolysis for 2.0 h. For stability evaluation, the current at 5.0 min was chosen as the initial steady-state current, and background current was subtracted to obtain the catalytic current. Clearly, in comparison to the control binding material of PCL, the use of RTILs resulted in a dramatic enhancement of the catalytic stability of the TEMPO composite. In particular, for butanol oxidation using CILEs, almost no current loss was achieved throughout all pH values. However, the current loss with PTPEs steadily increased from 47.9% current loss (pH 9.0) and reached up to 82.0% current loss at pH 12.0. In the case of glycerol oxidation, this drop became more significant, especially when the pH was higher than 10.0. With PTPEs, 83.2% and 84.6% catalytic current was lost at pH 11.0 and pH 12.0, respectively. However, this loss was considerably diminished *via* CILEs, where 30.0% and 41.1% current loss was observed for pH 11.0 and pH 12.0, respectively. These results demonstrate that the binder plays a crucial role in catalyst stability.

Aside from catalytic stability, it is also noteworthy that while high pH electrolyte facilitates substrate conversion, the increase of current density became diminishing return after pH 11.0. This slower increase might result from the increased rate of TEMPO degradation at high pH values. As a result, the competition between the base-induced degradation and the base-favored oxidation has to be considered to choose an optimal pH for alcohol oxidation.

Additionally, consistent with **Figure 1**, the additional alcohol groups in glycerol, in comparison to 1-butanol, did not result in faster conversion. In contrast, a decrease in current density was observed. This decreased anodic current was significantly mitigated by using CILEs. For instance, a 42.5% current density increase was observed for PTPEs when changing pH from 10.0 to 11.0, while a 121.6% increase in current density was observed for CILEs for the same pH change. Consequently, utilization of CILEs is not only capable of enhancing the catalytic stability, but also enables the improvement in reactivity.

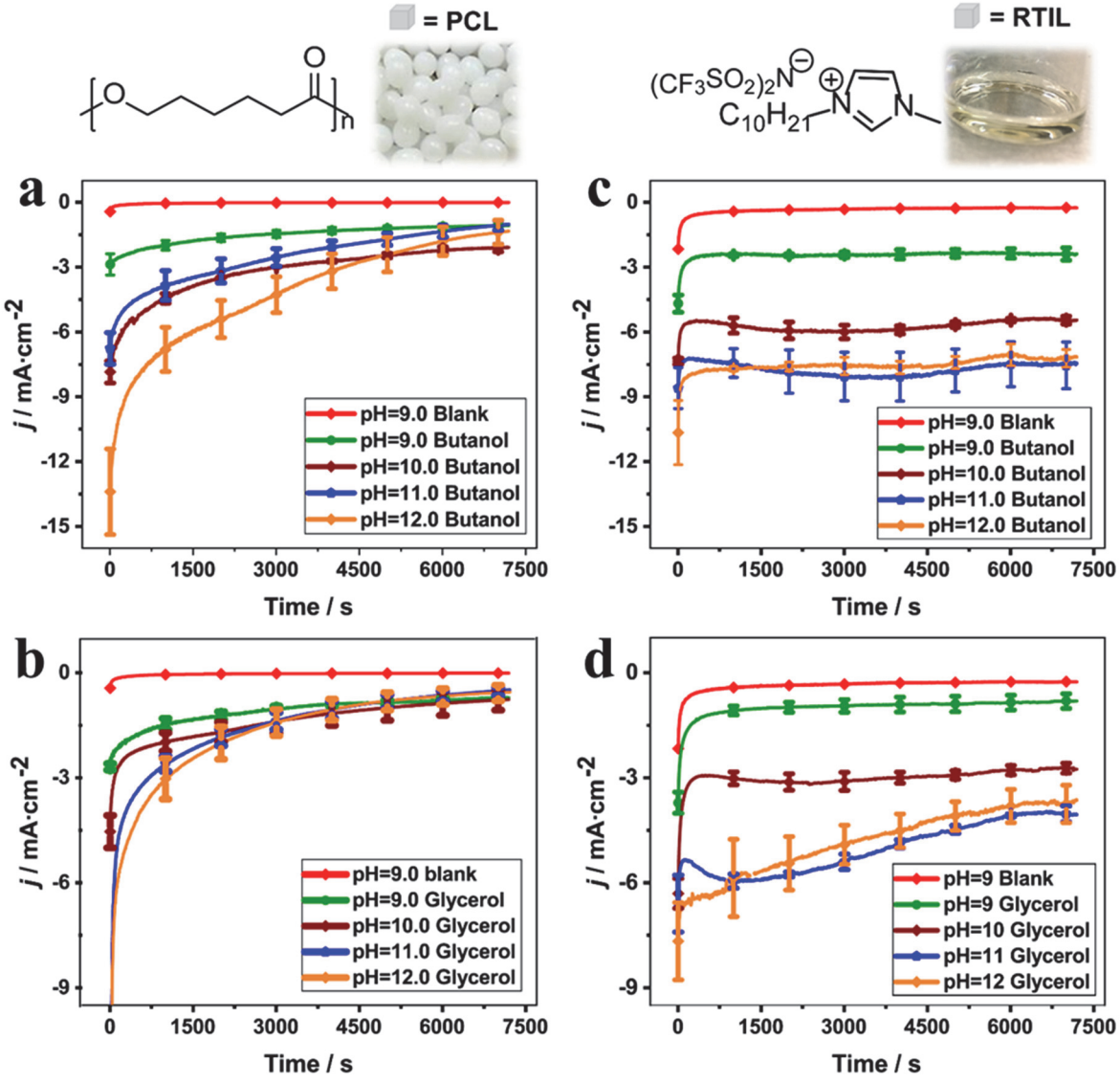


Figure 2. Effects of binders on the catalytic performance of TEMPO electrode composites. Amperometry results using PTPEs for butanol **(a)** and glycerol **(b). (c)** and **(d)** are the background subtracted current response using CILEs for butanol, and glycerol oxidation, respectively.

Electrochemical Behavior of Various Ionic Liquids. To unravel the structural effect of ILs on the composite catalysis, a series of ILs that possess different chain lengths and cations were studied. The ILs anion, bistriflimide, was fixed and the corresponding cation varied in chain length from C4 to C14. Bistriflimide anion was chosen due to its fast reaction kinetics and product selectivity for alcohol oxidations.[41] **Figure 3** shows the electrochemical behavior of the electrodes prepared with various ILs. Different from PTPEs, there appears to be two separate reduction peaks present in many of the IL-TEMPO combinations. It was hypothesized that TEMPO, from within the CILE matrix, that was not in contact with the solution triggered broadening or the appearance of two peaks. The TEMPO is essentially in a solution of electrolyte when buried in the electrode and should be able to be redox cycled, even when not in contact with the solution.

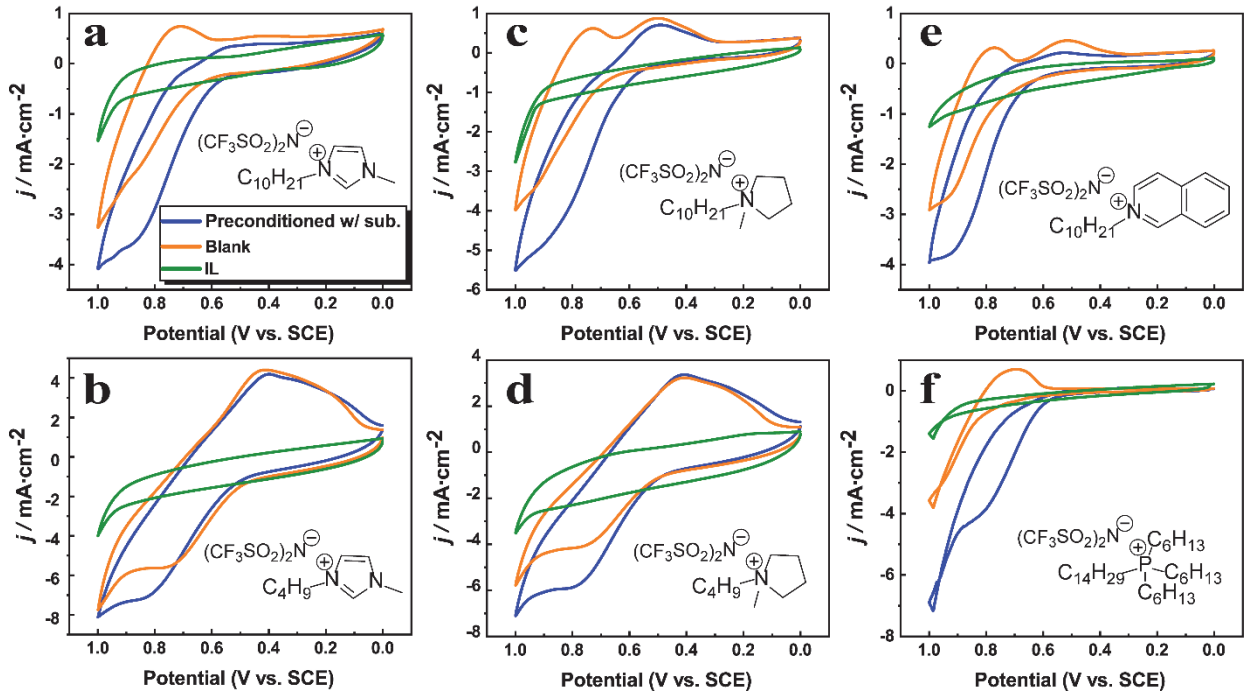


Figure 3. Electrochemical behavior of a variety of ionic liquids in TEMPO-mediated glycerol oxidation. The green trace is the CV of electrode composites consisting of only carbon and ionic liquids. The orange trace is the CV of CILEs with TEMPO embedded. The blue trace is the CV of CILEs with TEMPO using glycerol (55.5 mM) as a substrate. All the CVs were recorded using a scan rate of 5 mV/s, and 0.1 M carbonate buffer (pH 10.0).

Note that in **Figure 3a-e**, the secondary peak at lower potential maintained its reductive redox feature even in the presence of substrate. To study the effect of ILs on the redox nature of TEMPO, 4-acetamido-TEMPO (ACT) was selected as an analog for pyrene-TEMPO. ILs were used as the bulk electrolyte in a typical three-electrode electrochemical cell. This three-electrode cell experiment serves as an analog to what is happening within the CILE matrix. Acetonitrile was added in ILs to enhance the solubility of ACT, and adjust the viscosity of ILs – increasing the amount of acetonitrile decreases IL viscosity. The resulting IL solution used is 50% C_4mimNTf_2, 50% C_4mimBF_4, 50% C_{10}mimNTf_2, and 90% C_{10}mimNTf_2 (in the order of lowest

to highest). The chain length on the IL was adjusted from C4 to C10 which has a reported difference of ~ 4 – 4.5 in conductivity. Conductivity and viscosity values of the three ILs employed are listed in **Table S1**. The results from **Figure 4** indicate that peak separation is highly dependent on the viscosity of the IL. When nearly neat C_{10}mimNTf$_2$ was used, the peak current was severely diminished and the CV had the greatest peak separation, with a reductive peak at -0.5 V vs. SCE. This is near identical for the second peak location with CILEs in **Figure 3a, c, e**. Indeed, the blank CVs in **Figure 3b, d** with the C4 IL appear to be almost fully dominated by the presumed subsurface redox-active TEMPO. This is logical as the smaller IL is less viscous, thereby easier to rearrange. Viscosity is well known to affect the peak-to-peak separation (electron transfer kinetics), causing an increase in separation as viscosity increases.[42]

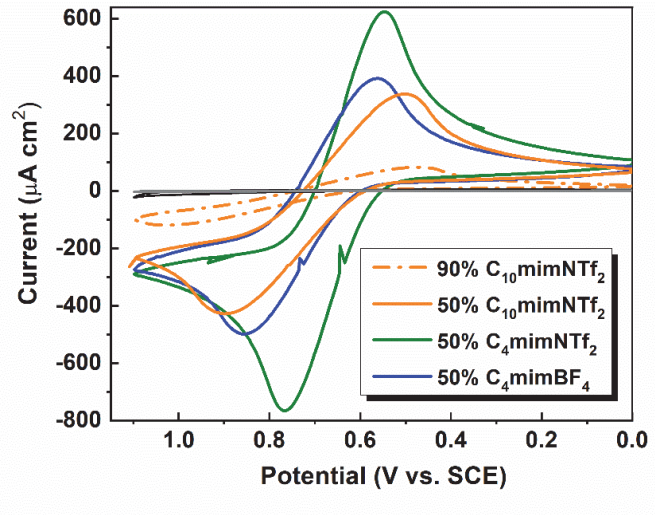


Figure 4. Cyclic voltammetry of 24 mM 4-acetamido-TEMPO dissolved in various ILs with 10 and 4 chain length and differing anion. 3mm diameter glassy carbon electrode at 300 mV/s.

While ILs with the short carbon chain (e.g., 1-butyl-1-methylimidazolinium bistrifliimide, C_4mimNTf$_2$, and 1-butyl-1-methylpyrrolidinium bistrifliimide, C_4mpyrNTf$_2$) displayed the least peak separation, the oxidative current only increased slightly with the

substrate, indicating that the catalytic reactivity of TEMPO in these ILs became slow. Therefore, ILs with long carbon chains were selected to further investigate the effect on the stability of electrodes (**Figure S2**). The results indicated that all electrode composites retained their catalytic activity after 100 cycles. However, after 300 cycles, electrodes composed of Trihexyltetradecylphosphonium bistrifliimide ($P_{66614}NTf_2$) and 2-decylisoquinolinium bis(trifluoromethanesulfonyl)imide ($[C_{10}qun]NTf_2$) degraded. In contrast, CILEs consisting of $C_{10}mpyrNTf_2$ and $C_{10}mimNTf_2$ showed consistent catalytic activity. These differences in electrochemical behavior in various CILEs were the direct evidence that the structure of ILs play a critical role in the TEMPO-mediated catalysis.

Effects of Ionic Liquid Structures on the Composite Conductivity. Besides the performance of CILEs in electrocatalytic activity and stability, the bulk electrical conductivity is another critical factor as electrode composites with high resistance lead to large ohmic drops. Thus, the conductivity of CILEs as a function of graphite-to-IL ratio was evaluated (**Figure 5**). Consistent with other composite materials, increasing the amount of carbon used results in an increase in the electrode conductivity. It is worth noting that structural changes of the ILs also alter the composite conductivity. This variation is mainly ascribed to the changes in viscosity. Particularly, ILs with short carbon chains display low viscosity, while ILs with imidazolium as cations are more viscous than that of pyrrolidinium. Consequently, at the same graphite/IL ratio, the conductivity rankings of the ILs tested (from highest to lowest) was $C_4mpyrNTf_2$, $C_4mimNTf_2$, $C_{10}mpyrNTf_2$, $C_{10}mimNTf_2$. This conductivity difference, as shown in **Figure 5**, was evident at low graphite/IL ratio, and attenuated when increasing the graphite percentage. Further, increasing the amount of graphite led to similar conductivity, regardless of IL structures. Although electrode composites with high conductivity are preferred, the homogeneous

distribution of IL and catalyst may become poor. On the other hand, graphite/IL ratio lower than 1:1 lost its mechanical stability. Overall, properties such as conductivity, composition, catalytical performance and mechanical stability should all be considered in order to select the appropriate graphite/IL ratio.

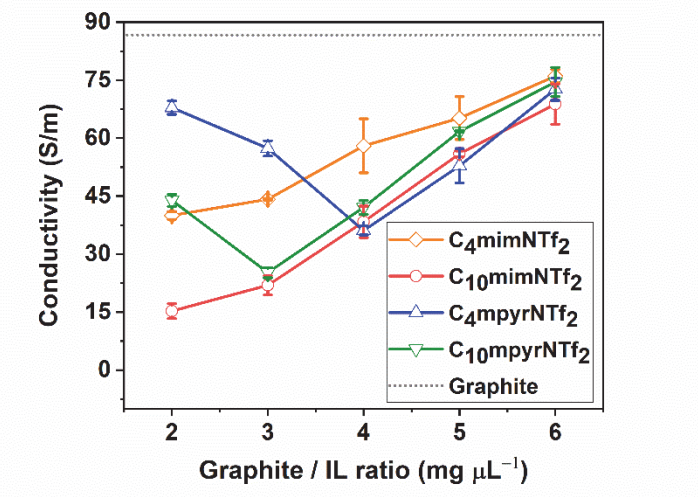


Figure 5. Measured conductivity values of CILEs containing various graphite/IL ratios. The conductivity of 100% carbon was also measured (dotted line) as a comparison.

Evaluation of Catalytic Stability in Bulk Glycerol Conversion. The amperometry results demonstrated that the incorporation of TEMPO in ILs improved the current stability. To further investigate whether the stabilized current practically translates to the conversion of TEMPO-based reactants, the oxidation of glycerol was studied and analyzed using UPLC-MS. A small volume, 800 μL three-electrode electrochemical cell was designed to facilitate glycerol detection in short-term experiments (**Figure 6a-b**). Using the 800 μL cell, a potential of 0.8 V (vs. SCE) was applied to the CILEs and PTPEs for 1 h, 2 h, 3 h, separately. As shown in **Figure 6c**, the conversion of glycerol in PTPEs plateaued after 2 h, which corroborates the chronoamperometry results shown in **Figure 2b**, suggesting that TEMPO was deactivated during the reaction

duration. In comparison, the IL-incorporated TEMPO CILEs displayed consistent increasing conversion to glyceric acid and tartronic acid throughout the reaction period (**Figure S5**). These results demonstrate TEMPO in C_{10}mimNTf_2, in comparison to TEMPO in PCL, exhibited improved catalytic stability.

It is worth mentioning that although upgrading glycerol to valuable products via product selectivity is of great interest, they are not the scope of the present work. Here we focus on improving catalytic stability by incorporating alkaline stable ionic liquids. Glycerol was selected as a model aliphatic alcohol. As discussed earlier, the low anodic current of CILEs when using glycerol as a substrate (**Figure 1**) underlines the critical need for developing highly stable catalyst systems. The results obtained by using glycerol as a model alcohol are expected to give insights into the current catalytic system (e.g., the choice of ionic liquids) and eventually serve as a universal tool to apply to other alcohols.

Catalytic stability, to some degree, can be revealed by the evaluation of certain products. However, the use of product analysis as a parameter for evaluating catalyst stability can be ambiguous as the mass balance obtained by-products hardly achieve 100%. Specifically, for glycerol oxidation, the mass balance is poor and sometimes can be as low as 20%.[43] This is mainly due to the fact that glycerol exhibits multiple oxidation pathways during the reaction duration. In alkaline conditions, it is reported that terminal carbons are more likely to be oxidized.[44,45] The generated C_3 products (e.g., glyceric acid, tartronic acid) may further undergo C-C cleavage in base, resulting in the formation of C_2 and C_1 products (e.g., glycolic acid, and formic acid).[46,47] Consequently, the catalytic current not only translates glycerol to glyceric acid, but also to other oxidation products. The formation of tartronic acid (**Figure S4**) is an indicator

of this multiple oxidation events. In this scenario, without knowing the kinetics of all potential oxidation pathways, the product analysis by itself cannot explain catalytic stability.

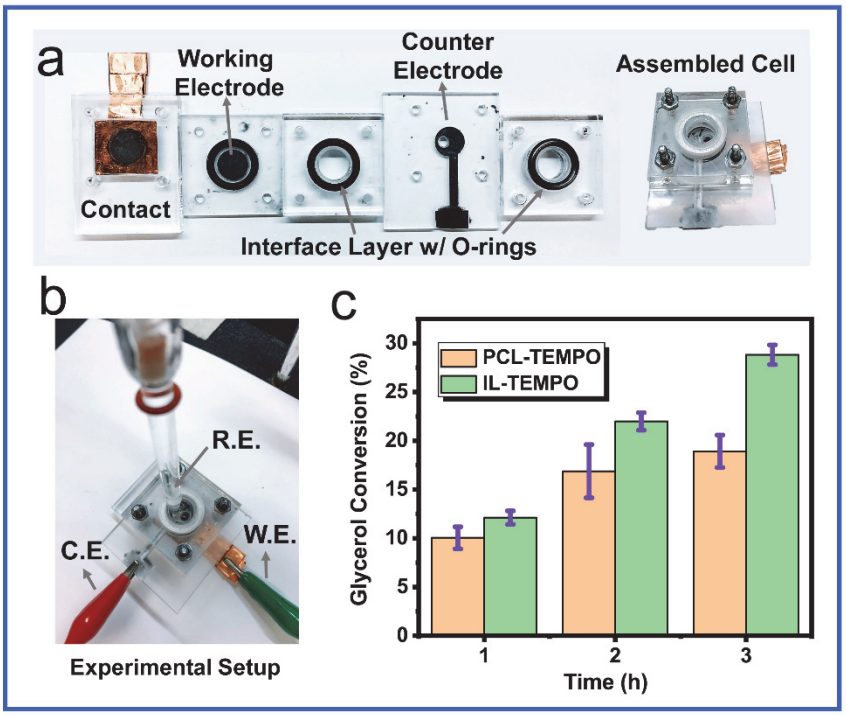


Figure 6. Electrochemical cell designed for glycerol conversion. **(a)** (left-to-right) Images of each layer and the assembled cell. Electrode composites of PTPEs or CILEs (1 cm^2) are sandwiched between the contact pad and interface layer. An off-center hole was made in the counter electrode to release bubbles formed during electrolysis from the cell without in touch with the reference electrode. **(b)** Experimental setup of the 800 µL electrochemical cell. **(c)** Results of the glycerol conversion using PTPEs and CILEs.

To further evaluate the stability and reusability of the CILEs, successive cycles of the glycerol oxidation were performed without any post-treatments of the electrode composite. Note that high substrate conversion (≥ 20%) can decelerate the reaction kinetics,[48] causing ambiguous results. Thus, 2 h was applied as one cycle period and the reaction mixture was refreshed after

each individual cycle. **Figure 6** has shown the anodic current translates to the conversion of glycerol. During the 2 h reaction duration, the current response was directly used to evaluate catalyst stability. As depicted in **Figure 7**, the minimal decay of current (4.4%) was observed between the second and the third cycle for CILEs. In contrast, TEMPO in PCL exhibited nearly 100 % degradation after the first cycle. This phenomenon is direct evidence that TEMPO incorporated in ionic liquids was not deactivated, while in PCL was. Since this C_{10}mimNTf_2 is reported to have 0.0% degradation at current pH values,[49] we expect stable catalytic current in the three cycles. The fact that the anodic current decreased at the extended reaction period might be attributed to ionic liquid dissolution in the electrolyte, which in turn, results in catalyst leaching. To investigate whether the ionic liquid dissolution actually occurs, NMR analysis was carried out. The presence of the characteristic peaks of 1-decyl-3-methylimidazolium in deuterated carbonate buffer after electrolysis indicates the loss of ionic liquid (**Figure 8a-b**). Although C_{10}mimNTf_2 is one of the most hydrophobic ionic liquids known (solubility in water is $< 3.2 \times 10^{-5}$ in mole fraction[50]), the effect of dissolution on catalyst leaching is non-trivial. In fact, the damage of the electrode surface after oxidation (**Figure 8e**) is another indicator of IL dissolution and catalyst leaching. Interestingly, this surface destruction is not observed when there is no potential applied, even under vigorous stirring overnight (**Figure S5**). This difference in the electrode surface change suggests that electrochemical events can accelerate IL dissolution. Nevertheless, the extreme hydrophobic nature of C_{10}mimNTf_2 enables slow dissolution, leading to stable catalytic current for a relatively long time period - after 7 cycles (14 h), about 50% of anodic current remained (**Figure 8e**), while the current loss was up to 50 % for CILEs within 1 h (**Figure 7**). Overall, these results suggest a 14-fold enhanced alkaline stability of TEMPO in ILs.

These differences in the catalytic stability between PTPEs and CILEs indicated the critical role the binding material plays in the TEMPO catalytic stability. More specifically, the binding materials exhibit two key functions – protection of TEMPO from being decomposed at high pH values, and maintaining the electrode composition throughout the electrolysis. To achieve this, the material needs to possess good alkaline chemical stability as well as extreme hydrophobicity. The IL used in this work enables preserving the TEMPO stability due to its high chemical stability in basic electrolyte. However, its dissolution into aqueous solution results in the loss of TEMPO. While PCL as a polymer is anticipated to retain the composite components without suffering from dissolution and TEMPO leaching, it is subjective to hydrolysis degradation. This hydrolysis due to the presence of carboxylate ester linkage is a common issue in polyesters.[51] Based on the above discussions, polymerization of chemically stable ILs could potentially further improve the stability and reusability of the electrode composite.[52] Such an improvement in the stability of the electrode components will, in turn, facilitate electrode applications and be critical for product isolation.

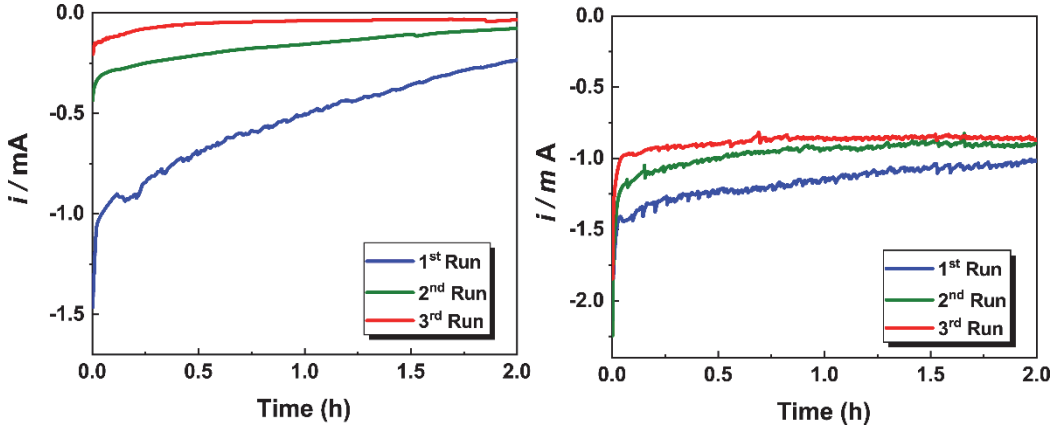


Figure 7. Comparison of the stability and reusability of the PTPEs and CILEs. For each run, 55.5 mM of glycerol in 0.1 M carbonate buffer (pH 10) was used with constant potential at 0.8 V. After each cycle, the reaction mixture was replaced with fresh glycerol solution.

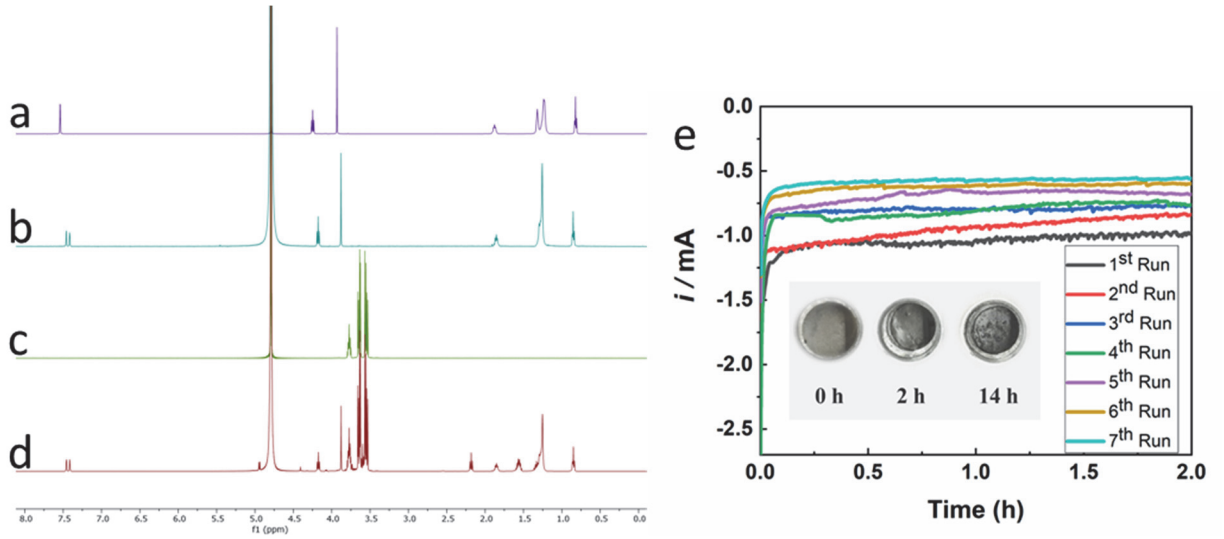


Figure 8. ^{1}H NMR spectrum of (a) C_{10}mimBr in deuterated carbonate buffer, (b) Supernatant of deuterated carbonate buffer solution with C_{10}mimNTf$_2$ being added. (c) Glycerol solution (55.5 mM) before (c) and after 2.0 h electrolysis (d). The concentration of the deuterated carbonate buffer used was 0.1 M (pH 10). Each spectrum was adjusted in different intensities to highlight the characteristic peaks of the 1-decyl-3-methylimidazolium cation. (e) Current responses of seven cycles using CILEs. For all runs, a solution of 55.5 mM glycerol in 0.1 M carbonate buffer (pH 10) was used, and refreshed after each cycle. The images shown represent the electrode surface before cycling, after first cycle, and seven cycle, respectively.

CONCLUSION

Among catalysts for alcohol oxidations, TEMPO has major advantages — it is selective, metal-free, and remarkably low-cost — yet it suffers from base-induced decomposition. This lack of stability hinders the widespread applications of TEMPO for electrosynthesis. In this work, we synthesized a TEMPO composite electrode with ionic liquid embedded for the enhancement of TEMPO-mediated oxidations under basic conditions. The results of this study demonstrate the continued reactivity of TEMPO for long time periods at high pH values, under which normally

results in TEMPO decomposition. For glycerol oxidation, electrodes with TEMPO in C_{10}mimNTf$_2$ displayed no loss of current at pH 10.0 after 2.0 h, while TEMPO in PCL degraded 67.1%. Further analysis of the bulk conversion of glycerol evidenced that the stabilized current practically translated to the oxidation of glycerol. Successive cycles of glycerol oxidation suggest that although ionic liquid dissolution and thus catalyst leaching occurs, the extreme hydrophobic nature of C_{10}mimNTf$_2$ permits stable current for a relatively long reaction period. About 50% catalytic current remained after 7 cycles (14 h) for CILEs, while in contrast; the current loss was up to 50 % for PTPEs within 1 h, leading to a 14-fold catalytic enhancement by applying IL in TEMPO electrode composite. The significant advancement in the catalytic stability by applying ILs reveals the critical role of the binding materials. A combination of the polymer nature of PCL with chemically stable functional groups of ILs is expected to generate next-generation binding materials – not only stable in catalytic turnover, but also stable in electrode components. Note that chemical dissolution present in the current work may complicate product isolation and purification. Such advancement in the stability of the electrode components is critical for the catalyst development and practical applications.

In addition to the enhanced catalytic stability, the present work enables the composite based catalyst to be attached to the electrode surface. This surface-attached catalyst system removes the requirement of catalyst separation from the reaction mixture. More importantly, the use of ILs enhances catalytic stability, rendering it applicable for electrode reuse and recycling. This can be particularly meaningful as ILs are expensive materials. Further, the current strategy only requires microliters of IL in electrode preparation. Accordingly, incorporation of ILs in electrode composite potentially can be a cost-effective approach. Therefore, the strategy is

expected to provide many opportunities for designing heterogeneous electrode composites with enhanced catalytic performance using other homogenous based systems.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Details of synthesis of ionic liquids, preparation of the two electrode composites, conductivity measurement, fabrication of the 800 μL electrochemical cell, chronoamperometry results of glycerol oxidation, and corresponding C_3 product analysis.

AUTHOR INFORMATION

Corresponding Author

*EMAIL: minteer@chem.utah.edu

NOTES

The authors declare no competing financial interest.

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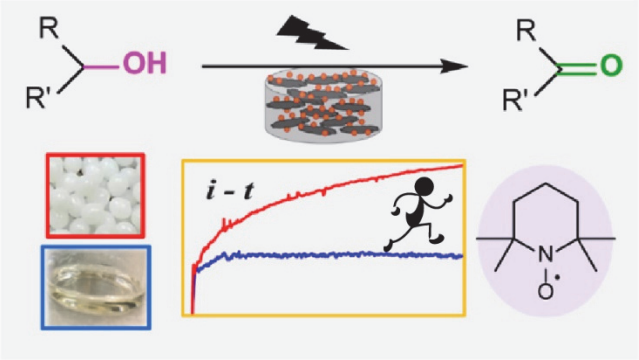

TEMPO mediated oxidations are used for a wide variety of biorenewables including alcohols. To improve the stability of TEMPO for these reactions, an ionic liquid-based catalyst was developed.