Ionic Liquids

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Polymeric Ionic Liquid and Carbon Black Composite as a Reusable Supporting Electrolyte: Modification of the Electrode Surface**

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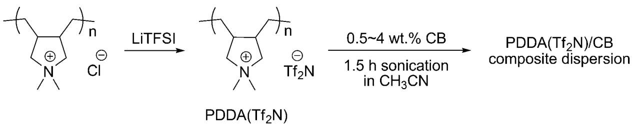
Abstract: *One of the major impediments to using electroorganic synthesis is the need for large amounts of a supporting electrolyte to ensure the passage of charge. Frequently this causes separation and waste problems. To address these issues, a polymeric ionic liquid–Super P carbon black composite has been formulated. The system enables electrolyses to be performed without adding an additional supporting electrolyte, and its efficient recovery and reuse. In addition, the ability of the composite to modify the electrode surface in situ leads to improved kinetics. A practical consequence is that one can decrease catalyst loading without sacrificing efficiency.*

Electroorganic chemistry provides a benign and practical approach to synthesis.[1] Unfortunately some applications necessitate the use of large amounts of supporting electrolyte to ensure ionic conductivity and the efficient movement of charge. As a result one can be faced with a tedious workup. In an effort to overcome this problem and the waste issues that accompany the use of supporting electrolytes, researchers have devised many solutions, including the use of ionic liquids.[2] While attractive, their high viscosity and low conductivity diminish the mass transport rate of the electroactive species, leading to low current flow and detracting from their utility.[3] Since the electroactive species must reach or be nearby the surface of an electrode for a heterogeneous electron transfer to occur, the overall efficiency of an electrolysis depends on the rate at which the species reach the surface.

Inspired by the discovery of an enhancement in the self-diffusion coefficient and conductivity of an ionic liquid containing nanoparticles,[4] and the intrinsic advantages of polymers, we turned our attention to the development of a polymeric ionic liquid (PIL)[5] and carbon nanoparticle composite featuring conductive Super P carbon black (CB). We report that the composite can be 1) used as a substitute for traditional supporting electrolytes, 2) recovered and reused, thereby simplifying product isolation and minimizing waste, and, with the formation of a composite dispersion, 3) used to avoid the high viscosity and low conductivity that is frequently encountered with ionic liquids. We also describe the dramatic change in current intensity and curve shape that is observed when voltammograms are recorded in the composite dispersion.

We selected the polymeric form of diallyldimethylammonium (PDDA) chloride, because the pyrrolidinium cation offers access to a wide electrochemical potential window.[6] Formation of the composite dispersion begins with an anion exchange to convert PDDA chloride to the easily handled solid, PDDA(Tf_2N), that is subsequently dissolved in acetonitrile (Scheme 1).[7,8] After the addition of CB to the solution, the resulting mixture is transformed to a dispersion by sonication,[9] and is stable for more than a year (see the Supporting Information (SI) for details). The composite system is electrochemically inert over a broad range of potentials (ca. $+2.8$ V to -2.7 V vs. Ag/$AgNO_3$), and therefore may constitute a reaction medium for a variety of applications (Figure S2).



Scheme 1. Formation of composite dispersion.

To study the influence of the composite dispersion upon voltammetry and to explore the possibility that the carbon nanoparticles might electrochemically deposit onto the electrode surface,[10] we chose the redox mediator tris(*p*-bromophenyl)amine (TBPA) for our investigation.[11]

Voltammograms of TBPA were obtained beginning with a scan rate of 500 $mV s^{-1}$ (Figure 1; curve a) and decreasing to 50 $mV s^{-1}$. Once completed, 300 additional cycles were recorded to allow time for the electrophoretic deposition[12] of nanoparticles to occur. Thereafter, the scan at 500 $mV s^{-1}$ was repeated (Figure 1; curve b) and compared with curve a. The contrast was dramatic, showing a significant increase in current intensity and change of curve shape.

We suggest that the changes are due to the formation of a nanoparticle assembly that creates a new conducting surface

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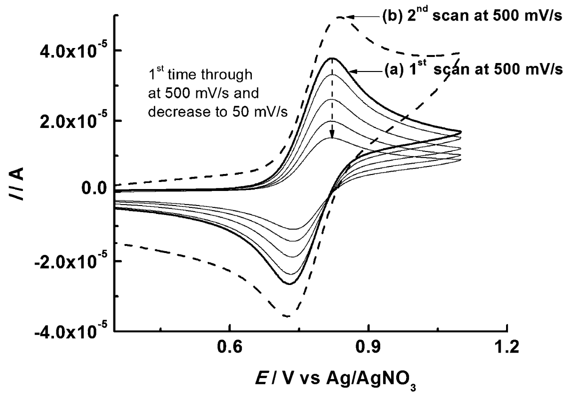


Figure 1. CV of TBPA in the composite dispersion. Pt working electrode, Pt wire counter electrode, and $Ag/AgNO_3$ reference electrode.

on the electrode, accompanied by an increase in the surface area, through in situ electrophoretic deposition of CB. The modification leads to a change in the flux of TBPA toward the surface through a combination of linear and radial diffusion,[13] and to an amplified current and change in the shape of the voltammogram. In contrast to the behavior just described, when the cyclic voltammetry (CV) of TBPA was examined in the PIL dissolved in acetonitrile, there was no change in the current intensity or the shape of the voltammogram (Figure S5). We conclude that in the absence of carbon nanoparticles the surface of the electrode remains unchanged.

To visually support our observations and rationale, we used an optical microscope to observe the surface changes on a carbon-coated aluminum foil electrode. Figure 2 shows the changes on the surface of the electrode after the application of a potential of 1.0 V (vs. $Ag/AgNO_3$) in the composite dispersion for 10 min. In contrast, no surface changes were observed when an electrolysis was conducted in a solution of the PIL dissolved in acetonitrile containing CB (no composite). The electrophoretic deposition of CB presumably results from attractive interactions between the anode surface and ions of PIL, as well as a cation–π interaction between the pyrrolidinium cation and π-electron-rich surface of CB in the composite dispersion.[9]

To determine whether the change in current intensity was mainly due to an increased Faradaic current of TBPA or was a manifestation of an increase in the double-layer charging (non-Faradaic current),[14] two chronoamperometry experiments were performed in the composite dispersion, one in the presence of TBPA, and the other in its absence. We capitalized upon the fact that the non-Faradaic current decays much more rapidly ($1/\exp(t)$; t = time) than the Faradaic current ($1/(t)^{1/2}$).[14] In each experiment, the potential was stepped from 0.5 V to 1.1 V, a potential in excess of that required to oxidize TBPA, and the current decay was monitored for 5 seconds. Next, repetitive CV scans were performed using the sequence described previously, to allow time for surface modification to occur. Figure 3 clearly shows that the current decays at a rate that is consistent with a Faradaic decay when TBPA is present and that the Faradaic current intensity is substantially higher with the surface-modified electrode (Figure 3; top). Meanwhile the use of a surface-modified electrode, but in the absence of TBPA, shows no difference in the current intensity over time, indicating that the current decays at a rate that is consistent with a non-Faradaic process (Figure 3; bottom). Together, these experiments illustrate that the increase is due to an increase of Faradaic current owing to an enhanced mass transport rate of TBPA to the surface of the in situ-modified electrode.

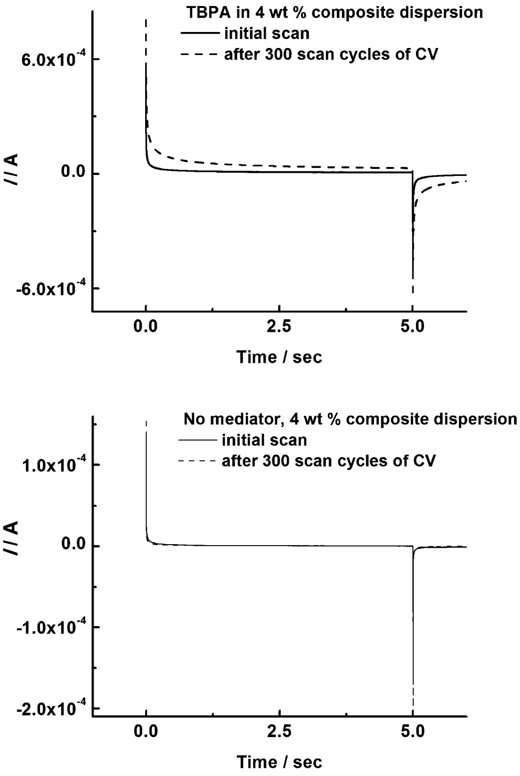


Figure 3. Chronoamperograms of the composite dispersion in the presence (top) and absence (bottom) of TBPA. Pt working electrode, Pt wire counter electrode, and $Ag/AgNO_3$ reference electrode.

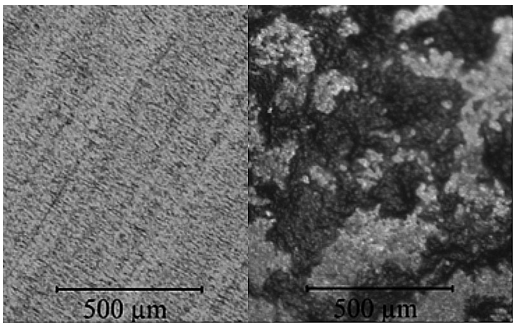


Figure 2. Optical microscope images of the electrode surface before (left) and after (right) application of a potential in the composite dispersion. Scale bar on each image indicates 500 µm.

To explore the applicability of the composite dispersion in synthesis, the voltammetric behavior of TBPA, and TBPA in the presence of 4-methoxybenzyl alcohol and 2,6-lutidine

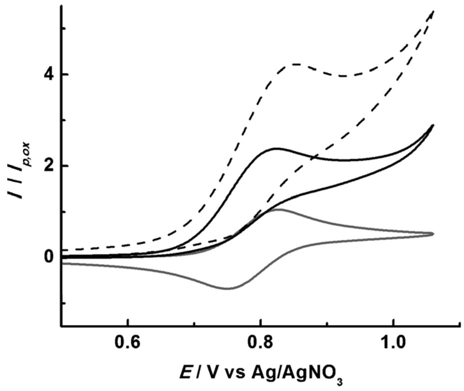


Figure 4. Comparison of catalytic effects; grey line: 2 mM TBPA; black solid line: 2 mM TBPA + 50 mM 4-methoxybenzyl alcohol + 100 mM 2,6-lutidine in the PDDA(Tf_2N) dissolved in acetonitrile; dashed line: 2 mM TBPA + 50 mM 4-methoxybenzyl alcohol + 100 mM 2,6-lutidine in the composite dispersion with surface modified electrode; scan rate, $\nu = 100\ mV\,s^{-1}$; all currents are normalized to the oxidation peak current $I_{p,ox}$ (28.1 μA) of the mediator (dotted line).

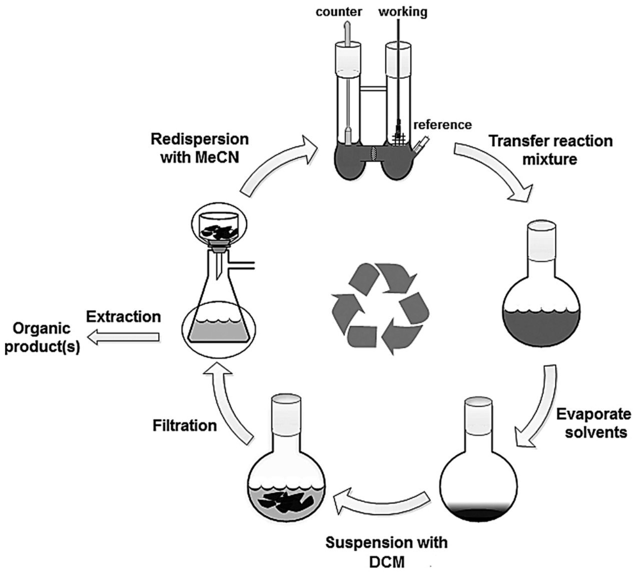
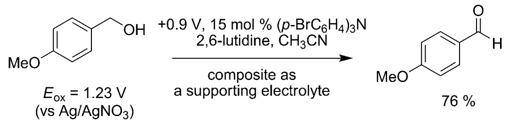


Figure 5. The workup procedure.

were examined in a) PDDA(Tf_2N) dissolved in acetonitrile, and b) in the composite dispersion in which the surface of the working electrode was modified in situ. Figure 4 portrays a dramatic increase in catalytic current[15] encountered when the CV of TBPA in the presence of substrate and base was measured in the composite dispersion with the surface-modified electrode (compare the black dashed and solid curves). The evidence suggests that the use of composite dispersion and in situ-modified electrode provides improved catalytic activity, and is kinetically more effective in the catalytic process.

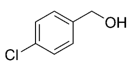
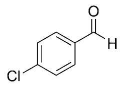
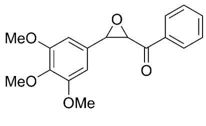
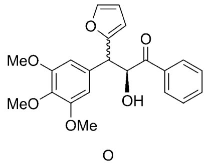
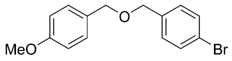
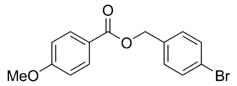
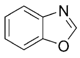
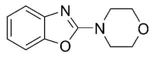
Encouraged by these results, we envisioned that the composite could be used in place of a traditional supporting electrolyte in preparative scale electrolyses. We performed an anodic oxidation of 4-methoxybenzyl alcohol in the composite dispersion to isolate 4-methoxybenzaldehyde in 76% yield.[16] Importantly, by following the simple workup procedure described below, a 95% recovery of the composite was achieved (Figure 5).

The workup illustrated in Figure 5 exploits that PDDA(Tf_2N) is insoluble in dichloromethane (DCM), but is soluble in acetonitrile. Thus, evaporation of the solvent is followed by suspension of the composite by adding DCM and filtration. The crude product(s) remains dissolved in DCM and can be isolated using standard workup procedures. Meanwhile, the recovered composite is simply redispersed and is ready for its next use. To explore its reusability, three successive oxidations were performed. Each led to product yields in the range of 65 to 76%, and to ca. 95% recovery of the composite. These examples clearly show that the composite can serve in place of a traditional supporting electrolyte and be reused with little sacrifice in efficiency.



To expand the scope of the composite system, we conducted oxidations of several dissimilar substrates (Table 1, see SI for details). Thus, the electrochemically mediated oxidation of 4-chlorobenzyl alcohol and an unsymmetrically substituted ether (entry 1 and 3), the arylation of an epoxy chalcone (entry 2),[17] and an oxidative amination of benzoxazole (entry 4),[18] each proceeded efficiently in controlled potential and constant current electrolyses. The oxidation of 4-chlorobenzyl alcohol is of special interest, because we operated at 0.9 V (vs. Ag/AgNO$_3$) and reduced the mediator loading to 5 mol%. Gratifyingly, the substrate

Table 1: Expanding the scope in synthesis.

Entry	Substrate	$E_{p,ox}$ vs. Ag/AgNO$_3$ [V]	Product	Yield[%]
1		1.94		74[a]
2		1.03		62[b]
3		1.44		45[b] (74)[c]
4[d]		1.02		60[a]

[a] Yields are of isolated products. [b] The yield was determined by ^1H NMR spectroscopy. [c] The yield is based on the recovered starting material. [d] Constant current electrolysis was conducted using nBu_4NI as a mediator; otherwise, controlled potential electrolysis using TBPA as a mediator was performed.

was converted to 4-chlorobenzaldehyde in 74 % yield revealing that the enhanced kinetics enabled a ca. 1.0 V thermodynamic impasse between TBPA and the substrate ($E_{\text{ox,sub}} =$ 1.94 V, $E_{\text{app}} = 0.9$ V) to be overcome and allowed mediator loading to be reduced significantly.[19]

In conclusion, a composite electrolyte has been developed that combines the features of a PIL with the properties of conductive CB. The result is a stable electrolyte that can be efficiently recovered and reused, and also improves the mass transport rate through modification of the electrode surface. Our approach promises to provide a general solution to problems associated with the use of conventional supporting electrolytes and ionic liquids. The system can be applied to a variety of synthetic transformations and will undoubtedly find use in a host of other applications that necessitate the use of an electrolyte.

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