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Finding balance with deep eutectic solvents: High concentrations and improved conductivities for the off-the-shelf nitroxide TEMPOL

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ABSTRACT

Viologens and the stable, water-soluble nitroxide radical known as TEMPOL have been studied extensively with respect to applications in energy storage. Here we report formulations wherein high concentrations of both are achieved in a single solution and the reversible electrochemistry of each is retained. We demonstrate one of several potential applications by constructing a high optical density electrochromic device.

1. Introduction

Stable nitroxide radicals have been put to use across diverse fields of science due to their ability to degrade reactive species [1], label spins [2], trap radicals [3], couple polymer units [4], and produce magnetic materials [5]. Extensive work has also been done to examine the potential of such molecules in energy storage [6–12], as they typically offer a chemically reversible oxidation and a reduction that can be either reversible or irreversible, depending on the molecule and the environment. The development of water-soluble TEMPO derivatives such as WS-TEMPO [13] and sulfonated [14] derivatives has expanded the scope of both biological and energy-driven research and development.

4-Hydroxy-TEMPO (or TEMPOL) in particular has garnered interest because it can readily be synthesized from phorone rather than derivatizing its nominal parent compound, the unsubstituted TEMPO backbone. Indeed, some have argued that the cost of production for TEMPOL could become low enough that it would be competitive as an active material for grid-scale energy storage applications, such as flow batteries [15].

To date, applications of TEMPO in aqueous solutions for energy storage have been limited by the need to achieve two technical goals: high active material concentrations and high solution conductivities. Researchers at Pacific Northwest National Laboratories (PNNL), for example, achieved excellent conductivities when using 1.5 M NaCl as an electrolyte, but they reported that such conditions allowed for only *ca.* 0.5 M TEMPOL [6].

More recently, Sinclair et al. reported high concentrations and reasonable conductivities for a different TEMPO derivative, 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO) in a low viscosity DES [12]. This approach elegantly solves many energy storage challenges at once, yet a transition from research to development and commercialization would require the development and scaling of new synthetic methods.

Here, we report formulations inspired by the deep eutectic solvent (DES) community that allow for progress in applications where high concentrations are required and high conductivities are still beneficial. We report both a formulation of TEMPOL in an electrochemically silent ionic melt and a formulation that includes a viologen. After consideration of other potential redox partners such as coordination compounds of titanium [16] or chromium [17] or sulfonated quinones [18], we selected a DES based on benzyl viologen (BV^{2+}, see Fig. 1 for structure). While the alternatives provide some advantages in aqueous media, the BV^{2+} formulation is one of very few DESs that exhibits well behaved reduction chemistry and the potential for improved solubility of both redox partners. Of particular relevance to the challenge at hand, the BV^{2+}-based DES was previously reported to maintain reversible electrochemistry at high concentrations of the active material (>4M) [19].

1. Materials and methods

All chemicals were purchased from Sigma Aldrich except benzyl viologen, which was purchased from TCI. All chemicals except tetraethylammonium chloride tetrahydrate and ethylene glycol

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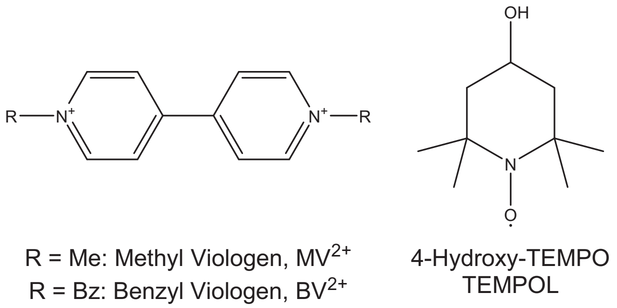

Fig. 1. Molecular structures and abbreviations used in the present study.

were dried to a constant mass at 50 °C under vacuum. Melting points were determined by slowly heating samples in a sand bath and measuring the sample temperature at the point of melting with an infrared thermometer.

Electrochemical measurements were performed with a CH Instruments 660e potentiostat. Voltammograms were acquired with a 11 μm diameter glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. The working electrode was polished, rinsed, and dried with filtered compressed air between experiments. Conductivities for small sample volumes were measured using a homemade pair of electrodes. In brief, two pieces of 0.7 mm pencil graphite were sealed into glass pipet tips with two-part epoxy with ~1 mm of carbon exposed, and the glass tips were glued together. Wires were wrapped around the back end of the carbon rods, and potentiostat leads were clipped to these wires. AC resistance measurements (1 kHz) were performed with the potentiostat, and calibration curves were produced for resistances measured for several conductivity standards. This calibration curve was then applied to the resistances measured for each sample to calculate the conductivity in mS/cm.

The demonstrative electrochromic device was produced by sandwiching two layers of indium-tin oxide on polyethylene (Sigma Aldrich) around an anion conducting membrane (Selemion, obtained from Ion Power). A pipet was used to add 10 μL of the liquid sample on each piece of ITO before making the sandwich.

2. Results & discussion

Table 1 shows molarities for TEMPOL and solution conductivities at 50 °C for several different molar ratios of TEMPOL / Et_4NCl / H_2O. A preparation with a 2:1:4 M ratio yielded a TEMPOL concentration of 3.5 M, only 15% lower than a sample of 1:4 TEMPOL/H_2O but with greatly improved conductivity. Unsurprisingly, formulations with greater relative concentrations of the ionic electrolyte melt $Et_4NCl{\cdot}4H_2O$ yielded higher conductivities at the expense of the active material concentration. The table includes an entry taken from the work of researchers at PNNL for context, further exemplifying the trade-offs available.

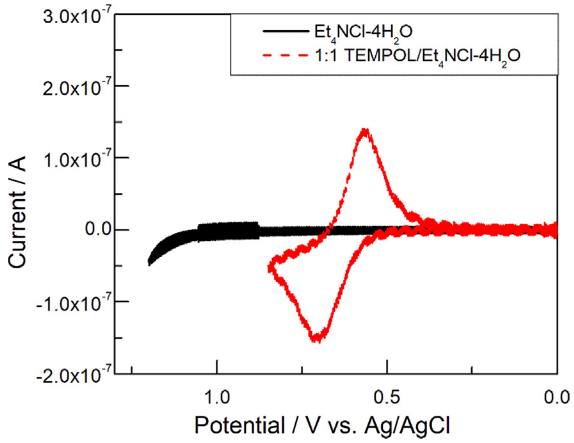

Fig. 2. Cyclic voltammetry of TEMPOL in an electrochemically silent DES.

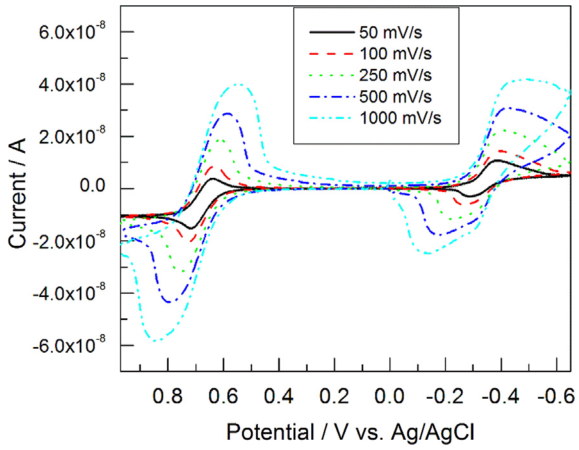

Fig. 3. Cyclic voltammetry of an electroactive DES containing high concentrations of TEMPOL. This formulation is an 8:1:1 M ratio of ethylene glycol:TEMPOL:benzyl viologen.

Voltammetry of 2:1:4 TEMPOL / Et_4NCl / H_2O exhibited a clean oxidation assigned to the transition of the nitroxide radical to the cation with an $E_{1/2}$ = +0.64 V vs. Ag/AgCl. The observed peak-to-peak splitting of 0.14 V at 100 mV/s is consistent with chemical reversibility and quasi-reversible electrochemistry. Fig. 2 shows the cyclic voltammetry of the sample with a background sweep of the ionic melt without the addition of TEMPOL (see Fig. 3).

To explore electrochemical applications of this class of formulations, we produced a sample of 8:1:1 ethylene glycol/TEMPOL/benzyl viologen inspired by our earlier work with viologen-based DESs [19]. This system yielded quasi-reversible electrochemistry for both the oxidation of the TEMPOL ($E_{1/2}$ = +0.68 V vs. Ag/AgCl) and the first reduction of the viologen ($E_{1/2}$ = −0.34 V vs. Ag/AgCl). For reference, the potentials observed for TEMPOL and the some-

Table 1
Formulations of the present study with molar concentrations, conductivities, and melting points.

Stoichiometry					
TEMPOL	Et_4NCl	H_2O	[TEMPOL] / M	Conductivity at 50 °C / mS/cm	Melting Point / °C
1	0	4	4.1	0.19	40
2	1	4	3.5	1.6	29
1	1	4	2.5	6.1	31
0.5	1	4	1.7	12	34
0	1	4	0	41	37
Work of Liu, et al., 1.5 M NaCl in water [6]			0.5	103	

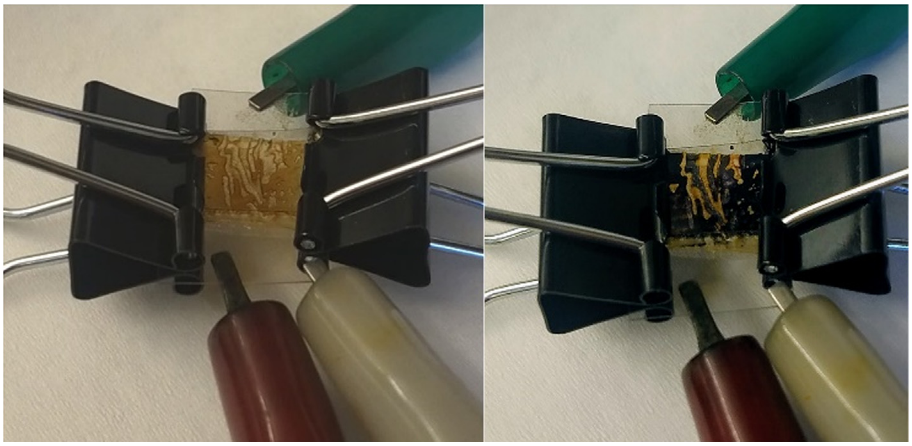

Fig. 4. High optical density electrochromic behavior of a TEMPOL/viologen DES. The image at left is the as-prepared sample, and the image at right is after application of a potential that oxidizes TEMPOL and reduces the viologen.

what more electron donating methyl viologen in previous studies of aqueous solutions were +0.6 V and −0.65 V, respectively [6].

The apparent cell voltage of 1.02 is a bit low for energy storage applications such as flow batteries [20], so we elected to build a rudimentary electrochromic device that would exhibit high optical densities upon application of modest voltages of *ca.* 1 V. Optically transparent ITO electrodes were used with a commercially available anion exchange membrane that would enable transport of chloride ions. A small amount of the electrolyte containing both TEMPOL and benzyl viologen was added to each side of the membrane before completing the sandwich. The potential between the two electrodes was ramped from 0 V to 1.1 V, and substantial darkening was observed as the viologen radical cation was produced with electrons from oxidizing the neutral TEMPOL species. Fig. 4 shows a picture before and after the application of the voltage, and a video of the device may be found as supporting information.

3. Conclusions

In this study, we have reported an advance in the parameter space of formulations of nitroxide radicals at high concentrations. In particular, formulations based on molten salts offer a new regime where high concentrations of TEMPOL are maintained in balance with ionic conductivity.

As DESs strike a curious balance between polar and non-polar, they appear to provide media that are miscible with TEMPOL and an enormous potential range of molecular combinations. We have reported an early venture into this space as well with a formulation the includes both TEMPOL and a viologen. Such formulations offer reversible oxidations and reductions. The separation of the redox potentials for these may be increased to provide battery active materials or decreased to provide high optical density, low voltage electrochromics.

Further work is required before these and similar formulations may find use in real-world devices. Modeling [21] of devices using such a formulation would benefit from a full characterization of solution viscosity and conductivity across a range of reasonable operating temperatures for e.g., flow batteries. Interestingly, each measurement across a range of temperatures would need to be repeated across the relevant range of states of charge for the device, leading to a useful but rather large information space. Additional progress towards devices also requires studies of the stability of each redox species in each oxidation state both chemically (e.g., by repeated NMR characterization in long term high temperature storage) [18] and in simple long-term cycling tests with highly instrumented test devices [22]. The present work also spurs us to create DES formulations with other redox-active species as major components, offering potential improvements in stability, cell voltage, and energy density.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.116556.

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