

Brewing up a Storm: Mixing Ionic Liquids to Optimise Electrochemical Reactions

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The intrinsic conductivity, negligible vapour pressure, and electrochemical stability of ionic liquids (ILs) have made them promising electrolytes for studying electrochemical reactions. However, variability in the viscosity, hygroscopicity, and electrochemical stability windows of ILs makes it difficult to find the most ideal candidate to use as an electrolyte. This can be mitigated by synthesising new ILs with desirable properties, but it can be costly and complex to produce ILs of adequate purity and at a practical scale. Alternatively, two ionic liquids can be mixed to alter the chemical properties of the electrolyte. The accessibility of commercial samples and simplicity relative to synthesising new ILs makes IL mixtures an approachable method for developing ‘task-specific’ electrolytes. Nonetheless, the limited insight into the effects of additional ions in the electrolyte on specific electrochemical reactions undermines the approachability of IL mixtures.

To address this, we have evaluated the effects of mixing the ionic liquids trihexyltetradecylphosphonium bis(trifluoromethyl)sulfonylimide ($[P_{14,6,6,6}][NTf_2]$) and 1-butyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide ($[C_4mim][NTf_2]$) on the oxygen-superoxide ($O_2/O_2^{\bullet-}$) redox couple. Surprisingly, the $O_2/O_2^{\bullet-}$ redox couple demonstrated faster redox kinetics in $[C_4mim]_x[P_{14,6,6,6}]_{1-x}[NTf_2]$ mixtures than both pure ILs on a Pt electrode.¹ Subsequent experiments also showed that the voltammetric response of the oxygen reduction reaction was more robust to changes in humidity in certain compositions of $[C_4mim]_x[P_{14,6,6,6}]_{1-x}[NTf_2]$ than both pure ILs. Changes to the hydrogen oxidation reaction in mixtures of 1-butyl-1-methylpyrrolidinium bis(trifluoromethyl)sulfonylimide ($[C_4mpyr][NTf_2]$) and 1-butyl-1-methylpyrrolidinium n-alkylsulfate ($[C_4mim][C_nSO_4]$, $n = 5, 8, 12$) were also studied to elucidate the effect of increased amphiphilicity in the mixture on the hydrogen-proton (H_2/H^+) redox couple. The conclusions from this work can be used to enhance the efficiency of electrochemical sensors for oxygen and hydrogen gas, and energy storage technologies that rely on these reactions like hydrogen fuel cells and metal-air batteries.

References

1. Mullen, J. W.; Li, H.; Atkin, R.; Silvester, D. S.* *ACS Phys. Chem. Au.* **2022**, *2*, 515-526.



Jesse Mullen is a final year PhD student at Curtin University, under the supervision of Prof. Debbie Silvester. His PhD research focuses on exploring electrochemistry in ionic liquids and their mixtures, and electrolyte effects on redox reactions.