**Towards All-Organic Radical Batteries**

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Ionic liquids have been shown to successfully replace traditional electrolytes electrochemical devices such as metal-ion batteries and solar cells. Particular interest has been paid to the improvement of performance, stability and longevity of metal-ion batteries using either lithium or sodium electrodes. Applications of organic-based electrodes based on polymers are relatively scarce due to their reduced electrochemical stability. Polymers synthesized from nitroxide or phenol radicals represent the most researched electrode materials to-date, with some showing significant promise. Nitroxide-based polymers have been successfully applied as a cathode material, reaching the operating potential of > 3.5 eV when paired with a lithium anode.1,2 Due to the susceptibility of nitroxide radicals to undergo hydrogen transfer reactions, their reduced form has been particularly difficult to stabilize in traditional electrolytes, thus limiting the advancement of nitroxide polymers as both cathode and anode material.

Recently in our group we have discovered that ionic liquids provide an ideal medium for stabilizing organic radicals, including carbon-based and nitroxides.3,4 This stability is achieved due to a strong interaction existing between a nitroxide radical and the ionic liquid cation. This interaction, driven by dispersion forces, has been successfully confirmed in EPR experiments.4 We have further explored this concept of imparting stabilization on nitroxide radicals by improving both reduction and oxidation potentials in imidazolium- and pyrrolidinium-based ionic liquids.5 In the case of the TEMPO radical, redox potentials were predicted to reach up to 5.5 eV in pyrrolidinium ionic liquids compared to that of 2.2 eV observed for TEMPO in aqueous electrolytes. More importantly, the reduced form of the TEMPO radical – the aminoxy anion - was found to be very stable in the presence of ionic liquid ions. This unprecedented stability was further confirmed by experiment, showcasing a new strategy for the development of all-organic radical batteries.

**References**

1. Nakahara, K.; Oyaizu, K.; Nishide, H., Organic radical battery approaching practical use. *Chem. Lett.* **2011,** *40* (3), 222-227.

2. Hansen, K.-A.; Nerkar, J.; Thomas, K.; Bottle, S. E.; O'Mullane, A. P.; Talbot, P. C.; Blinco, J. P., New Spin on Organic Radical Batteries-An Isoindoline Nitroxide-Based High-Voltage Cathode Material. *ACS Appl. Mater. Interfaces* **2018,** *10* (9), 7982.

3. Low, K.; Wylie, L.; Scarborough, D. L. A.; Izgorodina, E. I. Is it possible to control kinetic rates of radical polymerisation in ionic liquids? *Chemical Communications,* **BACK COVER***,* **2018**, *54* (80), 11226-11243.

4. Wylie, L.; Seeger, Z. L.; Hancock, A. N.; Izgorodina, E. I. Increased stability of nitroxide radicals in ionic liquids: more than a viscosity effect. *Physical Chemistry Chemical Physics,* **BACK COVER***,* 2019, *21* (6), 2882-2888.

5. Wylie, L; Oyaizu, K.; Karton, A.; Yoshizawa-Fujita, M. & Izgorodina, E. I.  **SUPPLEMENTARY COVER**, Towards Improved Performance of All- Organic Nitroxide Radical Batteries with Ionic Liquids: A Theoretical Perspective, *ACS Sustainable Chemistry & Engineering* 2019, *7* (5), 5367-5375.