

Supporting Information

Ionic Liquids and Plastic Crystals Utilising the Oxazolidinium Cation: The Effect of Ether Functionality in the Ring

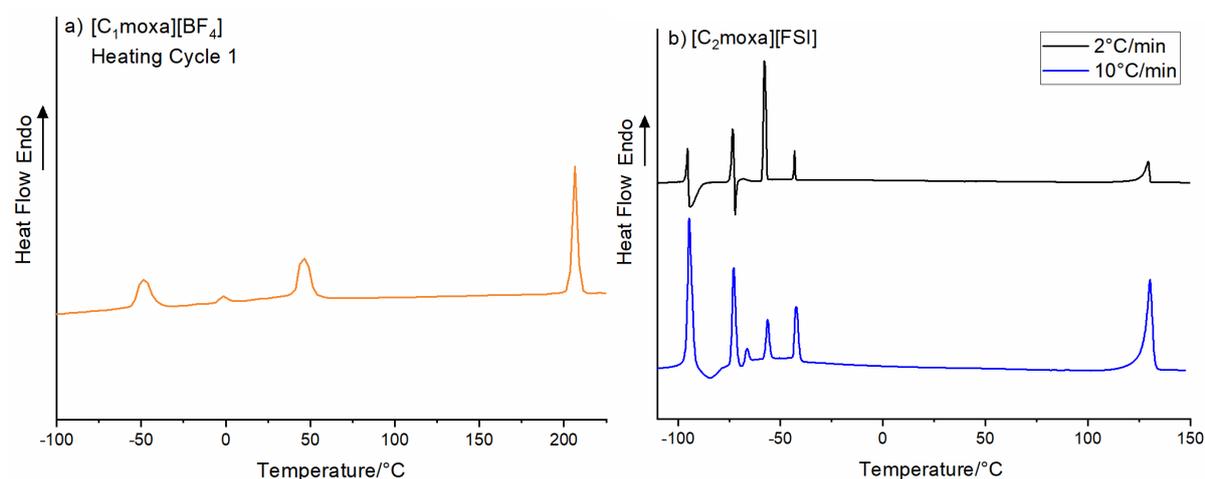
Colin S. M. Kang,^{a,b} Ruhamah Yunis,^a Haijin Zhu,^c Cara M. Doherty,^d Oliver E. Hutt,^b Jennifer M. Pringle^{a*}

^aInstitute for Frontier Materials, Deakin University, Burwood VIC, 3125, Australia

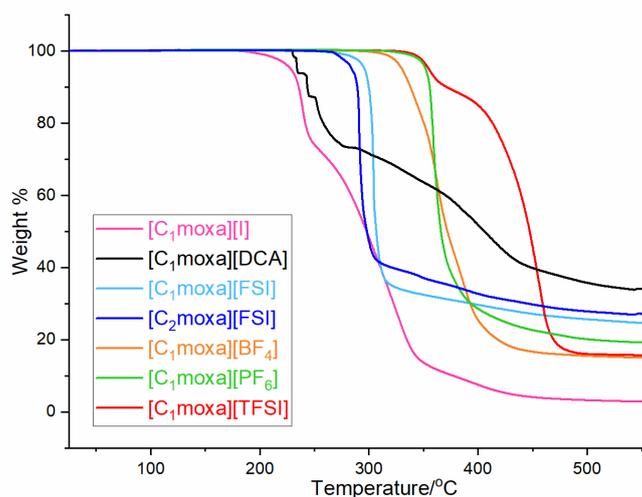
^bBoron Molecular, 500 Princes Hwy, Noble Park VIC, 3174, Australia

^cInstitute for Frontier Materials, Deakin University, Geelong VIC, 3220, Australia

^dCommonwealth Scientific and Industrial Research Organisation (CSIRO), Manufacturing, Clayton VIC, 3168, Australia



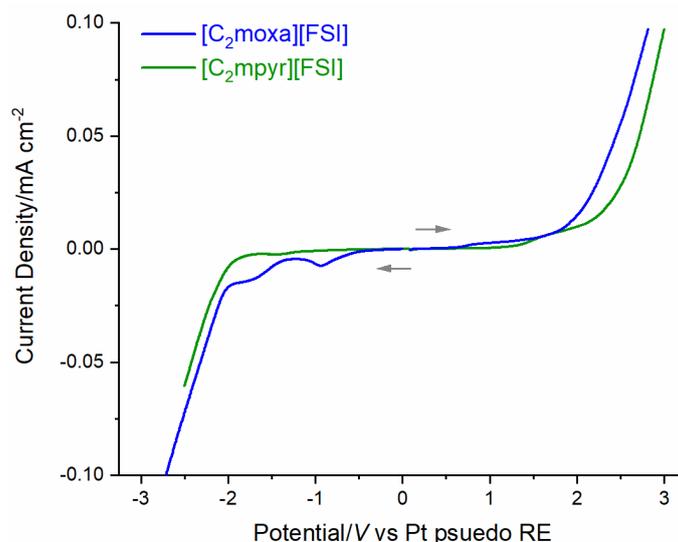
Supporting Figure S1: DSC trace of a) [C₁moxa][BF₄] at 10 °C min⁻¹ on the first heating cycle, and b) [C₂moxa][FSI] at 10°C min⁻¹ and 2°C min⁻¹.



Supporting Figure S2: Thermal gravimetric analysis of oxazolidinium-based salts.

Supporting Table S1: Comparison of thermal properties and ionic conductivity of oxazolidinium and pyrrolidinium-based salts. ($T_m \pm 1^\circ\text{C}$, $\Delta S_f \pm 10\%$ and conductivity $\pm 5\%$ for the data measured in the current work)

| Salt | T_m / $^\circ\text{C}$ | ΔS_f / $\text{J K}^{-1} \text{mol}^{-1}$ | $T_{d(\text{onset})}$ / $^\circ\text{C}$ | Conductivity at 30 $^\circ\text{C}$ / S cm^{-1} |
|--|-----------------------------|---|---|---|
| [C ₁ moxa][DCA] | 15 | 11 | 230 | 1.4×10^{-2} (melt) |
| [C ₁ mpyr][DCA] ¹ | 115 | 19 | - | 4.0×10^{-7} (phase I) |
| [C ₁ moxa][TFSI] | 72 | 24 | 340 | 2.3×10^{-7} (phase I) |
| [C ₁ mpyr][TFSI] ² | 132 | 40 | - | 2.0×10^{-9} (25 $^\circ\text{C}$, phase I) |
| [C ₁ moxa][BF ₄] | 204 | 12 | 323 | 3.8×10^{-7} (phase II) |
| [C ₁ mpyr][BF ₄] ^{3,4} | >340 | n/a | 340 | 1.0×10^{-7} (phase III) |
| [C ₁ moxa][PF ₆] | >343 | n/a | 343 | 2.7×10^{-9} (phase I) |
| [C ₁ mpyr][PF ₆] ⁵ | >390 | n/a | 390 | n/a |
| [C ₁ moxa][FSI] | 197 | 4 | 290 | 5.8×10^{-7} (phase I) |
| [C ₁ mpyr][FSI] ⁶ | 286 | 14 | 304 | 2.0×10^{-8} (phase I) |
| [C ₂ moxa][FSI] | 127 | 7 | 280 | 5.7×10^{-6} (phase I) |
| [C ₂ mpyr][FSI] ⁶ | 205 | 11 | 299 | 1.5×10^{-6} (phase I) |



Supporting Figure S3: Cyclic voltammetry of [C₁moxa][FSI] and [C₂mpyr][FSI] at 70°C at a scan rate of 2 mV s⁻¹, on a Pt working electrode, Pt coil counter electrode and Pt pseudo reference electrode. For clarity, only the forward sweep is shown.

References

- (1) Adebahr, J.; Forsyth, M.; MacFarlane, D. R. Cation Dynamics in Dimethyl-Pyrrolidinium-Based Solid-State Ion Conductors. *Electrochim. Acta* 2005, 50 (19), 3853–3858.
- (2) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. Pyrrolidinium Imides: A New Family of Molten Salts and Conductive Plastic Crystal Phases. *J. Phys. Chem. B* 1999, 103 (20), 4164–4170.
- (3) Forsyth, S.; Golding, J.; MacFarlane, D. R.; Forsyth, M. N-Methyl-N-Alkylpyrrolidinium Tetrafluoroborate Salts: Ionic Solvents and Solid Electrolytes. *Electrochim. Acta* 2001, 46 (10–11), 1753–1757.
- (4) Jin, L.; Howlett, P.; Efthimiadis, J.; Kar, M.; MacFarlane, D.; Forsyth, M. Lithium Doped N,N-Dimethyl Pyrrolidinium Tetrafluoroborate Organic Ionic Plastic Crystal Electrolytes for Solid State Lithium Batteries. *J. Mater. Chem.* 2011, 21 (27), 10171–10178.
- (5) Golding, J.; Hamid, N.; MacFarlane, D. R.; Forsyth, M.; Forsyth, C.; Collins, C.; Huang, J. N-Methyl-N-Alkylpyrrolidinium Hexafluorophosphate Salts: Novel Molten Salts and Plastic Crystal Phases. *Chem. Mater.* 2001, 13 (2), 558–564.
- (6) Yamada, H.; Miyachi, Y.; Takeoka, Y.; Rikukawa, M.; Yoshizawa-Fujita, M. Pyrrolidinium-Based Organic Ionic Plastic Crystals: Relationship between Side Chain Length and Properties. *Electrochim. Acta* 2019, 303, 293–298.