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PHYSICAL CHEMISTRY C**Elucidating the Impact of Sodium Salt Concentration on the Cathode-Electrolyte Interface of Na-Air Batteries**

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**Abstract**

A promising approach to improve the specific capacity and cyclability in a Na-O<sub>2</sub> cell using a pyrrolidinium-based ionic liquid electrolyte in a half-cell has been explored in this work. Increasing the concentration of sodium salt in an ionic liquid electrolyte produces a significant enhancement in the discharge capacity of up to 10 times, a reduction of the overpotential and an increase in long-term cyclability. Additionally, a distinct discharge morphology is also observed, which is demonstrated to be a result of a different oxygen reduction reaction (ORR) mechanisms. These improvements are likely due to the solvation of Na<sup>+</sup> in the electrolyte mixtures containing different Na<sup>+</sup> concentrations; the coordination of Na<sup>+</sup> by the anion of the ionic liquid dictates the discharge product morphology. At low Na<sup>+</sup> concentrations, Na<sup>+</sup> is strongly coordinated by the anion of the ionic liquid, and this also can have an effect on its mobility; however, at high Na<sup>+</sup> concentration this interaction is weakened, and favouring mass transport prior to product deposition. It therefore appears that the "highly-concentrated" electrolyte strategy is a useful route to enhance the performance of Na-O<sub>2</sub> batteries. Interestingly, when using a pressurized Swagelok-type cell the discharge product presents cubic morphology which is typical of NaO<sub>2</sub>. This is the first work where this characteristic morphology appears when using an ionic liquid which opens new venues for future research.