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Reactivity with superoxide radical of the $Pyr_{14}TFSI$ Ionic Liquid for $Li\text{-}O_2$ Cells

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Ionic liquids are attractive candidates as electrolyte solvents for $Li\text{-}O_2$ cells, primarily due to their low volatility, high anodic stability and low flammability. Specifically, the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($Pyr_{14}TFSI$) has attracted considerable attention, thanks to its electrochemical and chemical stability. In this contribution, the use of such ionic liquid as electrolyte in different $Li\text{-}O_2$ cell setups is investigated [1]. In a one-compartment $Li\text{-}O_2$ cell, the pyrrolidinium ion is reduced on metallic lithium, producing substantial amounts of alkenes and amines. To avoid this, an explored option was the substitution of lithium in the one-compartment cell with lithiated LTO (LLTO). Unfortunately, the absence of an SEI leads to the reduction of O_2 at LLTO, making it not useful as counter electrode for $Li\text{-}O_2$ cell evaluation. All the cell configurations are characterized by a first discharge specific capacity double than that obtained with unreactive electrolytes. The use of an edge-sealed two-compartment LLTO-Vulcan cell resulted in the usual discharge capacity of $\approx 200\ \mathrm{mAh\ g^{-1}_C}$ at the first cycle, eliminating the effects of $Pyr_{14}TFSI$ reduction; nevertheless, the poor cyclability even in this cell design suggests that $Pyr_{14}TFSI$ might not have sufficient long-term stability against the attack of O_2^- during discharge or of oxygen species during charge.

Afterwards we demonstrated, via our recently developed UV-Vis screening method, that $Pyr_{14}TFSI$ unfortunately reacts with the superoxide radical ($O_2^{\bullet-}$) which is produced during the discharge of $Li\text{-}O_2$ cells [2]. To clarify the reaction mechanism of $O_2^{\bullet-}$ with $Pyr_{14}TFSI$, we take advantage of the described formation of $O_2^{\bullet-}$ upon contact between LLTO and O_2 to produce a sufficient amount of degradation products from the reaction of $Pyr_{14}TFSI$ with $O_2^{\bullet-}$ that can be detected by NMR.

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[2] K. U. Schwenke, J. Herranz, H. A. Gasteiger and M. Piana, *J. Electrochem. Soc.*, **162** (6) A905-A914 (2015)

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