

Nitrate-Containing Electrolytes for Rechargeable Li-O₂ Batteries with Long Cycle Life

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Li-O₂ batteries with aprotic electrolytes have extremely high theoretical capacity, but practical implementation of this technology is hindered by myriad technical problems. For example, it is widely recognized that common electrolytes employed in Li-ion batteries are unstable in Li-O₂ cells. Moreover, the few solvent classes which evince stability in the O₂ electrode, such as amides and nitriles, generally do not form a stable solid-electrolyte interphase (SEI) on Li metal and other Li-based negative electrodes.¹ Conversely, certain Li salts with favorable SEI-forming properties, such as LiPF₆, have been shown to decompose in the O₂ electrode during cycling.²

This presentation addresses the goal of creating practical Li-O₂ batteries capable of long-term cycling through the use of nitrate-based electrolytes with enhanced stability toward both electrodes. The nitrate anion is thought to form a stable layer of Li₂O upon contact with Li metal.³ Previous work on Li-S batteries has shown that LiNO₃ incorporated as an electrolyte additive can suppress the phenomenon of polysulfide shuttling.⁴ In the current investigation, electrolytes employing LiNO₃ have been prepared and characterized for use in Li-O₂ batteries in combination with solvents that are incompatible with Li metal.

Evidence will be shown that dissolved O₂ and nitrate anions synergistically form a stable SEI between Li metal and dimethylacetamide (DMA).⁵ Cells employing an electrolyte composed of LiNO₃ and DMA have achieved high cycle number without evolving significant amounts of CO₂ or other gases that are indicative of side reactions. Mechanistic aspects of the behavior of nitrate anions in Li-O₂ cells are analyzed using a combination of *ex situ* and *in situ* techniques, including quantitative electrochemical mass spectrometry and electrochemical impedance spectroscopy.

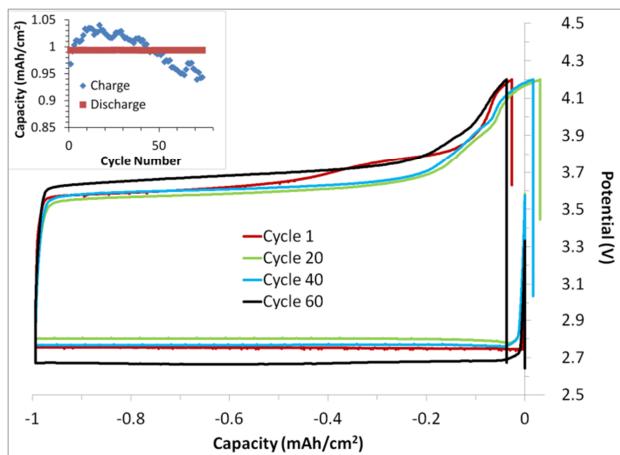


Figure 1: Discharge-charge curves obtained at cycles 1, 20, 40 and 60 for Li-O₂ cells containing 1.0 M LiNO₃ in DMA cycled at 0.1 mA/cm².

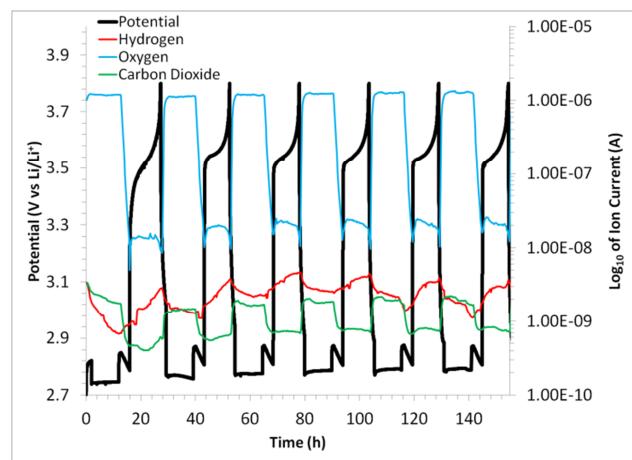


Fig. 2. In situ electrochemical mass spectrometry showing variations in evolved O₂, CO₂, and H₂ during cycling in Li-O₂ cells containing a LiNO₃/DMA electrolyte. The gas environment is switched between O₂ and Ar after each half cycle.

References:

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