Fluorinated Ether as an Electrolyte Additive for Lithium-Air Batteries

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Abstract:

Lithium-air batteries have shown promise as a next-generation battery technology due to their utilization of oxygen from ambient air. By using external oxygen instead of an internal oxidizer, the overall battery weight becomes reduced and more lithium can be used for energy storage. Thus, their energy density surpasses modern lithium-ion batteries' and even rivals gasoline fuels'. However, lithium-air batteries' current densities fall far behind industrial standards of at least 10 milliamps per centimeters squared (mA/cm^2) for high-discharge applications (e.g. electrical aircraft, medical devices, consumer electronics) due to the sluggish, diffusion-limited transport of oxygen across the liquid electrolyte. Here, we investigate the co-addition of a well-established fluorinated ether solvent 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl (TTE) due to increased oxygen solubility enabled by the molecule's nonpolar fluorocarbons. We find that current densities up to 7.5 mA/cm^2 can be achieved by optimizing the co-solvent ratio to around one-thirds TTE and two-thirds lithium nitrate ($LiNO_3$) in dimethylacetamide (DMA).

Summary of Research:

The lithium-air batteries were assembled as coin cells. The cathode side of the battery was primarily composed of a case with airholes, a stainless-steel spacer, and a porous carbon cathode. The carbon nanotube-based cathode was approximately 2 cm^2 in surface area, and it was wetted with approximately 32 microliters of electrolyte. Cathode materials were separated from the anode side by a membrane separator. The anode side of the battery was primarily composed of a lithium metal disk as the anode, a stainless spacer, and the anode case. The electrodes were connected via voltmeter inside a box connected to an oxygen input line and an exhaust output line.
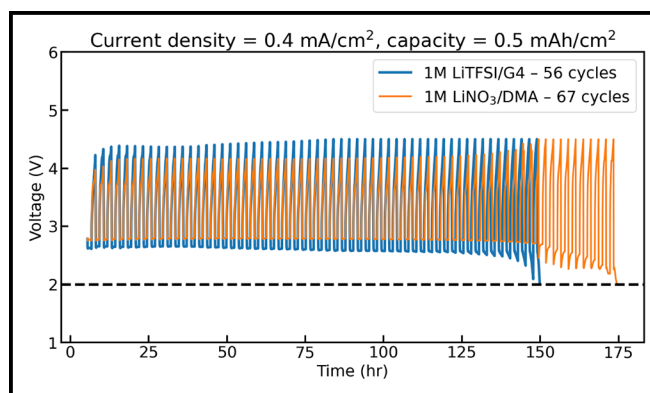

Figure 1: Comparison of lifecycles between 1 M LiTFSI/G4 and 1 M LiNO3/DMA.

Experimental conditions, i.e. current and capacity values, were controlled by an electrochemical workstation that multiple oxygen boxes were inserted in. Battery testing was conducted inside a dryroom with minimal moisture.

One molar (M) $LiNO_3$ in DMA has been known to be a robust candidate as a lithium-air electrolyte because of the stability of straight-chain alkyl amides like DMA in the oxygen electrode [1]. Although DMA is usually expected to be reactive towards lithium metal, the lithium nitrate salt facilitates the formation of a stable solid-electrolyte interphase primarily composed of lithium oxide (Li_2O). As shown in Figure 1, 1 M $LiNO_3$/DMA was demonstrated to boast exceptional cyclelife, or the number of discharge/recharge cycles before a cutoff voltage of 2 volts (V) was reached. At the cutoff voltage, it is expected that the overpotential, or the additional voltage required from the equilibrium potential in order to compensate for side reactions, has become large enough such that the battery has unstabilized due to degradation. At relatively shallow current density and capacity, the DMA-
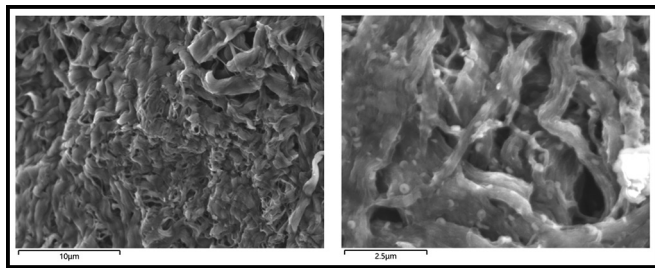
Figure 2: SEM images of a pristine porous carbon cathode (left) and Li$_2$O$_2$-deposited porous carbon cathode (right).

Figure 3: Comparison of lifecycles between 100% 1M LiNO$_3$/DMA and 67% 1M LiNO$_3$/DMA with 33% co-added TTE.

Figure 4: Comparison of lifecycles between 2.5 mA/cm^2 and 5 mA/cm^2 for 1 M LiNO$_3$/DMA with 30-minute intermittent rests between discharge and charge.

based electrolyte showed superior lifecycle compared to 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraglyme (G4) solvent: a well-established electrolyte. The electrolytes were prepared in an argon glovebox before being transferred to the dryroom. The discharge reaction between lithium and oxygen forms lithium peroxide (Li$_2$O$_2$) as a product with toroidal morphology. Figure 2 shows scanning electron microscopy (SEM) images of a pristine carbon cathode compared with a post-discharge carbon cathode, the latter being deposited with discrete, toroid Li$_2$O$_2$ particles.

For TTE experiments, TTE was co-added to G4 at various volume ratios in order to identify an approximate range for oxygen solubility. The oxygen solubilities were measured were an optical oxygen monitor, in which near-infrared emission detected from initial red-light excitation is correlated with oxygen concentration. A co-addition volume in the proximity of a range of 10 to 30% of TTE was shown to maximize oxygen solubility due to the nonpolar fluorocarbons in TTE [2]. 33% TTE was paired with 67% LiNO$_3$/DMA to test larger discharge currents and capacities.

As shown in Figure 3, the electrolyte combination was observed to sustain several cycles of discharge current densities up to 7.5 mA/cm^2. Lithium-air batteries typically cannot sustain current densities beyond 1 mA/cm^2, but the TTE/DMA-based electrolyte was able to approach a commercial benchmark of 10 mA/cm^2 [3,4]. In Figure 4, it was observed that counter-intuitively, larger current densities seem to prolong the cyclelife of lithium-air batteries rather than diminish it. This observation can be hypothesized to be due to formation of a disordered Li$_2$O$_2$ discharge product more facile to oxidize during the recharge process.

Conclusions and Future Steps:

Here, heavier discharge current densities up to 7.5 mA/cm^2 were sustainable for an electrolyte of two-thirds LiNO3/DMA and one-thirds TTE by volume. Future steps include a more rigorous optimization of the volume ratios, as the oxygen solubility measurements were conducted for pure solvents rather than lithium salt electrolytes. Furthermore, in order to investigate the hypothesis concerning the prolonged cyclelife at larger current densities, characterization techniques such as SEM and X-Ray Diffraction (XRD) can be employed to probe into the structural differences between the Li$_2$O$_2$ discharge product at various current densities.
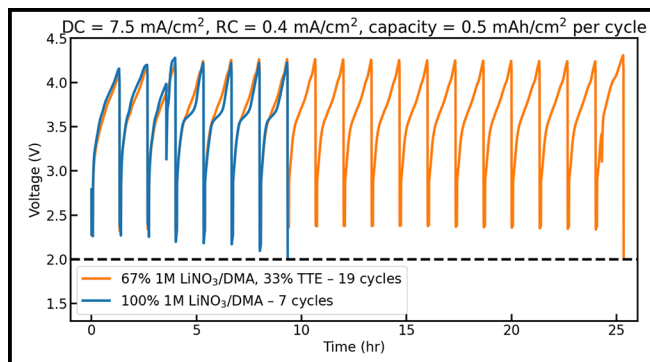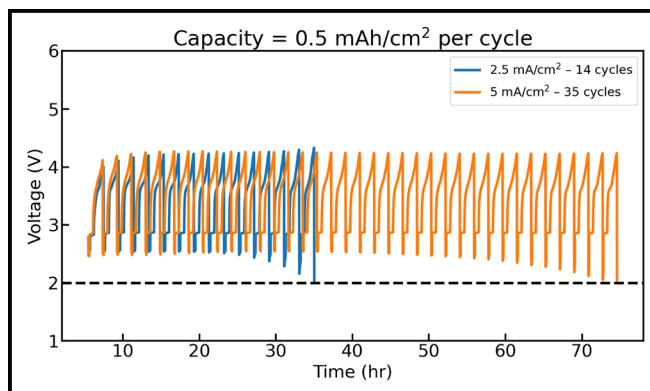
Acknowledgements:

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