



Short communication

Electrolyte optimization for the primary lithium metal air battery using an oxygen selective membrane

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ABSTRACT

The electrolyte solution for a primary nonaqueous lithium metal air battery is optimized. A novel oxygen selective membrane consisting of Teflon coated fiberglass cloth is used to prevent corrosion of the lithium metal negative electrode by water vapor during discharge in ambient air. The air electrode capacity is increased by increasing the amount of dimethyl carbonate and methoxybenzene in the electrolyte solvent, increasing the lithium tetrafluoroborate concentration to 1.5 M, and adding 4 mass % pentafluorophenylboron oxalate. Cells using either the starting or optimized electrolyte were discharged at a current density of 0.1 mA cm⁻² in air at 23 °C and 20% relative humidity. The discharge capacity (averaged for five discharges using each electrolyte solution) was increased by a factor of 2.2 for the cells using the optimized electrolyte solution of 1.5 M lithium tetrafluoroborate in propylene carbonate:dimethyl carbonate:methoxybenzene (1:5:1 by volume) + 4 mass % pentafluorophenylboron oxalate.

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1. Introduction

Lithium air (Li-air) batteries consist of a lithium (Li) metal negative electrode and a porous carbon positive electrode where oxygen (O₂) from air is reduced by lithium ions (Li⁺). Since O₂ is available freely from the air the theoretical energy density is higher than conventional lithium battery chemistries [1]. Therefore it is not surprising that many laboratories throughout the world, including this present laboratory, are currently researching primary [2–6] and secondary [7–9] Li-air battery systems. Water vapor from air must be prevented from corroding the Li metal negative electrode during discharge under ambient conditions, i.e. in humid air. One method of protecting the Li metal from corrosion is to use an O₂ selective membrane that allows O₂ into the cell while stopping or slowing the ingress of water vapor [6,10–12]. Fig. 1 is a schematic of this type of cell design. The optimization of the electrolyte for a cell using these types of O₂ selective membrane is discussed in this communication.

The electrolyte solution is known to have a large effect on the performance of a Li-air cell [13]. Researchers at the Pacific Northwest National Laboratories have previously published studies on the electrolyte optimization of the primary lithium metal air system [2,3]. However, two major differences between this study and

the previous warrant this additional publication. The previous publication selected 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in ethylene carbonate:propylene carbonate (1:1 by weight) based on its low evaporation rate [2]. The O₂ selective membrane used in this study has the additional advantage of significantly decreasing the evaporation rates of volatile solvents as discussed in greater detail below. This is important because volatile solvents tend to have higher O₂ solubility leading to better cell performance [13]. The second major difference is we have recently found the use of methoxybenzene as an electrolyte cosolvent can dramatically improve the discharge capacities of Li-air cells [14]. The use of this cosolvent will be included in this optimization while it was not considered in the former.

This communication will briefly discuss the use of O₂ selective membranes in Li-air batteries operating in ambient conditions. We previously have reported primary Li-air cathode performance in an electrolyte consisting of 1 M lithium tetrafluoroborate in propylene carbonate and dimethyl carbonate solvent mixture [6]. This paper deals with optimization of the electrolyte. Finally, the optimized electrolyte will be tested in ambient conditions, i.e. humid air.

2. Experimental

Electrolyte grade propylene carbonate (PC), 1,2-dimethoxyethane (DME), and dimethyl carbonate (DMC) were used as-received from Novolyte. Anhydrous tetraethylene glycol dimethyl ether (TEG-DME) and methoxybenzene (MOB) were

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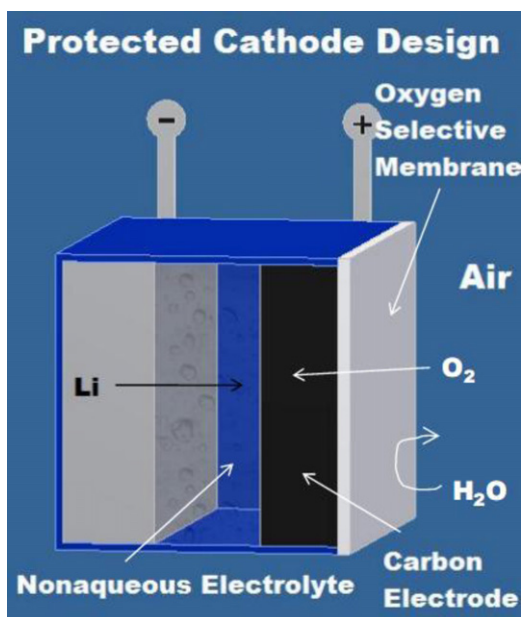


Fig. 1. Schematic of a Li-air cell using an O₂ selective membrane to allow for ambient operation.

purchased from Sigma Aldrich and dried over molecular sieves before use. High purity lithium tetrafluoroborate (LiBF₄) was used as-received from Sigma-Aldrich. Pentafluorophenylboron oxalate (PPFBO) was synthesized according to the procedure described in literature [15]. All electrolyte solutions were mixed in an argon filled glove box.

Full Li-air cells were constructed with a Li foil negative electrode separated from a porous carbon positive electrode by a cellulose separator (Nippon Kodoshi Corporation). The cathode pads, consisting of 95% Ketjen Black EC600G and 5% TE-3859 Teflon (DuPont), were fabricated via the “mineral spirits” method that we have previously described [6]. The cathode pad was pressed onto a titanium grid (Dexmet) that acts as a current collector. Cathodes with a geometric area of 10 cm² were punched from this larger pad. The cathodes were typically 150 μm thick and contained approximately 0.05 g of carbon. Cells were sealed into pouches that contained a 10 cm² Porex porous Teflon membrane window to prevent electrolyte solution from leaking out of the cell while freely allowing O₂ into the cell. Cells that were discharged in O₂ were placed in sealed bags filled with O₂ at 101 kPa. Cells discharged under ambient conditions had an additional Teflon coated fiberglass cloth (TCFC) membrane (McMaster Carr) adhered over the Porex window that acts as a selective O₂ membrane to allow ambient discharge [16]. These cells were discharged at 23 °C and 20% relative humidity (RH) in a Cincinnati Sub Zero Microclimate MCH-3-33-.33 H/AC Environmental Chamber. All cells were discharged galvanostatically to a cutoff voltage of 2 V using an Arbin BT-2000 battery tester. Five cells were discharged for each condition and the average discharge capacity based on mass of carbon in the electrode is reported. The error bars are the standard deviation for each set of tests. The cell with the median capacity was used for any graph that displays discharge curves. A lithium iron phosphate (LFP) electrode at a 50% state-of-charge was used as a pseudo-reference electrode in three electrode cells. This electrode was chosen because it demonstrates a stable open circuit voltage (3.44 V vs Li/Li⁺ at 23 °C) throughout most of its SOC and is stable in aqueous environments [17]. All half-cell potentials are reported vs. Li/Li⁺.

Table 1

Li-O₂ air electrode capacity (mAh g⁻¹ C) for various electrolyte solutions at current densities of 0.2 and 0.5 mA cm⁻².

Electrolyte solution (volume ratio)	0.2 mA cm ⁻²	0.5 mA cm ⁻²
1.0 M LiBF ₄ in PC:DMC (1:1)	3180 ± 260	1537 ± 99
0.1 M LiBF ₄ in PC	999 ± 139	590 ± 62
0.5 M LiBF ₄ in PC	790 ± 63	320 ± 47
1.0 M LiBF ₄ in PC	1333 ± 120	266 ± 52
1.5 M LiBF ₄ in PC	1031 ± 104	143 ± 32
1.0 M LiBF ₄ in TEG-DME	790 ± 170	
0.1 M LiBF ₄ in PC:DMC	1979 ± 82	1286 ± 39
0.1 M LiBF ₄ in TEG-DME:DME (1:1)	2684 ± 188	1052 ± 75
1.0 M LiBF ₄ in TEG-DME:DME (1:1)	2619 ± 609	1085 ± 214
0.1 M LiBF ₄ in PC:DMC:MOB (1:1:1)	2041 ± 88	1310 ± 53
1.0 M LiBF ₄ in PC:DMC:MOB (1:1:1)	4402 ± 279	1993 ± 347
0.1 M LiBF ₄ in TEG-DME:DME:MOB (1:1:1)	2047 ± 220	396 ± 81
1.0 M LiBF ₄ in TEG-DME:DME:MOB (1:1:1)	3006 ± 540	1028 ± 333
1.0 M LiBF ₄ in PC:DMC:MOB (1:3:1)	4645 ± 506	2319 ± 285
1.0 M LiBF ₄ in PC:DMC:MOB (1:3:3)	3888 ± 864	2292 ± 397
1.0 M LiBF ₄ in PC:DMC:MOB (1:1:3)	4764 ± 729	1750 ± 216
1.0 M LiBF ₄ in PC:DMC:MOB (1:5:3)	4439 ± 728	2571 ± 435
0.5 M LiBF ₄ in PC:DMC:MOB (1:5:1)	3163 ± 532	2606 ± 370
1.0 M LiBF ₄ in PC:DMC:MOB (1:5:1)	4639 ± 82	2492 ± 750
1.5 M LiBF ₄ in PC:DMC:MOB (1:5:1)	4970 ± 657	2704 ± 503
+1 wt% PFPBO	5210 ± 375	2673 ± 260
+2 wt% PFPBO	5388 ± 448	2881 ± 174
+4 wt% PFPBO	6180 ± 761	3014 ± 389

3. Results and discussion

3.1. O₂ selective membranes

Oxygen selective membranes are hydrophobic materials that demonstrate high O₂ solubilities and diffusion rates to allow O₂ into the cell where it is electrochemically reduced at the positive electrode. Additionally, the membrane must stop or slow the ingress of water vapor into the cell since it will corrode the Li metal negative electrode. A third feature of the membrane is it slows electrolyte evaporation to acceptable rates. Read et al. [13] showed that the use of electrolyte solvents with higher O₂ solubility like DMC and DME increased the discharge capacity. Table 1 lists the average discharge capacity obtained for all the electrolytes tested in this study. The average discharge capacity at 0.2 mA cm⁻² increases from 1331 for 1 M LiBF₄ in PC to 3180 mAh g⁻¹ C for 1 M LiBF₄ in PC:DMC (1:1 by volume) demonstrating Read's [13] conclusion. However, these solvents tend to be volatile and will lead to premature cell failure due to electrolyte evaporation. Therefore the use of a membrane that will slow electrolyte evaporation will lead to better cell performance.

Teflon coated fiberglass cloth is used as the O₂ selective membrane for cells discharged in ambient conditions in this study. We have found these membranes can transfer O₂ support a rate of approximately 0.2 mA cm⁻² if the air window is the same size as the cathode [16,18]. O₂ permeation measurements performed independently by Mocon Inc. and Illinois Instrument Company confirmed this observation. Fig. 2 shows the evaporation rate of a typical electrolyte through the TCFC membrane. Approximately 2% of the electrolyte evaporates out of the pouch over 40 days when the TCFC membrane is used. This is an acceptable loss for a primary cell. Fig. 3 shows a typical ambient discharge of a cell with a reference electrode. The cell failure is caused by a decrease in air electrode potential. The Li metal anode potential only increases from 13 to 24 mV vs. Li/Li⁺ over the course of the discharge, demonstrating minimal corrosion of the Li. Fig. 4 shows the Li anode for this cell after discharge compared to a cell discharged not using a membrane. The Li is pristine for the cell discharged using the TCFC membrane while completely consumed to form a white powder in the case with no membrane. This also demonstrates that the TCFC

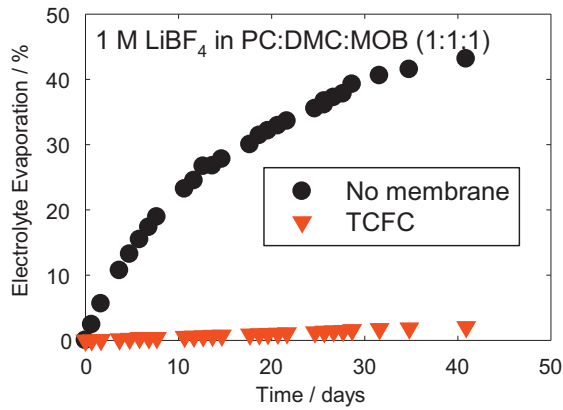


Fig. 2. Evaporation rates of a typical electrolyte from a pouch cell with and without a TCFC O₂ selective membrane.

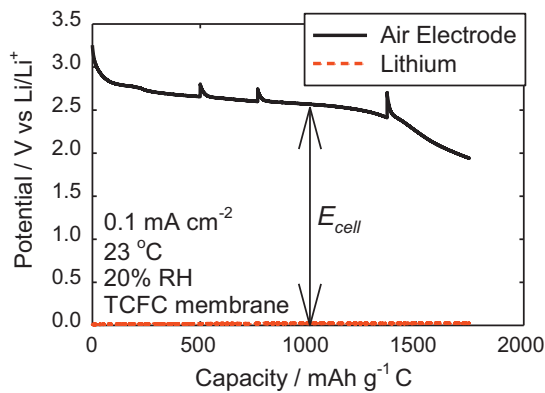


Fig. 3. Typical ambient discharge of a Li-air cell containing a reference electrode.

membrane slows the ingress of water vapor into the cell to rates acceptable for primary battery applications.

3.2. Alkyl carbonate verses ether based electrolytes

Abraham and Jiang [19] originally reported lithium peroxide (Li₂O₂) to be the major discharge product of a Li-air cell using a nonaqueous electrolyte consisting of lithium hexafluorophosphate (LiPF₆), ethylene carbonate, PC, and polyacrylonitrile. However, recent literature suggests that very little, if any, lithium peroxide or lithium oxide (Li₂O) is formed for cells discharged in alkyl carbonate based electrolytes [20–23]. Laoire et al. [24] showed ether based electrolyte solvents, specifically TEG-DME, formed mainly Li₂O₂ as the discharge product at potentials above 1.5 V vs. Li/Li⁺.

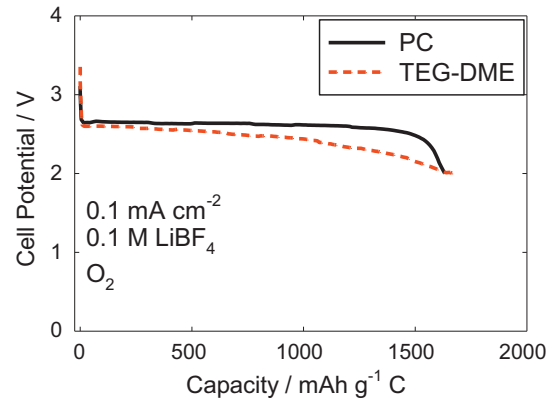


Fig. 5. Voltage profile during discharge at 0.1 mA cm⁻² of a Li-O₂ cell using either PC or TEG-DME as electrolyte solvent.

This is important for these studies that focus on secondary batteries, because Ogasawara et al. [25] showed Li₂O₂ formation to be reversible. However, there is very little research showing if this matters for primary batteries. Read [26] found ether based electrolytes, specifically containing 1,3-dioxolane and DME as solvent, to demonstrate higher discharge capacities than alkyl carbonates. He attributed this to the lower viscosity of the solvent compared to alkyl carbonate based solvents with similar O₂ solubility [26].

Fig. 5 shows a typical low rate discharge for an electrolyte solution with just PC or TEG-DME as solvent. The low current density, 0.1 mA cm⁻², was chosen to minimize differences caused by O₂ transport in the different electrolytes. There is no significant difference in discharge capacity, though the PC based electrolyte has a higher discharge voltage. This shows that the actual discharge product, whatever it is, has no significant effect on the primary performance of Li-air batteries. We compared mixtures of PC and DMC to that of TEG-DME and DME. LiBF₄ was used as the electrolyte salt and studied with and without MOB for both the alkyl carbonate and ether based mixtures. All electrolyte solvents were studied in equivolume mixtures. The addition of MOB to the carbonate based mixtures causes an increase in discharge capacity; however, MOB causes no change or even decreases the capacity when added to the ether based mixtures. 1 M LiBF₄ in a PC:DMC:MOB solvent mixture was chosen because it demonstrates the highest discharge capacities of the mixtures studied as seen in Table 1. The next section optimizes the volumetric ratio of each cosolvent.

3.3. Optimal electrolyte solvent volume ratio

The electrolyte solvent mixture consisting of PC, DMC, and MOB was optimized for an electrolyte of 1 M LiBF₄ since the electrolyte

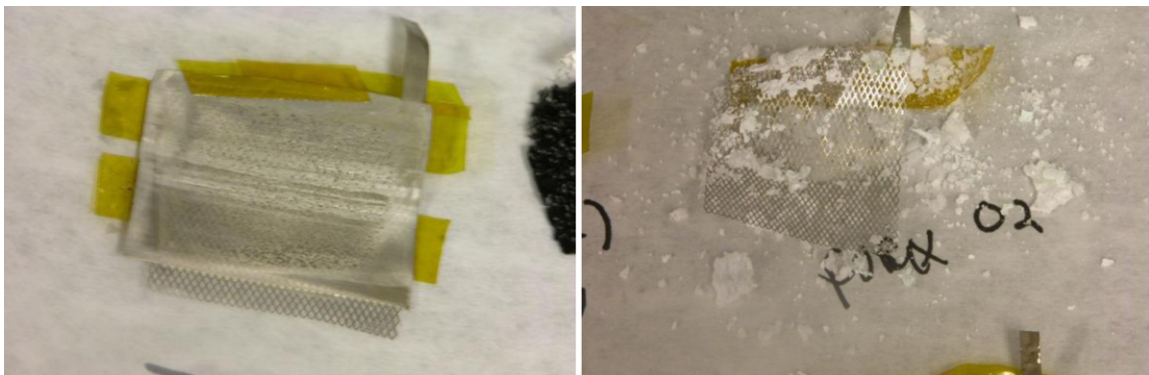


Fig. 4. Pictures of a Li metal negative electrode after cell discharge in humid air at 23 °C and 20% RH for a cell using a TCFC membrane (left) and with no membrane (right).

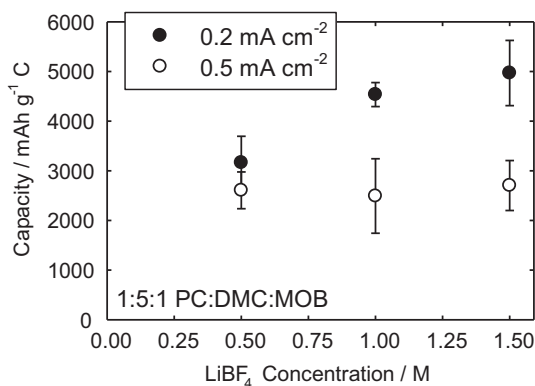


Fig. 6. Effect of LiBF₄ concentration on discharge capacity of Li-O₂ air electrodes.

solvent has been shown to have a larger effect on Li-air cathode performance (compared to salt type) [2,3,13]. The amount of PC was kept at the minimum quantity to allow the electrolyte salt into solution. In addition, PC has a high dielectric constant thus minimizing ion association [27]. The discharge capacity increases with an increasing amount of DMC and MOB. There is no significant difference between the volumetric ratios of 1:3:1, 1:1:3, 1:5:1, and 1:5:3 PC:DMC:MOB as seen in Table 1. We selected the 1:5:1 PC:DMC:MOB solvent volumetric ratio to use in this optimization because it demonstrated the highest single cell capacities at both current densities.

3.4. Electrolyte salt optimization

The next step in this optimization was to determine the optimum salt type and concentration. We looked at using LiTFSI, lithium triflate, and LiBF₄ since these salts are known to be stable in organic solvents containing small amounts of water [27]. We found no significant difference in performance for the different salts so we continued to use LiBF₄ (data not shown). Fig. 6 shows the effect of LiBF₄ concentration on discharge capacity. The concentration affects the bulk concentration of Li⁺, the transport number, the ionic conductivity and O₂ solubility [13,27]. The discharge capacity increases with LiBF₄ concentration for a current density of 0.2 mA cm⁻².

3.5. PFPBO additive

It has been suggested that increasing the solubility of Li₂O and Li₂O₂ in the electrolyte solution will result in an increase in Li-air cell performance [3,14]. One method to increase the solubility of these lithium oxides is adding boron-based anion receptors to the electrolyte solution [15]. PFPBO is a boron-based anion receptor that has been shown to increase the solubility of Li₂O, Li₂O₂, and lithium fluoride in PC and DMC based electrolyte solutions [15]. Fig. 7 shows the effect of increasing PFPBO concentration on Li-air discharge capacity at rates of 0.2 and 0.5 mA cm⁻². The addition of 4 mass percent PFPBO to the electrolyte solution increases the discharge capacity by 24% at 0.2 mA cm⁻² and 11% at 0.5 mA cm⁻².

3.6. Electrolyte optimization summary

Fig. 8 shows the achieved discharge capacities as a function of current density for the starting electrolyte, 1 M LiBF₄ in PC:DMC (1:1), and the optimized electrolyte, 1.5 M LiBF₄ in PC:DMC:MOB (1:5:1) + 4 mass % PFPBO. The capacity is significantly increased for all current densities. The average capacity is increased by 94.3% at 0.2 mA cm⁻², 96.2% at 0.5 mA cm⁻², and 433.1% at 1 mA cm⁻² when cells are discharged in O₂. The high capacity demonstrated

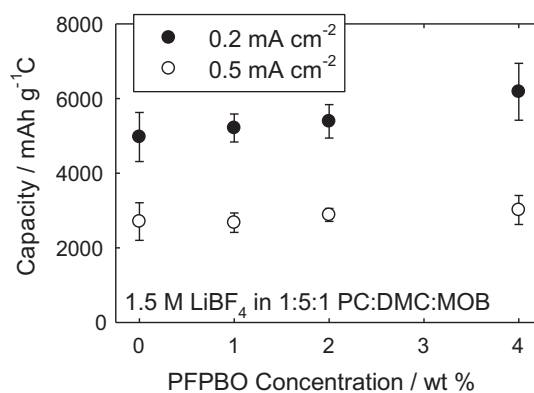


Fig. 7. Effect of additive concentration on Li-O₂ air electrode capacities at different rates.

at 1 mA cm⁻² (~200 mA g⁻¹ C) of approximately 1500 mAh g⁻¹ C for uncatalyzed air electrode shows that the Li-air cell may be able to provide reasonable power capability. However, better O₂ selective membranes must be developed that transport a sufficient amount of O₂ to the air electrode from ambient air to support these higher current densities. We are currently determining the physical properties of the starting and optimized electrolyte, including O₂ solubility and the solubility of various proposed discharge products to better understand the mechanism for this increase. Regardless of mechanism, cells discharged using the optimized electrolyte demonstrate significantly higher capacities.

3.7. Ambient cell performance

The electrolyte optimization performed above in O₂ atmosphere has no value if the electrolyte solution does not improve Li-air performance under practical operating conditions, i.e. discharge in ambient environments of humid air. For example, electrolyte evaporation may occur quicker because of the increased amount of DMC (relative to Fig. 2) leading to drying out of the air electrode. Also the MOB or PFPBO may not be stable with water or carbon dioxide. Therefore we discharged cells using the TCFC membrane at a current density of 0.1 mA cm⁻² in an environmental chamber maintained at 23 °C and 20% RH. The electrolyte solutions tested were 1 M LiBF₄ in PC:DMC (1:1) and 1.5 M LiBF₄ in PC:DMC:MOB (1:5:1) with and without 4 mass percent of the PFPBO additive. Fig. 9 shows the typical discharge profile for these three electrolyte solutions. The optimized electrolyte has the highest capacity and also demonstrates a more flat discharge than the other electrolyte solutions. The optimized electrolyte solution with the additive increases the

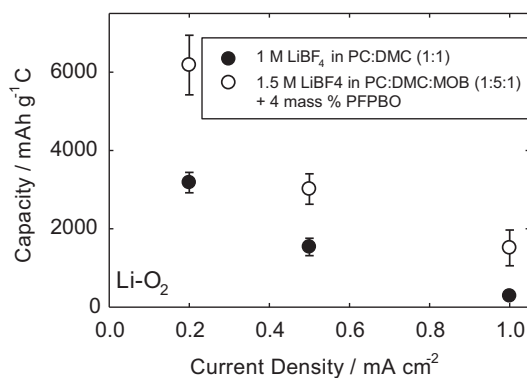


Fig. 8. Effect of current density on Li-O₂ air electrode capacity for cells with an electrolyte consisting of either 1 M LiBF₄ in PC:DMC (1:1) or the optimized electrolyte, 1.5 M LiBF₄ in PC:DMC:MOB (1:5:1) + 4 mass % PFPBO.

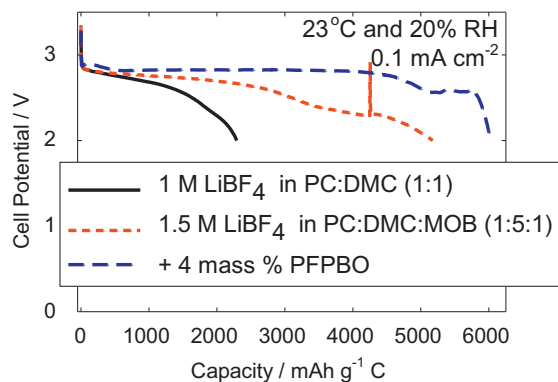


Fig. 9. Ambient discharge of Li-air cells using TCFC O₂ selective membranes at 0.1 mA cm⁻² in humid air at 23 °C and 20% RH.

discharge capacity by an average factor of 2.2 compared to the starting electrolyte solution under these discharge conditions.

4. Conclusions

The electrolyte for a primary nonaqueous Li-air cell is optimized. A novel O₂ selective membrane consisting of Teflon coated fiber-glass cloth is used to discharge the Li-air cells in ambient conditions. The air electrode capacity is increased by optimizing the solvent components, the concentration of electrolyte salt, and the concentration of PFPBO additive. The capacity is significantly increased for all current densities. The average capacity is increased by 94.3% at 0.2 mA cm⁻², 96.2% at 0.5 mA cm⁻², and 433.1% at 1 mA cm⁻² when cells are discharged in O₂. The uncatalyzed air electrodes demonstrated a large capacity of 1500 mAh g⁻¹ C at a relatively high rate of 1 mA cm⁻² (~200 mA g⁻¹ C) when discharged in pure O₂ demonstrating that this system may provide better power density than originally believed. However, to realize this improved power density better O₂ selective membranes must be developed that transport O₂ at rates high enough to support these current densities while still stopping the corrosion of the Li metal anode from water vapor in ambient air. The optimized electrolyte solution is stable for discharge under typical ambient conditions. The optimized electrolyte of 1.5 M LiBF₄ in PC:DMC:MOB (1:5:1) + 4 mass % PFPBO increases the discharge capacity by an average factor of 2.2 compared to the starting electrolyte solution for a discharge at a rate of 0.1 mA cm⁻² in humid air at 23 °C and 20% RH.

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