



Short communication

A non-aqueous electrolyte for the operation of Li/air battery in ambient environment

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ABSTRACT

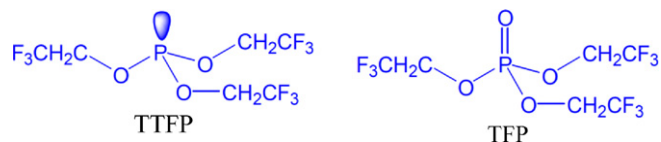
In this work we report a non-aqueous electrolyte that supports long-term operation of the Li/air battery in dry ambient environments based on a non-hydrolytic LiSO_3CF_3 salt and a low volatility propylene carbonate (PC)/tris(2,2,2-trifluoroethyl) phosphate (TFP) solvent blend. By measuring and analyzing the viscosity of PC/TFP solvent blends, the ionic conductivity of electrolytes, and the discharge performance of Li/air cells as a function of the PC/TFP weight ratio, we determined the best composition of the electrolyte is 0.2 m (molality) LiSO_3CF_3 7:3 wt. PC/TFP for Li/O₂ cells and 0.2 m LiSO_3CF_3 3:2 wt. PC/TFP for Li/air cells. Discharge results indicate that Li/air cells with the optimized electrolyte are significantly superior in specific capacity and rate capability to those with baseline electrolytes. More interestingly, the improvement in discharge performance becomes more significant as the discharge current increases or the oxygen partial pressure decreases. These results agree neither with the viscosity of the solvent blends nor the ionic conductivity of the electrolytes. We consider that the most likely reason for the performance improvement is due to the increased dissolution kinetics and solubility of oxygen in TFP-containing electrolytes. In addition, the electrolyte has a 5.15 V electrochemical window, which is suitable for use in rechargeable Li/air batteries.

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1. Introduction

Since the first report on a non-aqueous electrolyte Li/air battery by Abraham and Jiang [1], many electrolytes have been proposed for long-term operation of the Li/air battery in ambient environments, including non-aqueous electrolytes [2–9], polymer gel electrolytes [1,10] and hydrophobic ionic liquids [11]. All these electrolytes, featured with either low volatility or non-volatility, are highly viscous, which makes the diffusion of dissolved oxygen in electrolytes difficult and hence results in poor power capability of the Li/air battery. In a recent work [12], we have demonstrated that use of a partially fluorinated co-solvent in the non-aqueous electrolyte can significantly improve discharge performance of Li/air batteries. In particular, adding 30 wt.% tris(2,2,2-trifluoroethyl) phosphite (TTFP) into a propylene carbonate (PC) electrolyte significantly increases the specific capacity and rate capability of Li/air cells although the addition of TTFP only causes a small change in the viscosity of solvent blends while inversely the ionic conductivity of liquid electrolytes is reduced. We attribute this improvement to the increased dissolution kinetics and solubility of oxygen in the

liquid electrolyte as a result of the addition of partially fluorinated solvent. Furthermore, we have shown that the Li/air cells based on PC/TTFP electrolyte are able to operate a long time in dry ambient environments due to the low volatility of TTFP and PC solvents [12]. However, the TTFP-based electrolytes may not be suitable for use in a rechargeable Li/air battery since the valence of phosphorus in TTFP is +3, it can potentially be oxidized into +5 to form tris(2,2,2-trifluoroethyl) phosphate (TFP) with the following chemical structures:



Based on the radical-scavenging mechanism, we have successfully used TTFP and TFP to formulate non-flammable electrolytes for Li-ion batteries [13–15]. This feature also may benefit the development of a non-aqueous electrolyte for a rechargeable Li/air battery. It has been reported [16,17] that most carbonate solvents are unstable in rechargeable Li/air batteries because the charging process produces oxygen anionic radicals, which are highly reactive and attack carbonate molecules. Due to the excellent radical-scavenging property of phosphate compounds, we predict that the chemical stability of carbonate solvents in rechargeable Li/air batteries can be improved by using TFP or other phosphate com-

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pounds as a co-solvent of the non-aqueous electrolytes. Our goal in this work is to develop a non-aqueous electrolyte for long-term operation of Li/air primary batteries in dry ambient environments. For this reason, we have formulated an electrolyte by using non-hydrolytic LiSO_3CF_3 as the Li salt and low volatility PC and TFP as the solvent. In this paper we report optimization of the composition of the electrolytes and discuss the discharge performance of Li/air cells by comparing the optimized electrolyte with PC and PC/TTFP baseline electrolytes.

2. Experimental

Lithium triflate (LiSO_3CF_3 , 96%, Aldrich) was dried at 100°C under vacuum for 8 h. Electrolyte grade propylene carbonate (PC, Ferro) was used as received and tris(2,2,2-trifluoroethyl) phosphite (TTFP, 99%, Aldrich) was dried over activated aluminum oxide for a week prior to use. Tris(2,2,2-trifluoroethyl) phosphate (TFP) was synthesized by reacting sodium trifluoroethoxide with phosphorus oxychloride and purified by repeated fractionation under reduced pressure. Detailed descriptions on the synthesis and characterization of TFP are referred to Refs. [14,15], and the basic physical properties of TTFP and TFP are summarized in Table 1.

Electrolytes with different compositions were prepared in a glove-box and expressed as a molality (m) for the concentration of lithium salt and a weight ratio for the composition of solvent blends. Kinematic viscosity of the solvents and solvent blends was measured in a 25°C constant temperature bath using a Ubbelohde viscometer (Cannon Instrument Company). A Solartron SI 1287 electrochemical interface and a SI 1260 impedance/gain-phase analyzer were used for impedance and cyclic voltammetry measurements. Ionic conductivity of the electrolytes was calculated from the impedance of solution measured using a two-platinum-electrode cell. Electrochemical window of the electrolyte was measured on a Pt electrode and a Ni electrode using a three-electrode cell with Li foils as the counter and reference electrodes. The working electrode was a 1 cm long Pt or Ni wire (both having a 0.5 mm diameter), and each scan (to anodic and cathodic, respectively) used a new wire. A Li/Ni cell with a 1.27 cm^2 active area was assembled in a glove-box to measure the plating/stripping cycling efficiency of Li. The cell was discharged (i.e., Li plating on Ni electrode) at 0.5 mA cm^{-2} for 1 h, and then charged (i.e., Li stripping) using the same current density until the cell voltage rose to 1.0 V. The cycling efficiency of Li was defined as the percentage of charging time over discharging time.

A carbon air cathode with a composition of 90 wt.% super P carbon and 10 wt.% polytetrafluoroethylene (PTFE) was prepared by mixing calculated amounts of super P and PTFE emulsion (Teflon[®], solid content = 61.5%, DuPont Co.) and rolling the mixed paste into a free-standing cathode sheet. The resultant air cathode sheet was punched into small disks with an area of 0.97 cm^2 and dried at 100°C under vacuum for at least 8 h. Typically, the air cathode has a thickness of 0.5–0.6 mm and a porosity of $2.9\text{--}3.2\text{ cm}^3\text{ g}^{-1}$ (vs. super P). In a dry-room having a dew point of below -90°C , Li/air cells with an air window of 0.97 cm^2 were assembled by stacking a Li foil, a Celgard[®] 3500 membrane, a carbon air cathode, a Ni mesh

as the current collector, and an air window in sequence into a coin cell cap. To activate the cell, $200\ \mu\text{L}$ of liquid electrolyte was added through the air-window, followed by applying a vacuum for 20 s to ensure complete wetting. Extra liquid electrolyte was removed by gently swiping a filter paper on the top of Ni mesh. The electrolyte-activated cell was clamped on a cell holder to discharge as a Li/air cell or sealed in an O_2 -filled plastic bag to discharge as a Li/ O_2 cell. Before discharging, the cells rested for 2 h to reach equilibrium of oxygen concentration between the air cathode and gaseous atmosphere in the cell. In the dry room cells were discharged on an Arbin BT-2000 cyler with a 1.5 V cutoff voltage. Specific capacity of the cell was calculated based on the weight of super P carbon in the air cathode. All discharging tests were carried out at room temperature (22°C).

3. Results and discussion

3.1. Viscosity and ionic conductivity of solvent blend and electrolyte

The viscosities at 25°C of PC/TFP solvent blends together with the ionic conductivities at room temperature (22°C) of $0.2\text{ m LiSO}_3\text{CF}_3$ electrolytes are plotted as a function of the solvent composition in Fig. 1. First, we see that the viscosity of PC/TFP solvent blends displays a maximum value at the composition of 1:4 PC/TFP (i.e. $x=0.8$). This observation differs from the PC/TTFP system, which shows a general trend of the viscosity decreasing with the fraction of TTFP as a result of the addition of less viscous TTFP (i.e., kinematic viscosity at $25^\circ\text{C}=0.98\text{ mm}^2\text{ s}^{-1}$ vs. $2.1\text{ mm}^2\text{ s}^{-1}$ of PC) [12]. However, such correlations of viscosity with the solvent composition have been observed in many aqueous solvent systems and their related electrolytes [18–20] and have been well modeled by Wang et al. [21]. Second, we see that ionic conductivity of the electrolytes is linearly decreased with an increase in the fraction of TFP in the PC/TFP solvent blend. This result is in good agreement with the viscosity data of solvent blends, which shows a linear increase with the fraction of TFP as the x value in $(1-x):x$ PC/TTFP is less than 0.8. On the other hand, the decrease in ionic conductivity is also associated with the reduced dielectric constant of the PC/TFP solvent blends as a result of the addition of TFP having lower dielectric constant, that is, 10.5 vs. 66.1 of PC at 20°C [14,22]. Just judging from the solvent viscosity and electrolyte conductivity data, one would predict that the use of PC/TFP electrolytes is unfavorable to the discharge performance of Li/air batteries.

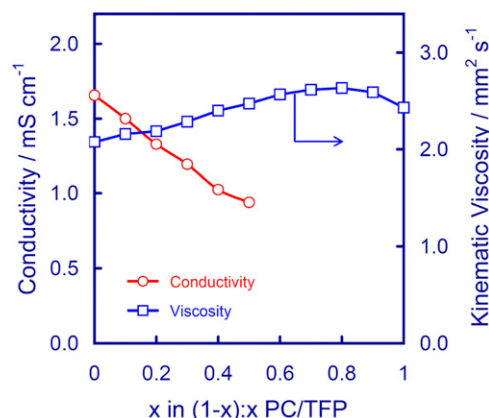


Fig. 1. Viscosity of PC/TFP solvent blend and ionic conductivity of $0.2\text{ m LiSO}_3\text{CF}_3$ electrolyte as a function of the solvent composition for $(1-x):x$ PC/TTFP solvent blends, in which the viscosity was measured at 25°C and ionic conductivity was measured at room temperature (22°C).

Table 1
Physical properties of TTFP and TFP.

	TTFP	TFP
Molecular weight	328.064	344.07
Boiling point ($^\circ\text{C}$)	130–131 (743 mmHg)	178
Density (g mL^{-1})	1.4870 (25°C)	1.5941 (20°C)
Viscosity ($\text{mm}^2\text{ s}^{-1}$ at 25°C)	0.9830	2.4332

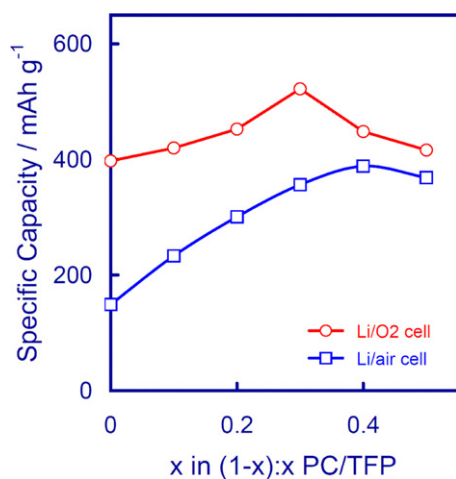


Fig. 2. Correlation of the specific capacity of a Li/O₂ cell and a Li/air cell with the solvent composition for a 0.2 m LiSO₃CF₃ (1-x):x PC/TFP electrolyte, in which all capacities were measured at 0.2 mA cm⁻² and room temperature (22 °C).

3.2. Relationship of discharge capacity and electrolyte composition

Correlations of the specific capacity with electrolyte composition (i.e., x value in (1-x):x PC/TFP solvent blends) for Li/O₂ cells and Li/air cells, respectively, are compared in Fig. 2. In low x range, the specific capacities of both Li/O₂ and Li/air cells are increased with the x value. This phenomenon disagrees with the solvent viscosity and electrolyte conductivity data as indicated in Fig. 1. For the same reason as proposed for 0.2 m LiSO₃CF₃ PC/TFP electrolytes [12], the obtained improvement in specific capacity by TFP can be attributed to the increased dissolution kinetics and solubility of oxygen in TFP-containing electrolyte. Here, the dissolution of oxygen is such a process that the liquid electrolyte first forms a large enough cavity for accommodating the oxygen molecule and then the oxygen molecule inserts into the liquid's cavity, and the dissolution kinetics corresponds to a mass transferring rate of oxygen molecule from gas phase into the liquid electrolyte phase. As shown in Fig. 2, the highest capacity appears at $x=0.3$ for Li/O₂ cells and at $x=0.4$ for Li/air cells. This means that when the oxygen partial pressure is low, more TFP is needed for high capacity although the solvent viscosity and electrolyte conductivity become worse.

In an early paper [12], we have shown that the best composition for the PC/TFP solvent system is 0.2 m LiSO₃CF₃ 7:3 wt. PC/TFP. Therefore, in the present work we use this electrolyte as one of the baseline electrolytes. Fig. 3 compares the effect of TTFP and TFP on the discharge performance of Li/O₂ and Li/air

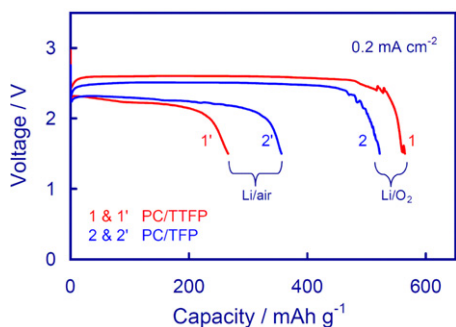


Fig. 3. Comparison of the discharge performances of Li/O₂ cells and Li/air cells with different electrolytes, in which all measurements were conducted at room temperature (22 °C). (1 and 1') 0.2 m LiSO₃CF₃ 7:3 PC/TFP, and (2 and 2') 0.2 m LiSO₃CF₃ 7:3 PC/TTFP.

cells, in which the composition of 0.2 m LiSO₃CF₃ 7:3 wt. PC/TFP was selected for the PC/TFP solvent system. It can be seen from Fig. 3 that for both solvent systems, the Li/O₂ cell has much higher specific capacity than the Li/air cell. This phenomenon can be easily explained by the effect of oxygen partial pressure. That is, the high oxygen partial pressure in Li/O₂ cell not only enhances dissolution kinetics of oxygen but also increases solubility of oxygen in liquid electrolyte. A very interesting phenomenon we can see from Fig. 3 is that the specific capacity of carbon in Li/O₂ cells is lower with TFP electrolyte than with TTFP electrolyte. However, the order of the specific capacity is reversed in Li/air cells. This is because the TFP co-solvent is more favorable than TTFP for the dissolution and solubility of oxygen. At low oxygen partial pressures, the dissolution and solubility of oxygen play more important role than the viscosity of the electrolyte solution in determining the discharge performance of Li/air cells. The facts above suggest that the TFP electrolyte be more suitable for the operation of Li/air cells in low oxygen partial pressure environments, as compared with TTFP electrolyte.

3.3. Discharge rate capability of Li/air cells

The discharge performances of Li/air cells with PC, PC/TTFP, and PC/TFP electrolyte, respectively, at various discharge current densities are compared in Fig. 4(a)–(d). At low current density (0.05 mA cm⁻², Fig. 4(a)), PC and PC/TFP electrolyte cells have nearly the same capacities. As the current increases to 0.1 mA cm⁻² and higher (Fig. 4(b)–(d)), the PC/TFP electrolyte cells show significantly higher capacity than PC and PC/TTFP baseline cells although PC/TFP solvent has the highest viscosity and its related electrolyte has the lowest ionic conductivity (see Fig. 1, and Figs. 3 and 4 of Ref. [12]). More interestingly, the performance improvement becomes more significant when the discharge current density is increased. These facts reveal that TFP must play an important role in the dissolution process and solubility of oxygen in liquid electrolyte. Fig. 4(b)–(d) indicates that the specific capacities of Li/air cells are increased in the order of PC/TFP > PC/TTFP > PC. The performance improvement by TTFP and TFP co-solvent is because the fluorinated solvents increase the dissolution kinetics and solubility of oxygen in liquid electrolyte.

In addition, we should mention that PC/TFP electrolyte is quite suitable for long-term operation of Li/air cells in dry ambient environments due to the low volatility of PC and TFP. As evidence, the air electrode and separator of the Li/air cells still remained electrolyte-wetted even after the cells were discharged at low current density (0.05 mA cm⁻²) and then exposed to air in the dry-room for a week.

3.4. Electrochemical window and Li cycling efficiency of electrolyte

With interest in the application of PC/TFP electrolytes in rechargeable Li/air batteries, we examined the electrochemical window of PC/TFP electrolyte using cyclic voltammetry (CV). Fig. 5 shows cyclic voltammograms of Pt electrode and Ni electrode in a 0.2 m LiSO₃CF₃ 7:3 PC/TFP electrolyte, in which each CV curve consists of two scans (i.e., anodic and cathodic) and each scan used a new electrode. For the Pt electrode (Fig. 5(a)), the anodic stability is limited by the potential of oxidative decomposition of electrolyte components, which occurs at 5.1 V vs. Li⁺/Li. The cathodic stability is limited by the potential of Li plating, which starts at -0.05 V vs. Li⁺/Li. As shown in Fig. 5(a), in the cathodic scanning there are no visible reductive current peaks above 0 V, while multiple oxidative current peaks between 0.4 and 2.4 V in the subsequent anodic scanning are the characteristic of anodic dissolution of Pt–Li alloy. These facts indicate that Li–Pt alloy is formed chemically between Pt and Li metals after Li plating. Therefore, a 5.15 V electrochemical

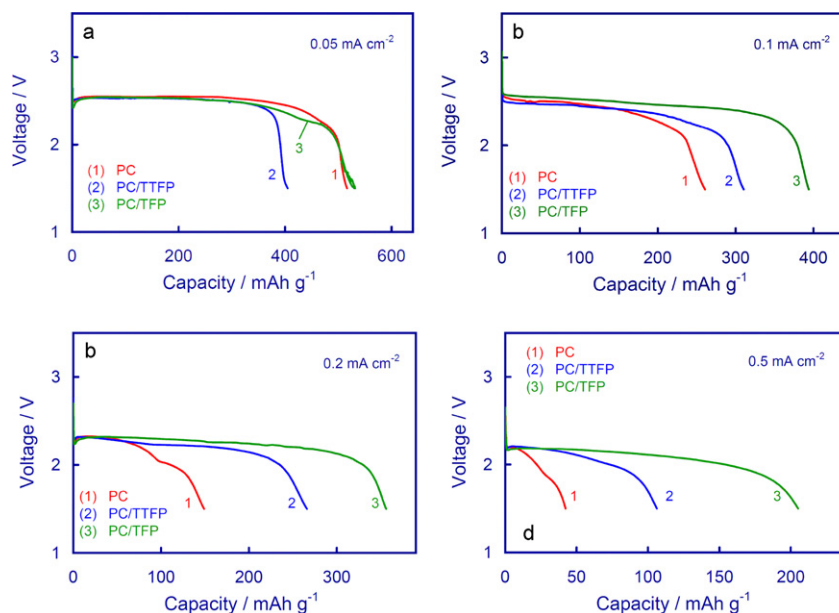


Fig. 4. Comparison of the discharge performances of Li/air cells with a PC electrolyte, a 7:3 PC/TFP electrolyte, and a 7:3 PC/TFP electrolyte, respectively, in which all electrolytes had a 0.2 m LiSO₃CF₃ concentration. (a) 0.05 mA cm⁻², (b) 0.1 mA cm⁻², (c) 0.2 mA cm⁻², and (d) 0.5 mA cm⁻².

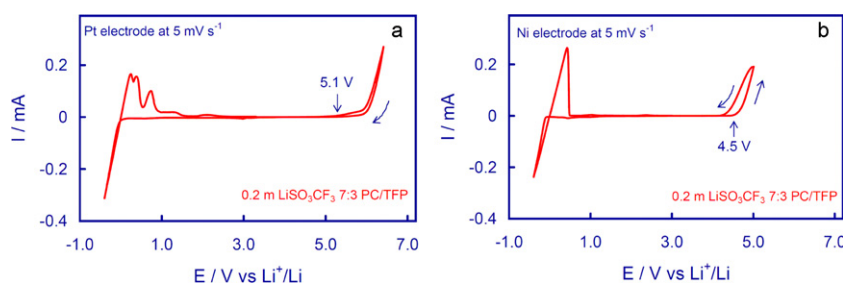


Fig. 5. Electrochemical window of a 0.2 m LiSO₃CF₃ 7:3 PC/TFP electrolyte measured by using a (a) Pt electrode and (b) Ni electrode at a potential scanning rate of 5 mV s⁻¹.

window can be calculated from the potential difference between electrolyte oxidative decomposition and Li plating. For the Ni electrode (Fig. 5(b)), dramatic increase in the oxidative current occurs at 4.5 V vs. Li⁺/Li, being 0.6 V lower than that observed from Pt electrode. This is due to the anodic dissolution of Ni metal. This fact reminds us that the charge voltage must not exceed 4.5 V when Ni mesh is used as the current collector of carbon air electrode in the rechargeable Li/air batteries. The cathodic stability is limited by the potential of Li plating. Since no alloy is formed between Ni and Li, there is only an oxidative current peak at 0.43 V vs. Li⁺/Li, which corresponds to the stripping of Li.

The cycling ability of Li metal in 0.2 m LiSO₃CF₃ 7:3 PC/TFP electrolyte is evaluated by cycling a Li/Ni cell with an active electrode area of 1.27 cm². The voltage profiles of Li plating and stripping on Ni foil are shown in Fig. 6, and the coulomb efficiencies are plotted against cycle number in the inset of Fig. 6. As shown in the inset, Coulomb efficiency in the first cycle is rather low (48%), it keeps increasing in subsequent cycles and reaches a maximum (83%) in the sixth cycle. Further cycling results in a steady decline in the coulomb efficiency. This phenomenon is common for Li cycling on the smooth Ni surface and it is known because of these two factors: (1) poor morphology of the plated Li on Ni surface, and (2) high reactivity of newly plated Li with electrolyte components [23–25]. The coulomb efficiency and its retention against cycle number as shown in the inset of Fig. 6 are very similar with those obtained from 1 M LiClO₄ PC electrolyte [24,25]. Further work on the rechargeable Li/air battery with PC/TFP electrolytes is in progress and the results will be reported separately.

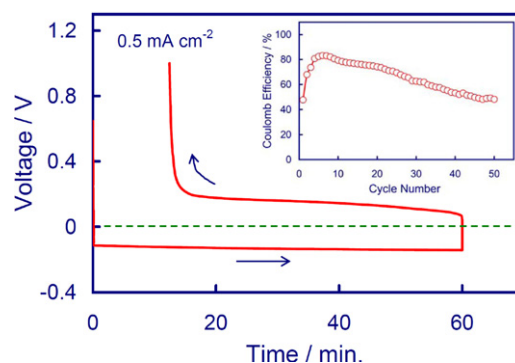


Fig. 6. Voltage profile of Li plating and stripping on Ni foil with a 0.2 m LiSO₃CF₃ 7:3 PC/TFP electrolyte, in which the inset shows cycling efficiency of Li as a function of cycle number.

4. Conclusions

Due to the low volatility of PC and TFP, the PC/TFP electrolyte is a good choice for the long-term operation of Li/air batteries in dry ambient environments. Although the use of TFP increases viscosity of the solvent blend and reduces ionic conductivity of the electrolyte, the Li/air battery with PC/TFP electrolyte still shows increased specific capacity and improved power capability. More importantly, the use of TFP has benefits for the Li/air battery operating in a low oxygen partial pressure environment. The performance

improvement by TFP is attributed to the increased dissolution kinetics and solubility of oxygen in TFP-containing electrolyte. In addition, PC/TFP electrolyte has a 5.15 V electrochemical window, which makes it suitable for use in rechargeable Li/air batteries.

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