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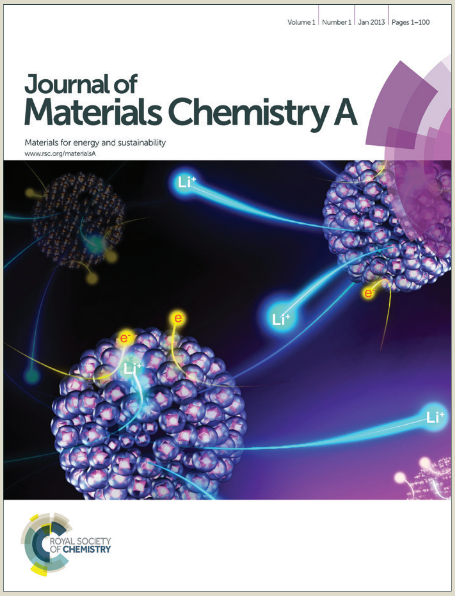

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Oxygen-Enriched Electrolytes Based on Perfluorochemicals for a High-Capacity Lithium-Oxygen Battery

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Highly oxygen-enriched electrolytes for a lithium-oxygen (Li-O_2) battery were prepared by combining perfluorohexyl bromide as an oxygen-uptake perfluorochemical (PFC) medium with lithium perfluorooctane sulfonate (LiPFOS) as a perfluoro-surfactant and a supporting electrolyte, which allowed exceptionally high miscibility of PFC with tetraethylene glycol dimethyl ether (TEGDME). The electrochemical reduction current of oxygen was three times enhanced in the LiPFOS-TEGDME electrolyte with ca. 60 wt% PFC content in comparison with that of a conventional Li-O_2 battery electrolyte, which was ascribed to high oxygen solubility of the electrolyte. A Li-O_2 cell fabricated with the PFC-based electrolyte exhibited excellent discharging capacity of 6500 mAh/g which was approximately 1.5 times larger than that obtained with the conventional electrolyte.

Introduction

Lithium-oxygen (Li-O_2) batteries have received considerable attention because they could offer extremely high energy density derived from the utilization of a light and highly oxidizable lithium metal as an anode-active material, and oxygen in the air as a cathode-active material.[1–4] The discharging process of the Li-O_2 battery involves oxygen reduction at an air cathode; the efficiency of the oxygen reduction often dominates the discharging performance. Recently, it has been described that for the aprotic Li-O_2 batteries, the oxygen reduction occurs at a two-phase boundary composed of an electrolyte and the air cathode,[5] suggesting that oxygen is dissolved into the electrolyte and then diffuse to the surface of the catalyst. Oxygen solubility and diffusivity in the aprotic electrolytes could be a crucial factor in facilitating the oxygen reduction. However, the oxygen solubility and diffusivity of the most aprotic solvents were insufficient to apply them to the Li-O_2 batteries. [6–10]

One possible approach to enhance the oxygen solubility and diffusivity is the utilization of oxygen-enriching materials as electrolyte components. The authors have intensively examined the oxygen-enriching materials such as cobalt porphyrin complexes for an oxygen absorbent,[11] an artificial hemoglobin[12] and an oxygen facilitated membrane.[13–16] We also reported their oxygen enrichment effect at the electrodes for enhanced oxygen reduction in aqueous solutions,[17,18] which was significant in the development of fuel cells.[19] Moreover, Sun *et al*. reported the use of iron phthalocyanine, the possible oxygen-enriching material, as an electrolyte additive improved the performance of the Li-O_2 battery.[20] In this paper, we focused on perfluorochemicals (PFCs), well-investigated oxygen-enriching media for liquid breathing[21,22] and blood substitutes.[23,24] The most notable feature of PFCs is their high gas solubility derived from weak intermolecular forces. Oxygen solubility in the PFC media is 3−10 times higher than those in the corresponding hydrocarbons or water.[25–27] The weak intermolecular interaction of PFCs also offers low viscosity and surface tension which could improve the performance of the Li-O_2 batteries by enhancing the mass transfer of oxygen and ionic species, and by increasing the active surface area at the air cathode. PFCs exhibit other distinct properties such as high chemical and thermal stability, low flammability and hydrophobicity. By considering hush conditions of the Li-O_2 battery operation including highly oxidative and water-sensitive environment, these properties could make PFCs suitable for the electrolyte components.

Few reports have investigated PFCs as an electrolyte additive[28] and as modifiers of the air cathodes[29,30] in the Li-O_2 batteries. However, the content of PFCs in the electrolyte solvents was limited to be <1.0 wt/vol%[28,29] because PFCs with the inherent low polarity were immiscible with the polar electrolyte solvents. Read *et al*. reported that partially fluorinated phosphate esters, which showed high miscibility with organic carbonates, were useful as co-solvents in the Li-O_2 batteries to result in enhanced discharging capacity and rate performance.[31,32] But, the organic carbonate solvents are considered undesirable for the Li-O_2 battery application owing to their susceptibility to nucleophilic attacks by discharging products ($O_2^{\bullet-}$).[33] Moreover, rechargeability of the cells fabricated with the electrolytes containing the fluorinated compounds has not been noted, which might be due to the solvent instability. The preparation of highly PFC-miscible electrolytes which possess high tolerance toward $O_2^{\bullet -}$ has remained to be challenging. We anticipated that the exploration of the $O_2^{\bullet -}$-stable electrolytes with the high PFC content should be accomplished by employing perfluoro-surfactants which have been examined to form stable PFC emulsions in the blood substitutes.[23]

In this paper, we found lithium perfluorooctane sulfonate (LiPFOS) acted not only as the perfluoro-surfactant but also as the supporting electrolyte and have succeeded in preparing highly oxygen-dissolved electrolytes composed of PFCs. LiPFOS allowed exceptionally high miscibility of PFCs with tetraethylene glycol dimethyl ether (TEGDME) which is commonly used as the electrolyte solvent in the Li-O_2 batteries[34,35] due to its high chemical stability toward the discharging products[36] and the lithium metal anode.[37] To our surprise, the obtained electrolytes were homogeneous solutions rather than emulsions. Upon the exploration of the various PFCs, perfluorohexyl bromide (BrC_6F_{13}) was found to exhibit the highest miscibility of 60 wt% and distinct physicochemical properties of the BrC_6F_{13}-based electrolyte were examined. Electrochemical analysis of the BrC_6F_{13}-based electrolyte revealed its oxygen enrichment effect on the oxygen reduction. We also report enhanced discharging capacity of the Li-O_2 cells fabricated with the BrC_6F_{13}-based electrolyte in comparison with the conventional electrolyte along with their cyclability.

Experimental

Materials

All perfluorochemicals such as perfluorohexyl bromide (BrC_6F_{13}), lithium perfluorooctane sulfonate (LiPFOS), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) of electrochemical grade, and tetraethylene glycol dimethyl ether (TEGDME) were purchased from Tokyo Kasei Co. *N*-Methyl-2-pyrrolidone (NMP) was purchased from Kanto Chemical Co. A Pt/C catalyst (TEC10EA50E, 47 wt% Pt) was purchased from Tanaka Kikinzoku Kogyo Co. Polyvinylidene fluoride (PVDF, KF polymer) was supplied from Kureha Chemical Co. A gas diffusion layer (GDL, SIGRACET© GDL34BC) was obtained from SGL Group Co. LiPFOS and LiTFSI were vacuum-dried at 80 °C for 1 h and all solvents were purified by distillation prior to use.

Preparation of PFC-based electrolytes

The following procedures were carried out in an argon-filled glovebox. To a TEGDME solution containing a prescribed amount of a supporting electrolyte salt, LiTFSI or LiPFOS, was added PFC and stirred at room temperature for 1 h. The resulting homogenous solution was stable during storage in the glovebox for at least three months.

Electrolyte property measurements

All measurements were conducted at 25 °C and repeated three times. Oxygen solubility was measured using a galvanic dissolved oxygen meter (Iijima Electronics, B-506). Viscosity was estimated with a Kusano Cannon-Manning Semi-Micro viscometer using silicon as a standard. Ionic conductivity was measured with a ZAHNER Zennium conductivity meter with respect to a 0.1 M KCl standard, using a couple of Pt disk electrodes with a diameter of 1.0 cm. Surface tension was obtained with a Surfgauge capillary-rise method surface tensiometer (Dyne Gauge, DG-1).

Electrochemical measurements

Voltammetric measurements were conducted using an ALS electrochemical analyzer Model 760D with a conventional cell. A glassy carbon disk (ϕ = 3.0 mm), coiled platinum wire, and Ag/AgCl were used as the working, auxiliary, and reference electrodes, respectively. The ferrocene/ferrocenium redox couple was used as a standard electrochemical reference. For electrochemical stability analysis, measurements were performed in an argon-filled glovebox while for oxygen reduction, the electrolytes were saturated with O_2 by bubbling for 30 min prior to measurements. To examine stability in the presence of Li_2O_2, the electrolytes containing Li_2O_2 were stored for one month prior to measurements.

Li-cation transference number (T_{Li+}) of the electrolytes was analyzed with a potentiostatic polarization method[38] on an Autolab potentiostat/galvanostat (PGSTAT128N) using coin-type cells with symmetrical configuration of Li | Li^+X^-, solvent | Li. DC polarization measurements were performed with an applied voltage of 10 mV for 2 h until the potential profile reached steady-state. Before and after the DC polarization, AC impedances were measured in the frequency range of 0.1–100 kHz with 10 mV of potentiostatic perturbation. The AC impedance measurements of the symmetrical Li coin cells were also performed to determine compatibility of the electrolytes with a Li metal. The frequency range of 0.1–1.0 MHz with 10 mV was applied.

Li-O_2 cell assembly and charging/discharging measurement

An air electrode was prepared by casting an ink containing a Pt/C catalyst and PVDF (100/3 in w/w) in NMP onto a GDL. The average Pt loading was ca. 0.5 mg/cm^2.

Swagelok-type Li-O_2 cells were employed for charging/discharging measurements. The cells consisted of a lithium foil (ϕ = 15 mm), two glass-fiber separators (GF/A, Whatman, ϕ = 15 mm) presoaked in the electrolytes, the air electrode (ϕ = 12 mm), and an Al mesh current collector. A gas outlet of the cell was connected to a latex balloon (ca. 50 mL) to supply an extra amount of oxygen. The cells were assembled in an argon-filled glovebox and purged with pure oxygen for 10 min. Charging/discharging characteristics of the cells were measured using a Hokuto Denko charging/discharging analytical instrument (HJ1001SD8).

Results and discussion

Preparation of TEGDME electrolytes with high PFC content

Miscibility of a series of PFCs with the TEGDME solutions was investigated (Table 1). Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was chosen as the reference supporting electrolyte because it has been often employed in the Li-O_2 batteries to give rise to high cell performance.[10] Only small amounts of PFCs were stably dispersed but not miscible in pristine TEGDME and the LiTFSI-TEGDME electrolyte, which could be attributed to the low polarity of PFCs. On the other hand, LiPFOS allowed miscibilization of PFCs with TEGDME to yield homogenous electrolyte solutions (Fig. S1). This indicated that its perfluoro-surfactant nature contributed to the miscibility enhancement. The miscibilization effect by LiPFOS was more prominent for bromide-terminated linear perfluorocarbons in comparison with other PFCs including a perfluoroamine and linear/cyclic perfluorocarbons, and the miscibility significantly increased with the LiPFOS concentration (Fig. S2). It could be noted that an iodine-terminated perfluorocarbon was highly miscible, but underwent iodine release. Perfluorohexyl bromide (BrC_6F_{13}) in the TEGDME solution containing 2.0 M LiPFOS exhibited the highest miscibility of 60 wt%, which was an approximately twenty-fold increase from that of the LiTFSI electrolyte. In contrast, PFCs displayed low miscibility with DMSO, a commonly-investigated electrolyte solvent for the Li-O_2 battery,[39,40] even with the high LiPFOS concentration (Fig. S3), suggesting that the solvent polarity plays an important role in the miscibilization process.

Table 1 Miscibility of PFCs with the TEGDME electrolyte solutions

electrolyte	miscibility of PFC (wt%)					
	$N(C_4F_9)_3$	$C_{10}F_{18}$ [a)]	C_8F_{18}	Br-C_6F_{13}	Br-C_7F_{15}	Br-C_8F_{17}
TEGDME	insoluble	insoluble	insoluble	5.7	insoluble	insoluble
1.0 M LiTFSI TEGDME	< 0.5	< 0.5	< 0.5	3.5	1.5	1.0
1.0 M LiPFOS TEGDME	1.0	3.5	1.5	45	33	13
2.0 M LiPFOS TEGDME	1.5	7.0	3.4	60	57	31

a) $C_{10}F_{18}$: perfluorodecalin

Electrolyte properties of PFC-based electrolytes

The physically dissolved amount of oxygen in the obtained electrolytes was measured using a galvanic oxygen meter. The oxygen solubility of 1.0 M LiTFSI and 2.0 M LiPFOS TEGDME electrolyte solutions was 8.4 and 8.9 mg/L, respectively and enhanced up to 13 mg/L for a 60 wt% BrC_6F_{13}-containing LiPFOS electrolyte solution, which was significantly higher than those reported for common aprotic LiTFSI electrolytes (Table S1).[41] These results demonstrated that BrC_6F_{13} enhanced the oxygen dissolving ability of the electrolyte.

Ionic conductivity and viscosity of the electrolyte solutions were also examined. The conductivity of the electrolyte solutions containing 1.0 and 2.0 M LiPFOS was 0.51 and 0.45 mS/cm, respectively, which decreased in one order of the magnitude from that of the 1.0 M LiTFSI electrolyte (2.8 mS/cm). The solution viscosity increased in highly concentrated LiPFOS electrolyte solution (74 cP for 2.0 M LiPFOS) compared with those for the 1.0 M LiPFOS and LiTFSI electrolytes (15 and 9.3 cP, respectively). These results could be ascribed to the surfactant nature of LiPFOS; PFOS anions most likely aggregated in the highly concentrated electrolyte solution, giving rise to the increased viscosity and reduced mass transfer. Another factor in determining the conductivity was the degree of dissociation of the electrolyte salt. Charge localization was more pronounced on the PFOS anion in comparison with the TFSI anion, and the LiPFOS salt had the lesser degree of the dissociation.

BrC_6F_{13} further influenced the conductivity and viscosity of the electrolytes, as shown in Fig. 1. The conductivity of the LiPFOS electrolytes decreased along with the BrC_6F_{13} content, suggesting that the introduction of BrC_6F_{13} reduced the polarity of the electrolytes and suppressed the dissociation of the electrolyte salt. These results supported the formation of PFC-miscible solutions rather than emulsions. On the other hand, low viscous BrC_6F_{13} significantly reduced the solution viscosity of the LiPFOS electrolytes, achieving 11 cP for 60 wt% BrC_6F_{13} which was comparable to that of the LiTFSI electrolyte (9.3 cP). The reduction in the viscosity could compensate for the conductivity decrease, leading to enhanced electrochemical performance of the BrC_6F_{13}-based electrolyte (*vide infra*).

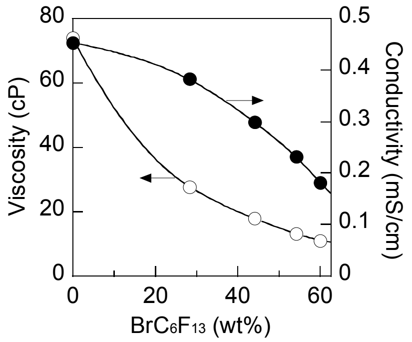

Fig. 1 Viscosity (○) and conductivity (●) of the 2.0 M LiPFOS TEGDME solutions containing BrC_6F_{13}. The measurements were conducted at 25 °C.

Surface tension was employed to evaluate the wettability of the electrolyte solution on the air cathode. The surface tension of the LiPFOS electrolytes (26 and 24 mN/m for 1.0 and 2.0 M LiPFOS, respectively) was smaller than that obtained for the LiTFSI electrolyte (36 mN/m for 1.0 M LiTFSI) as a consequence of the surfactant property of LiPFOS. As expected, BrC_6F_{13} further reduced the surface tension, reaching 17 mN/m with the addition of 60 wt% BrC_6F_{13}. The high wettability of the BrC_6F_{13}-containing electrolyte could lead to an increase in the active surface area at the porous air cathode, which may be a crucial advantage for the effective oxygen reduction in the Li-O_2 battery.

Electrochemical properties of PFC-based electrolytes

Electrochemical stability of the LiTFSI and BrC_6F_{13}-contining LiPFOS electrolytes was examined with cyclic voltammetry (Fig. S4–5). The BrC_6F_{13}-based electrolyte exhibited oxidative stability superior to that of the LiTFSI while reductive stability was slightly inferior. However, a cathodic peak observed in the BrC_6F_{13}-based electrolyte was much smaller than that for the oxygen reduction. A cyclic voltammogram obtained for the BrC_6F_{13}-containing electrolyte in the presence of Li_2O_2 revealed that an only small anodic peak was observed after storage for one month, indicating that the significant decomposition of the electrolyte hardly occurred during the battery operation in this experiment. Based on the above results, we described that the BrC_6F_{13}-containing electrolyte were suitable for our Li-O_2 battery testing. Fig. 2 depicts linear sweep voltammograms for oxygen reduction in the electrolytes. The oxygen reduction current density for the LiPFOS-TEGDME electrolytes (210 and 310 μA/cm^2 for 1.0 and 2.0 M LiPFOS, respectively) was higher than that for the conventional LiTFSI-TEGDME electrolyte (140 μA/cm^2 for 1.0 M LiTFSI) in spite of the undesirable properties of the LiPFOS electrolytes, including its low conductivity and high viscosity. The fluorous nature of LiPFOS, such as its high oxygen affinity may contribute to the oxygen reduction improvement. The oxygen reduction was further enhanced with the addition of BrC_6F_{13} (the oxygen reduction current density: 300 and 390 μA/cm^2 for 45 and 60 wt% BrC_6F_{13} in 1.0 and 2.0 M LiPFOS electrolytes, respectively), achieving the current density of up to ca. 280 % vs the LiTFSI electrolyte. The increased oxygen reduction current density originated from the enhanced oxygen solubility. It could be suggested that the LiPFOS electrolyte possessed insufficient ionic conductivity despite enhanced oxygen reduction current density, and the rate-determining step for the oxygen reduction was the supply of oxygen on the electrode surface. These results clearly demonstrated that the highly PFC-containing electrolyte was an effective approach for the enhanced oxygen reduction in the aprotic media.

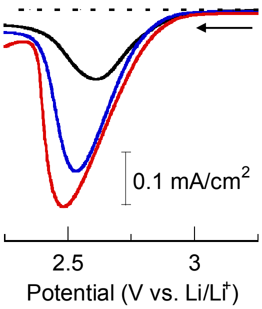

Fig. 2 Linear sweep voltammograms recorded for the oxygen reduction in the TEGDME solutions containing 1.0 M LiTFSI (black), and 2.0 M LiPFOS in the absence (blue) or presence (red) of 60 wt% BrC_6F_{13} at a scan rate of 10 mV/s.

Li-cation transference number (T_{Li+}) of the electrolytes was estimated using a potentiostatic polarization method (Fig. S6).[38] The transference number was defined as follows: $T_{Li+} = I_{ss}(\Delta V - I_0R_0)/I_0(\Delta V - I_{ss}R_{ss})$, where I_{ss} is the steady-state current, I_0 the initial current, ΔV the applied potential, R_0 and R_{ss} the electrode-electrolyte interfacial resistances before and after polarization, respectively. While ionic conductivity was the consequence of the total mobility of both cations and anions, the Li-cation transference number represented the fraction of the ionic conductivity resulting from a Li cation. The Li-cation transference number could be considered an important parameter to prevent concentration polarization in the Li-O_2 battery where the charging/discharging process involves Li-cation migration. The PFOS anions may aggregate in the highly concentrated solutions of LiPFOS leading to reduction in the anion mobility and improvement of the Li-cation transference number. The T_{Li+} values for the LiPFOS and BrC_6F_{13}-contining electrolytes were higher than that of the LiTFSI electrolyte (Table 2). It should be mentioned that even though the Li-cation mobility value of the LiTFSI electrolyte (1.1 mS/cm) was still higher than that of the BrC_6F_{13}-contining electrolyte (0.12 mS/cm), the high T_{Li+} value could alleviate the effect of the concentration polarization. These electrochemical and electrolyte properties prompted us to examine the BrC_6F_{13}-containing electrolyte in a Li-O_2 cell.

Table 2 Li-cation transference number (T_{Li+}) of the electrolytes

electrolyte	conductivity (mS/cm)	T_{Li+} (-)
1.0 M LiTFSI	2.8	0.40±0.05
0.1 M LiPFOS	0.05	0.52±0.07
2.0 M LiPFOS + BrC_6F_{13}	0.18	0.69±0.05

Charging/discharging characteristics of the Li-O_2 cells fabricated with PFC-based electrolytes

Li-O_2 cells were fabricated with a Li metal anode, an air cathode composed of a Pt/C catalyst and a gas diffusion layer, and two glass-fiber separators presoaked with the electrolyte. Compatibility of the BrC_6F_{13}-based electrolyte with the Li metal was preliminarily examined by impedance measurements of symmetric Li coin cells demonstrating no occurrence of side reactions (Fig. S7). It should be mentioned that the TEGDME-based electrolyte may undergo decomposition in the presence of the Pt/C catalyst.[42] However, it served our investigation of the PFC-based electrolyte and the use of alternative catalysts would further improve the cell performance. Capacity-limited galvanostatic measurement of the Li-O_2 cell using the LiPFOS-TEGDME electrolyte with 60 wt% BrC_6F_{13} was performed along with the reference cell of the LiTFSI-TEGDME electrolyte to examine charging/discharging cyclability, as shown in Fig. 3. The measurements were performed with the upper-limited capacity of 200 mAh/g and the voltage range of 2.0−5.0 V. Cycle testing revealed that the BrC_6F_{13}-containing LiPFOS electrolyte exhibited cyclability up to 38 cycles, which was slightly lower than that of the LiTFSI electrolyte (50 cycles). A possible reason could be the decomposition of the BrC_6F_{13}-containing electrolyte over the cycles. It should be noted that the BrC_6F_{13}-based electrolyte exhibited the performance compatible with that of the LiTFSI when the different condition was applied; larger upper-limited capacity at higher rate in the voltage range of 2.0−4.2 V which was within the electrochemical windows of the electrolytes (Fig. S8).

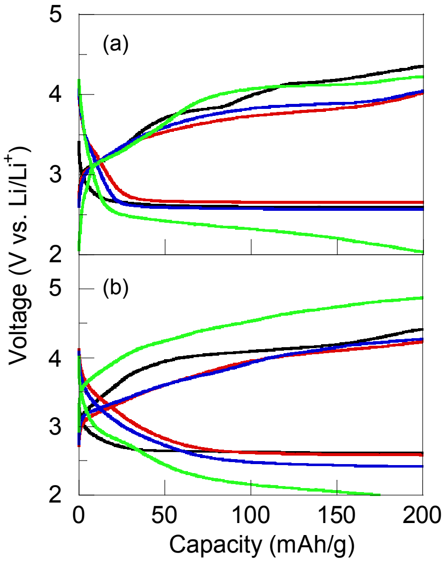

Fig. 3 Examples of charging/discharging curves of the Li-O_2 cells composed of the TEGDME solutions containing (a) 1.0 M LiTFSI, and (b) 2.0 M LiPFOS and 60 wt% BrC_6F_{13} at a current density of 0.1 mA/cm^2 in the 2.0−5.0 V voltage range when the charging/discharging capacity was limited to 200 mAh/g. The curves for 1st (black), 10th (red), 20th (blue), and 40th or 50th (green) cycle are shown (40th for the LiPFOS electrolyte and 50th for the LiTFSI electrolyte, respectively).

The Li-O_2 cells were fully charged/discharged in the voltage range of 2.0−4.2 V vs. Li/Li$^+$, as shown in Fig. 4. Discharging capacity of the cell using the TEGDME electrolyte with 2.0 M LiPFOS in the absence of BrC_6F_{13} was unexpectedly low in comparison with that for the LiTFSI electrolyte, which was incompatible with the result mentioned above for the electrochemical oxygen reduction, i.e. at least in part, due to the unfavourable physical properties of the LiPFOS electrolyte, such as low ionic conductivity and high viscosity. Enhanced discharging capacity of 6500 mAh/g was accomplished by introducing 60 wt% BrC_6F_{13} into the 2.0 M LiPFOS electrolyte by virtue of the improved oxygen solubility, viscosity and wettability. Moreover, the charging overpotential was suppressed for the BrC_6F_{13}-based electrolyte, which was attributed to its low surface tension. A possible high wettability on the porous air cathode could allow an increased catalytic surface area and enhanced oxidation of the insulating solid discharging product (Li_2O_2), resulting in the reduction of the charging overpotential. It should be emphasized that the cell using the BrC_6F_{13}-based electrolyte exhibited the discharging capacity larger than those obtained for other bromo-terminated PFCs with lower miscibility (Fig. S9). These results supported the conclusion that the BrC_6F_{13}-based electrolyte with the unique physicochemical properties contributed to the enhancement of the discharging and charging performance of the Li-O_2 cell.

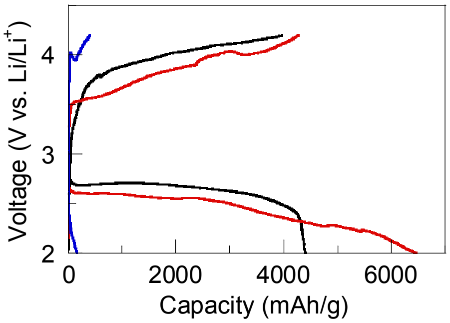

Fig. 4 Examples of charging/discharging curves of the Li-O_2 cells composed of the TEGDME solutions containing 1.0 M LiTFSI (black), and 2.0 M LiPFOS in the absence (blue) or presence (red) of 60 wt% BrC_6F_{13} at a current density of 0.1 mA/cm^2 in the 2.0−4.2 V voltage range.

Conclusions

We described a new approach to provide an oxygen-enriched electrolyte for a high-capacity Li-O_2 battery. BrC_6F_{13} was found to exhibit the unprecedentedly high miscibility with TEGDME in the presence of LiPFOS. The electrochemical analysis revealed the effective oxygen enrichment in the highly BrC_6F_{13}-containing electrolytes. The enhanced discharging performance was accomplished for the BrC_6F_{13}-based electrolyte in comparison with the conventional Li-O_2 battery electrolyte, as a result of the improved oxygen solubility and wettability. To the best of our knowledge, the present study is the first report applying the PFC-based (>50 wt%) electrolytes to the rechargeable Li-O_2 batteries. The distinct properties of the PFC-based electrolyte such as flammability, and compatibility with Li metal will expand their potential applications in Li batteries including Li-ion and Li-S batteries.

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Notes and references

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