Supplementary Information

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

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Contents:

1. Miscibilization of PFC with aprotic solvents in the presence of LiPFOS

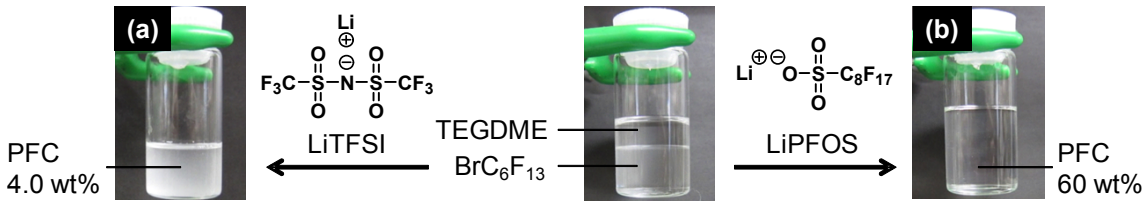

Fig. S1 Images of TEGDME solutions containing BrC_6F_{13} in the presence of (a) 1.0 M LiTFSI and (b) 2.0 M LiPFOS.

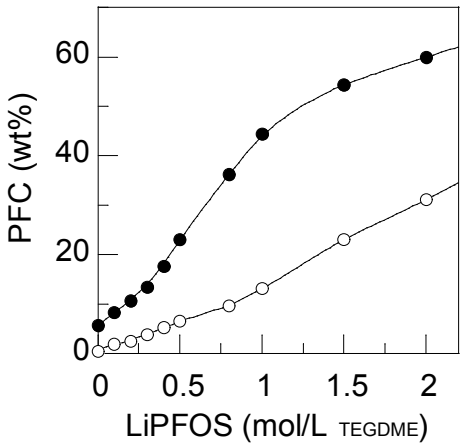

Fig. S2 Miscibility of BrC_8F_{17} (○) and BrC_6F_{13} (●) with TEGDME depending on the LiPFOS concentration.

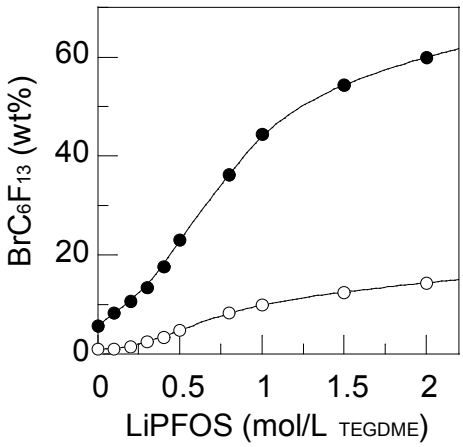

Fig. S3 Miscibility of BrC_6F_{13} with DMSO (○) and TEGDME (●) depending on the LiPFOS concentration.

2. Comparison of oxygen solubility among the different electrolytes

Table S1 Oxygen solubility of the electrolytes

supporting electrolyte	solvent	oxygen solubility (mg/L)
1.0 M LiTFSI	PC-EC[a)]	5.7[c)]
1.0 M LiTFSI	DMSO	6.2[c)]
1.0 M LiTFSI	Triglyme	7.3[c)]
1.0 M LiTFSI	TEGDME	8.4
2.0 M LiPFOS	TEGDME	8.9
2.0 M LiPFOS	TEGDME-BrC_6F_{13}[b)]	13

a) 1:1 wt. b) 60 wt% BrC_6F_{13}. c) Zhang *et al*.[1]

3. Electrochemical stability analysis of PFC-based electrolytes

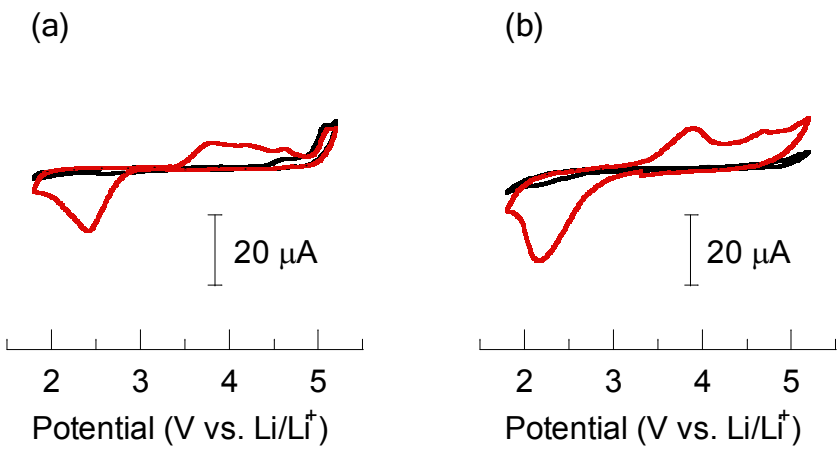

Fig. S4 Cyclic voltammograms recorded for TEGDME solutions containing (a) 1.0 M LiTFSI, and (b) 2.0 M LiPFOS with 60 wt% BrC_6F_{13} under an argon (black) and an oxygen (red) atmosphere at a scan rate of 50 mV/s.

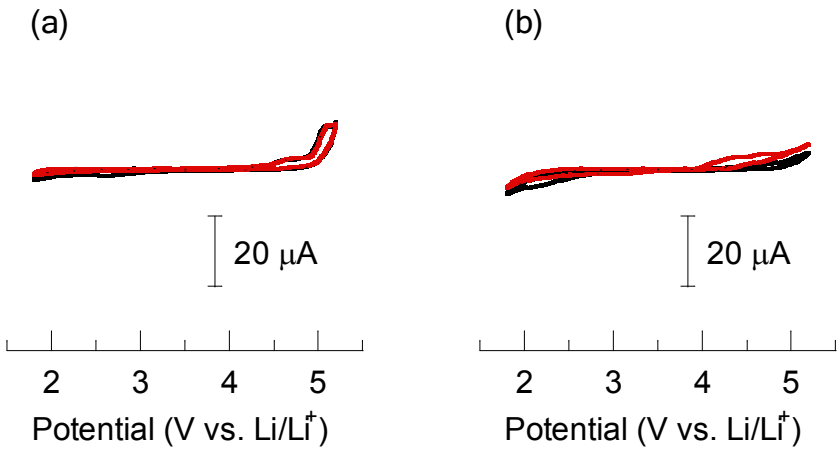

Fig. S5 Cyclic voltammograms recorded for TEGDME solutions containing (a) 1.0 M LiTFSI, and (b) 2.0 M LiPFOS with 60 wt% BrC_6F_{13} in the absence (black) and presence (red) of Li_2O_2 under an argon atmosphere at a scan rate of 50 mV/s. The solutions were stored with Li_2O_2 for one month prior to the measurements.

4. DC polarization and AC impedance measurements of PFC-based electrolytes

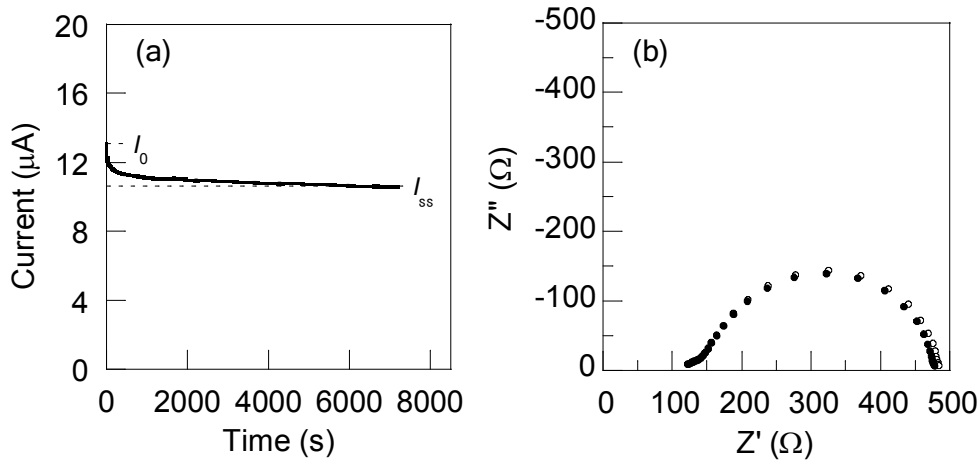

Fig. S6 (a) A chronoamperogram for the DC polarization and (b) AC impedance spectra before (○) and after (●) polarization obtained for the symmetric Li coin cell fabricated with a TEGDME solution containing 2.0 M LiPFOS with 60 wt% BrC_6F_{13}. I_0 and I_{ss} represent the initial and steady-state current, respectively.

5. Compatibility analysis of PFC-based electrolyte with Li metal

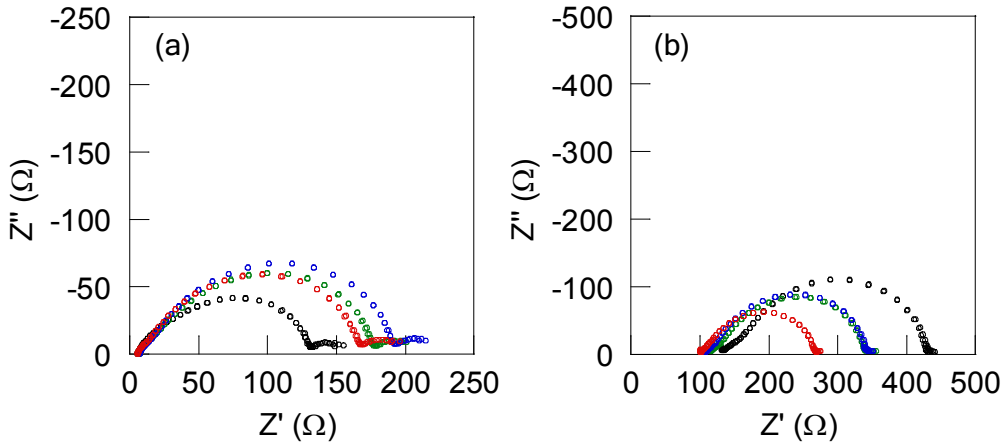

Fig. S7 AC impedance spectra obtained for the symmetric Li coin cells fabricated with TEGDME solutions containing (a) 1.0 M LiTFSI, and (b) 2.0 M LiPFOS with 60 wt% BrC_6F_{13} recorded with storage time of 1 (black), 10 (green), 20 (blue) and 30 (red) days.

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

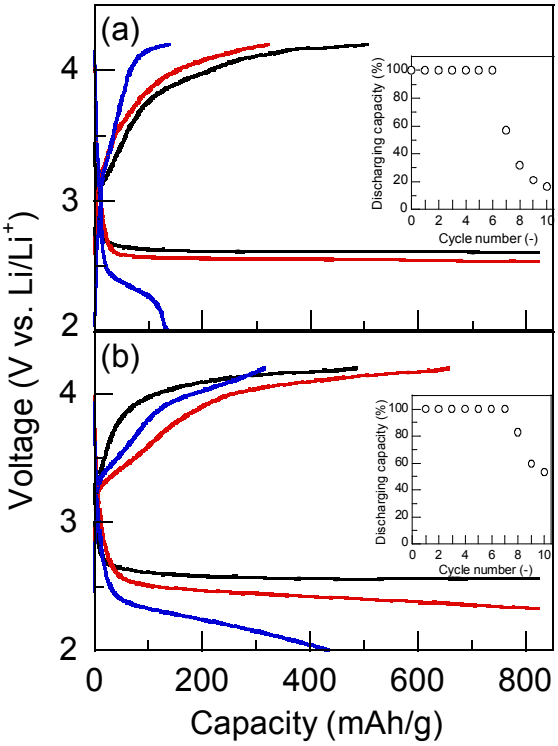

Fig. S8 Examples of charging/discharging curves of the Li-O_2 cells composed of TEGDME solutions containing (a) 1.0 M LiTFSI, and (b) 2.0 M LiPFOS and 60 wt% BrC_6F_{13} at a current density of 0.2 mA/cm^2 in the 2.0−4.2 V voltage range when the charging/discharging capacity was limited to ca. 800 mAh/g. Black, red and blue curves represent 1st, 5th and 10th cycle, respectively. Inset: Discharging capacity dependence on the cycle number.

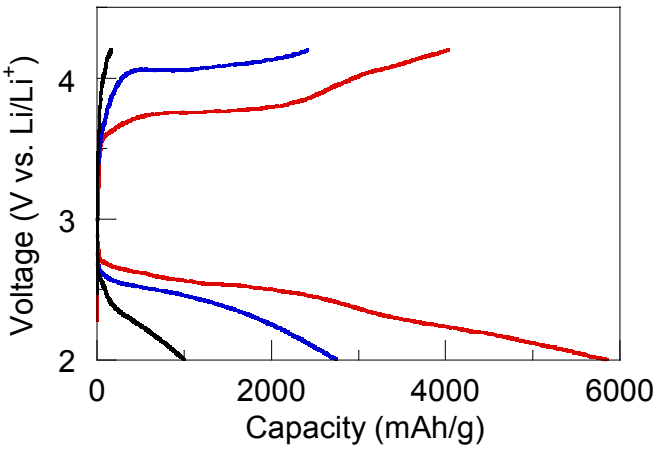

Fig. S9 Examples of charging/discharging curves of the Li-O_2 cells composed of TEGDME solutions containing 2.0 M LiPFOS with 25 wt% BrC_9F_{19} (black), 31 wt% BrC_8F_{17} (blue), and 60 wt% BrC_6F_{13} (red) at a current density of 0.2 mA/cm^2 in the 2.0−4.2 V voltage range.

Reference

1 W. Xu, J. Hu, M. H. Engelhard, S. A. Towne, J. S. Hardy, J. Xiao, J. Feng, M. Y. Hu, J. Zhang, F. Ding, M. E. Gross and J.-G. Zhang, *J. Power Sources*, 2012, **215**, 240–247.