

Expanding the Design Flexibility of Electrolyte Solvents for Li–O₂ Secondary Batteries by Incorporating Fluorine Groups

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KEYWORDS

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ABSTRACT

The development of chemically stable electrolytes is crucial for lithium-oxygen battery design. However, modifying electrolyte solvents to enhance the specific properties often increases the number of constituent atoms per molecule, potentially reducing chemical stability by providing more initiation sites for bond cleavage. This study demonstrates that introducing fluorine moieties into amide-based electrolyte solvents mitigates this trade-off while maintaining lower charging voltages over extended cycles. This effect was consistently observed across various amide-based solvents, including diamides. These findings suggest that introducing fluorine moieties can relax constraints related to the number of constituent atoms, thereby increasing the range of molecular designs.

In conjunction with the growing demand for electric, unmanned aerial vehicles, there is an increasing requirement for next-generation batteries providing higher energy densities than lithium-ion batteries. Among these new devices, lithium-oxygen batteries (LOBs) exhibit especially high theoretical gravimetric energy densities^{1,2}. However, to date, no LOB has demonstrated sufficient cycle performance at the benchmark energy density value of 500 Wh kg⁻¹. Achieving the superior specific energy density expected from LOBs will require increases in the charge and discharge capacities of these batteries while minimizing the overall battery mass³. Specifically, the amount of electrolyte solvent in each battery, which tends to have a higher density than metallic lithium, must be as low as possible. Unfortunately, reducing the amount of electrolyte to increase gravimetric energy density often results in undesirable effects due to the decomposition of the electrolyte solvent, leading to a significant deterioration in cycle performance. Therefore, the development of chemically stable electrolyte solvents that resist decomposition would be helpful.

The need for chemically stable electrolyte solvents has been widely recognized since the first LOB prototype was reported in 1996⁴⁻⁷. Recently, it has been reported that by using an appropriate lithium salt, a high-quality solid-electrolyte interface can be formed on the Li anode, enabling amide-based electrolytes to exhibit superior cycle performance and oxygen evolution efficiency compared to tetraglyme-based electrolytes⁸⁻¹⁰. On the other hand, research to date has demonstrated that smaller molecules having shorter carbon chains tend to exhibit greater chemical stability¹⁰⁻¹⁵. This effect occurs because electrolyte solvents with lower molecular weights generally have lower viscosities along with higher ionic conductivities. In addition, oxygen is more soluble and diffuses more readily in these materials¹⁶ and these solvent molecules contain fewer initiation sites for bond cleavage. As an example, among the amide-

based solvents, *N,N*-dimethylacetamide (DMA), which has the fewest atoms per molecule among the amides investigated, has demonstrated the best cycle performance¹⁰. This principle, based on empirical evidence, greatly restricts the design of electrolyte solvents. This is because modifications to the molecular structure of electrolyte solvents, intended to enhance their properties, typically result in an increase in the number of constituent atoms per molecule. On this basis, the present study assessed the effects of introducing fluorine atoms into electrolyte solvents to work around this limitation. The results show the feasibility of using larger solvent molecules and that the charging voltage can be maintained at a lower level for a longer period of time during cycle tests with such compounds.

Tables 1 and 2 summarize the electrolyte solvents and electrolyte compositions used in this study. Note that some of the solvents were not commercially available and so were synthesized for the purpose of this work (see the Supporting Information for synthesis details). The compounds in Table 1 were all liquids at room temperature. LiNO₃ was employed as the lithium salt component of the electrolyte because this compound is known to form a high-quality solid electrolyte interphase layer on the anode^{17,18}. Prior work has demonstrated that the incorporation of LiNO₃ in the electrolyte typically enables the use of amide-based solvents that are often unstable when combined with metallic lithium^{19,20}. Even so, LiNO₃ was found to be poorly soluble in some of the solvents employed in this work. In such cases, DMA, in which LiNO₃ is readily soluble, was also added to the electrolyte solution. Unless otherwise specified, the mixing ratio between the solvent and the DMA was set to 1:1 v:v.

Table 1 Solvents used in this work and associated abbreviations

Abbreviations	Name of the solvent	CAS Number	Molecular structure
G4	Tetraglyme	143-24-8	
DMA	<i>N,N</i> -Dimethylacetamide	127-19-5	
DMTFA	2,2,2-Trifluoro- <i>N,N</i> -dimethylacetamide	1547-87-1	
DEA	<i>N,N</i> -Diethylacetamide	685-91-6	
DETFA	<i>N,N</i> -Diethyl-2,2,2-trifluoroacetamide	360-92-9	
TEDFPA	<i>N</i> ¹ , <i>N</i> ¹ , <i>N</i> ³ , <i>N</i> ³ -Tetraethyl-2,2-difluoropropanediamide	1357624-59-9	
TEBA	<i>N</i> ¹ , <i>N</i> ¹ , <i>N</i> ⁴ , <i>N</i> ⁴ -Tetraethylbutanediamide	22692-57-5	
TETFBA	<i>N</i> ¹ , <i>N</i> ¹ , <i>N</i> ⁴ , <i>N</i> ⁴ -Tetraethyl-2,2,3,3-tetrafluorobutanediamide	548451-05-4	
DEDMBA	<i>N</i> ¹ , <i>N</i> ⁴ -Diethyl- <i>N</i> ¹ , <i>N</i> ⁴ -dimethylbutanediamide	97856-77-4	
DETFDMBA	<i>N</i> ¹ , <i>N</i> ⁴ -Diethyl-2,2,3,3-tetrafluoro- <i>N</i> ¹ , <i>N</i> ⁴ -dimethylbutanediamide	-	
HFTMPA	2,2,3,3,4,4-Hexafluoro- <i>N</i> ¹ , <i>N</i> ¹ , <i>N</i> ⁵ , <i>N</i> ⁵ -tetramethylpentanediamide	904055-14-7	
DEHFDMPA	<i>N</i> ¹ , <i>N</i> ⁵ -Diethyl-2,2,3,3,4,4-hexafluoro- <i>N</i> ¹ , <i>N</i> ⁵ -dimethylpentanediamide	-	
DEDMPA	<i>N</i> ¹ , <i>N</i> ⁵ -Diethyl- <i>N</i> ¹ , <i>N</i> ⁵ -dimethylpentanediamide	-	

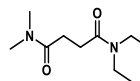


Table 2 Electrolyte compositions used in this work and terms used to refer to these compositions

Given names	Electrolyte composition
DMA	100 vol% DMA + 1 M LiNO ₃
DMTFA-50	50 vol% DMTFA+ 50 vol% DMA + 1 M LiNO ₃
DEA-50	50 vol% DEA+ 50 vol% DMA + 1 M LiNO ₃
DETFA-50	50 vol% DETFA+ 50 vol% DMA + 1 M LiNO ₃
TEBA-50	50 vol% TEBA+ 50 vol% DMA + 1 M LiNO ₃
TETFBA-50	50 vol% TETFBA+ 50 vol% DMA + 1 M LiNO ₃

It should be noted that, in the case that LiNO₃ was used, the reaction between the metallic lithium anode and NO₃[−] anions generated NO₂[−]. The presence of these ions induced electrode reactions based on the NO₂[−]/NO₂ redox couple over the voltage range of approximately 3.6 to 3.8 V²¹. Prior work has shown that, at suitably high concentrations, this redox couple can function as a redox mediator that promotes the decomposition of the discharge product lithium peroxide (Li₂O₂) at low voltages²¹. Despite this, the redox peaks in the voltage range of 3.6 to 3.8 V were found to be either negligibly small or completely absent (Figures S1 and S2). These results suggest that, in the present system, the concentration of the NO₂[−]/NO₂ redox couple generated by the reaction between the Li anode and NO₃[−] ions was sufficiently low and so any associated redox mediator effect can be considered negligible.

Figures 1a, c, e and g compare the charge-discharge cycle performances obtained using amide-based electrolytes with and without fluorine moieties at a current density of 0.4 mA cm^{-2} and a capacity of 4 mAh cm^{-2} . Figures 1b, d, f and h present the dQ/dV plots derived from the charging profiles. In tests using fluorine-free electrolytes, the results were consistent with data from previous studies. That is, trials with DMA, which had fewer constituent atoms with two CH_3 groups attached to the nitrogen atom, provided lower charging voltages and better cycle performance compared with the DEA-50, which had a higher molecular weight with two C_2H_5 groups attached to the nitrogen atom. However, when using fluorine-containing electrolytes, the trend was reversed. That is, the DETFA-50 maintained a lower charging voltage for a longer duration compared with the DMTFA-50, resulting in superior cycle performance. A sustained low charging voltage plateau was also observed in trials with the former solvent in previous work by the authors²². (The cycle performance of a G4-based electrolyte, one of the standard electrolytes in LOB research²³, under the same conditions can be found in Figure 1c in ref 10.) These findings suggest that the introduction of fluorine atoms can allow a greater range of electrolyte solvents to be employed. It should be noted that fluorinated amides may exhibit greater volatility due to reduced intermolecular forces, potentially leading to a shorter cycle life²². An effective approach to reducing the volatility of the electrolyte solvent is to increase the molecular weight by incorporating longer alkyl chains. Unfortunately, the additional carbon-hydrogen bonds can provide more initiation sites for bond cleavage so that the electrolyte is more likely to decompose.

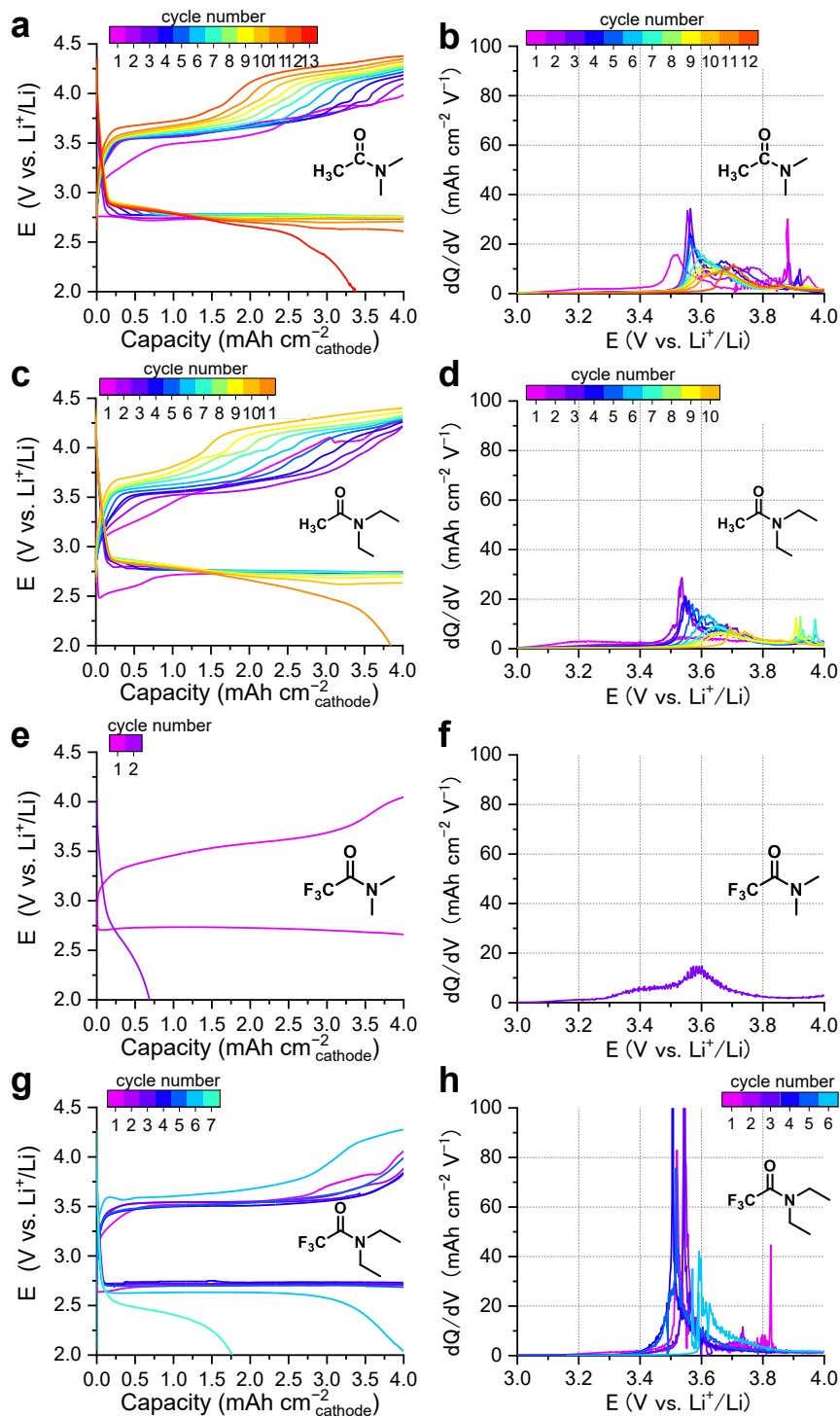


Figure 1. (a, c, e, g) Discharge-charge cycles and (b, d, f, h) the corresponding dQ/dV plots constructed from charging profiles acquired under current-controlled conditions at 0.4 mA cm^{-2} with a fixed capacity of 4.0 mA h cm^{-2} using the (a,b) DMA, (c, d) DEA-50, (e, f) DMTFA-50,

and (g, h) DETFA-50 electrolytes. KB-based porous carbon was used as the positive electrode in these trials. (Reproduced from ref. 22. Copyright 2024 American Chemical Society.)

To address this issue, this work attempted to suppress both decomposition and volatility by increasing the molecular weight through the incorporation of a diamide-like structure. For this purpose, TETFBA $((\text{C}_2\text{H}_5)_2\text{NCO-C}(\text{CF}_3)_2\text{-(CF}_2)_2\text{-CON-(C}_2\text{H}_5)_2)$ was synthesized as a dimer of DETFA. The boiling point of TETFBA was determined to be approximately 180 °C at 1 mmHg, indicating much lower volatility compared with that of DETFA. For comparison purposes, TEBA was also synthesized as the fluorine-free analogue of TETFBA, along with DETFDMBA $((\text{CH}_3)(\text{C}_2\text{H}_5)\text{-NCO-(CF}_2)_2\text{-CON-(C}_2\text{H}_5)(\text{CH}_3))$, in which two of the four C_2H_5 groups in TETFBA were replaced with CH_3 groups. Tables S1 and S2 summarize the physical properties of the various electrolyte solvents including those examined in this work. It should be noted that the diamides listed in Table 1 and used in the present work, including TETFBA, DETFDMBA and TEBA, were all liquids at room temperature even though many diamides are solids at room temperature. Table S3 summarizes the compounds that were synthesized and found to be solids near room temperature. Interestingly, it appears that diamides tend to solidify more readily than monoamides due to the increased rotational symmetry of the former molecules²⁴.

Figures 2a and b present the discharge-charge cycle data obtained with the fluorine-free electrolyte TEBA-50 and the fluorine-containing electrolyte TETFBA-50. Prior to the cycling tests, each electrolyte was subjected to cyclic voltammetry trials under Ar to confirm stability over the range of 2.4 to 4.0 V (Figures S1 and S2). The TEBA-50 exhibited higher charging overvoltages and a shorter cycle life compared with the DEA-50, in agreement with prior reports that larger molecules show shorter discharge-charge cycle lifespans. However, the TETFBA-50 showed a lower charging voltage and longer cycle life than the TEBA-50 (Figure S3). Notably,

the TETFBA-50 demonstrated a longer cycle life than both the DETFA-50 and TEBA-50. These results indicate that fluorine-containing electrolytes do not exhibit the behavior observed in previous studies. Similar results were observed with other diamide molecules, confirming the general effect of introducing the fluorine moiety (Figures 2c-f, S4).

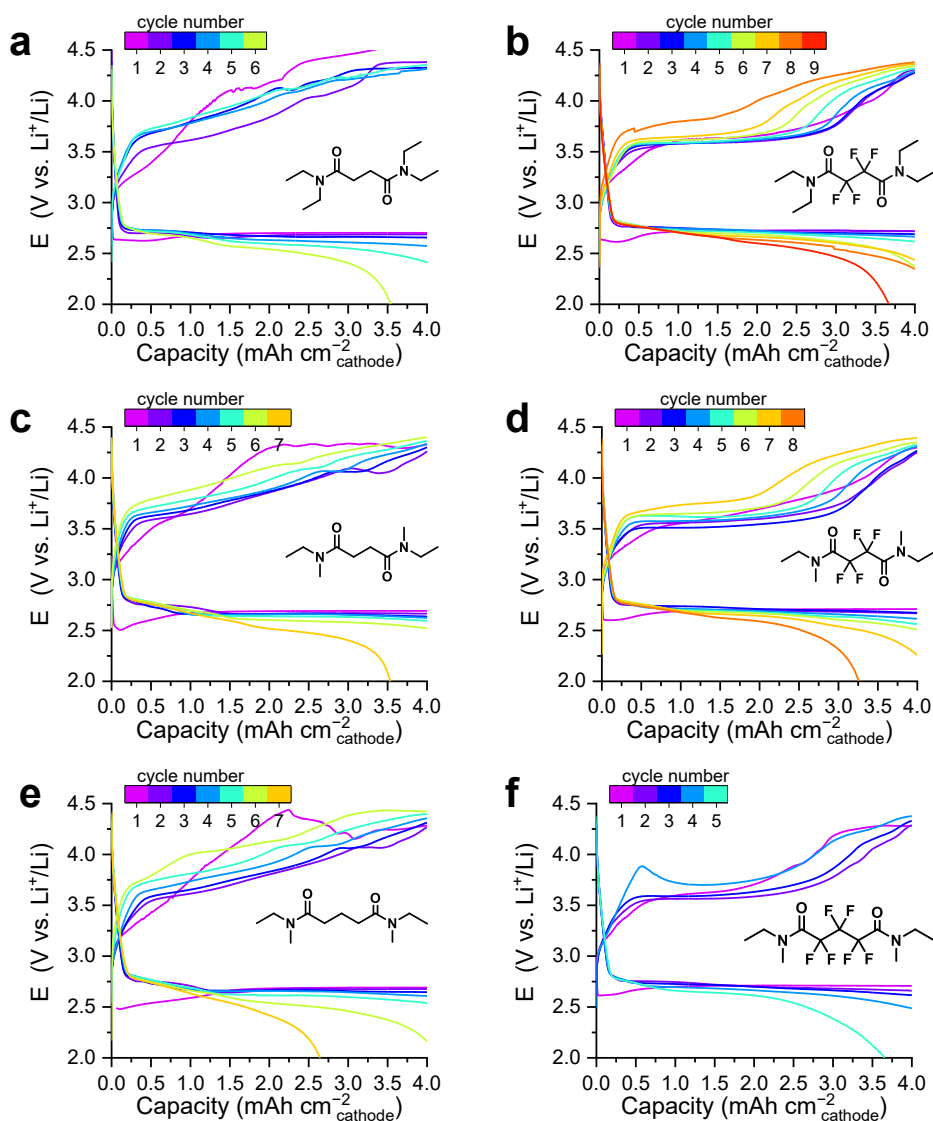


Figure 2. (a, b) Discharge-charge cycle data acquired under current-controlled conditions at 0.4 mA cm⁻² with a fixed capacity of 4.0 mA h cm⁻² using the (a) TEBA-50, (b) TETFBA-50, (c)

DEDMBA-50, (d) DETFDMBA-50, (e) DEMPDA-50, and (f) DEHFDMPA-50 electrolytes.

KB-based porous carbon was used as the positive electrode in these trials.

This work also conducted structural characterizations of the discharge products formed in the fluorinated diamide-based electrolytes. Figure S5 provides scanning electron microscopy (SEM) images of positive electrode surfaces after discharge and charge processes in the electrolytes based on the TETFBA-50 and DETFDMBA-50, fluorinated diamides. It is challenging to differentiate between the discharge products and carbon particles due to their similar particle sizes (approximately 34 nm). However, after discharge, particles with diameters in the range of approximately 50 to 200 nm were observed, which disappeared after charging. Figure 3 shows the synchrotron X-ray diffraction (XRD) patterns of the discharge products obtained using the DETFA-50 or the corresponding diamide TETFBA-50. The diffraction lines at 21.2° and 22.5° , corresponding to the 100 and 101 planes, confirm the presence of lithium peroxide in these materials. Although similar discharge capacities were obtained, the lithium peroxide formed in the TETFBA-50 electrolyte was more highly crystalline. The degree of lithium deficiency (the X value in $\text{Li}_{2-x}\text{O}_2$) in each discharge product was ascertained by a Rietveld analysis of the XRD pattern. The results demonstrated that the discharge product formed in the TETFBA-50 had a smaller X value compared with that generated in the DETFA-50 (details of the Rietveld analysis can be found in the Supporting Information). It is known that discharge products that are more crystalline and have smaller X values typically result in higher charging voltages. Indeed, a higher charging voltage was obtained with the TETFBA-50 electrolyte compared with that in the DETFA-50 trials (Figures 1g and 2b).

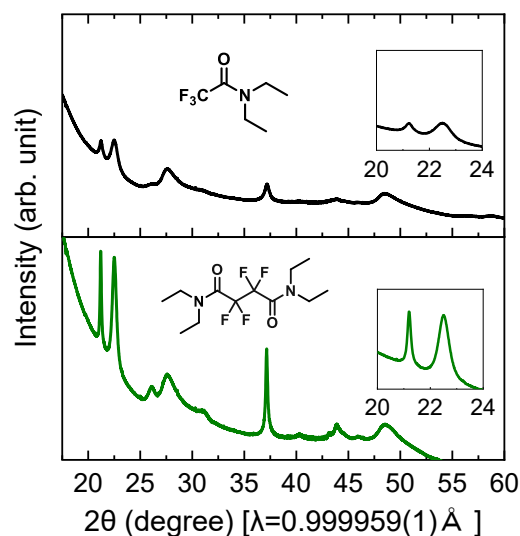


Figure 3. Synchrotron XRD patterns of discharge products formed on graphene mesosponge-based porous carbon electrodes after discharge at 0.2 mA cm^{-2} and 2.0 mAh cm^{-2} in the DETFA-50 (black) and TETFBA-50 (green) electrolytes. (The DETFA-50 data are reproduced from ref. 22. Copyright 2024 American Chemical Society.)

The extent to which the lithium peroxide formed during the discharge process was oxidatively decomposed during charging was assessed by monitoring the O_2 generation rate using differential electrochemical mass spectrometry (DEMS) (Figure 4). The O_2 generation efficiency values during charging in the TEBA $((\text{C}_2\text{H}_5)_2\text{NCO}-(\text{CH}_2)_2\text{CON}-(\text{C}_2\text{H}_5)_2)$ and TETFBA $((\text{C}_2\text{H}_5)_2\text{NCO}-(\text{CF}_2)_2\text{CON}-(\text{C}_2\text{H}_5)_2)$ were determined to be 54.5% and 62.2%, respectively, and so were both lower than the value of approximately 80.0% associated with the DETFA-50. This decrease in efficiency is ascribed to the greater number of decomposition initiation points when using a diamide. In fact, it was observed in the present work that more CO_2 was measured below

4.0 V in trials using the diamide-based electrolytes compared with the monoamide-based electrolytes. Even so, an analysis of the data obtained from the diamides indicates that introducing the fluorine moiety improved the O₂ generation efficiency. Experiments using isotopic O₂ showed that the O₂ used in the latter half of the discharge was primarily detected in the first half of the charging process, consistent with previous reports^{25–27} and observations when using the monoamide-based electrolytes (Figure S6). Hence, it appears that, when using the diamide solvents, the lithium peroxide underwent oxidative decomposition through a similar mechanism as occurs with other electrolyte solvents such as monoamides. These results demonstrate that, although the extent of the effect may have varied, the introduction of fluorine atoms into the diamide solvents generally provided greater O₂ generation efficiencies relative to the values for the corresponding fluorine-free molecules.

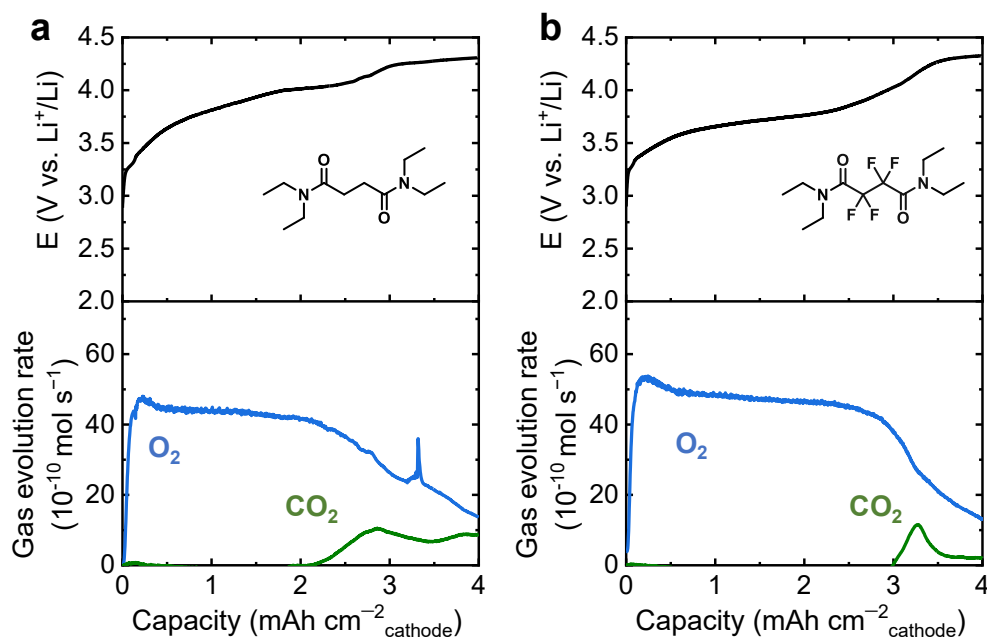


Figure 4. (a,b) Data from DEMS analyses during charging. The cells were discharged and subsequently charged in the (a) TEBA-50 and (b) TETFBA-50 electrolytes at 0.4 mA cm^{-2} and 4.0 mAh cm^{-2} . KB-based porous carbon was used as the positive electrode in all trials.

Prior work has shown that improved charge-discharge cycle characteristics can be obtained using electrolytes based on low molecular weight molecules^{10–15}. This work demonstrates that the adverse effects associated with larger solvent molecules can be mitigated by introducing a fluorine moiety, thus permitting a wider range of molecular designs. This phenomenon might originate from the inherent properties of fluorine-containing amide electrolyte solvents, which exhibit superior O_2 transport properties and enhanced oxidation tolerance^{16,22}. Additionally, the introduction of fluorine into the electrolyte may modulate its properties, potentially influencing the decomposability of Li_2O_2 by inducing structural changes in the discharge products. Although the reduction in the charging voltage when using fluorinated diamides is minimal at present, the development of mixed solvents that combine fluorinated amides and other solvents to provide synergistic effects could be a promising direction for future research. The increased molecular design flexibility provided by the incorporation of a fluorine moiety also significantly expands the options for selecting counterpart solvents. Additionally, it is expected that fluorinated amides that are normally solids at room temperature could be utilized in electrolytes by employing deep eutectic formulations.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at <http://pubs.acs.org>.

Experimental section, Synthesis of electrolyte solvents, Characterization of electrolytes, Rietveld analysis to estimate Li deficiency, Cyclic voltammograms under an Ar atmosphere, linear sweep voltammograms, dQ/dV plots, Discharge–charge cycles, DEMS analyses during charge, Plot of viscosities, Compounds synthesized in this work and found to be solids close to room temperature, Selected physical properties of the electrolyte solvents used in this work, Crystal structure parameters of samples discharged in different electrolytes as determined through Rietveld analyses, Copies of NMR spectra for synthesized diamides

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Notes

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