

Fluorinated Amide-Based Electrolytes Induce a Sustained Low Charging Voltage Plateau in Conditions Verifying the Feasibility of Achieving 500 Wh kg⁻¹ Class Li–O₂ Batteries

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ABSTRACT

Although Lithium–oxygen batteries (LOBs) hold the promise of high gravimetric energy density, this potential is hindered by high charging voltages. To ensure that the charging voltage remains low, it is crucial to generate discharge products that can be easily decomposed during the successive charge process. In this study, we discovered that the use of amide-based electrolyte solvents containing a fluorinated moiety can notably establish a sustained voltage plateau at low-charging voltages at around 3.5 V. This occurs under conditions that can verify the feasibility of achieving the benchmark energy density value of 500 Wh kg⁻¹. Notably, the achievement of the low-voltage plateau was accomplished solely relying on the intrinsic properties of the electrolyte

solvent. Indeed, synchrotron X-ray diffraction measurements have shown that the use of fluorine-containing amide-based electrolyte solvents results in the formation of highly decomposable discharge products, such as amorphous and Li-deficient lithium peroxides.

INTRODUCTION

Lithium–oxygen batteries (LOBs) hold promise for practical applications such as electric vehicles, drones, and unmanned aircrafts^{1,2}. During the discharging process of LOBs, solid-state lithium peroxide is formed on the positive electrode via the electrochemical reduction of O₂. Ideally, the lithium peroxide is oxidatively decomposed during the subsequent charging process. However, various side reactions proceed when the charging voltage increases. This increase in charging voltage is partly due to the fact that lithium peroxide is an insulating solid and hence less decomposable. In addition, the decomposition of the electrolytes induced by super oxide anion radical and/or singlet oxygen generated during charge and discharge leads to the formation of insulative byproducts at the positive electrode, suppressing the battery reaction^{3–5}. The decomposition of the electrolytes also leads to the electrolyte depletion within the porous electrode, resulting in a reduction of the effective electrode surface area. These factors cause the increase in charging voltage^{6–10}. The increase in charging voltage consequences in a further increase in charging voltage via electrochemical oxidation of the electrolytes.

Based on the negative cycle described above, achieving the long-lasting plateaus of low-charging voltage is crucial for the enhanced cyclability. In order to induce this, it is effective to obtain highly decomposable discharge products. Previous studies have revealed that Li-deficient and amorphous lithium peroxide significantly enhance their electronic and ionic conductivities, resulting in their oxidative decomposition at low voltages^{11–13}. The main approach reported so far to form highly decomposable lithium peroxide has been chemical and/or structural modifications of the positive electrode^{14–17}. However, we have recently shown that the appropriate choice of electrolyte can lead to the formation of highly decomposable lithium peroxide¹⁸. This is a new

option that is compatible with the conventional approach of structural-chemical modifications of the positive electrode. In this study, we report that introducing fluorocarbon moiety into the amide-based solvent enables the appearance of a long-lasting plateau of low-charging voltage.

RESULTS AND DISCUSSION

Cycle characteristics.

Among the electrolyte solvents summarized in Table 1, we first focused on *N,N*-Diethyl-2,2,2-trifluoroacetamide (DETFA), a commercially available fluorine-containing amide. Note that DETFA, as well as 2,2,2-Trifluoro-*N,N*-dimethylacetamide (DMTFA), were previously used at only approximately 2% of the total liquid volume, indicating their contribution to stabilization of the lithium/electrolyte interface¹⁹. However, in the present study, DMTFA and DETFA were used as the main solvents in the electrolyte. The effects obtained in this case are significantly different from the previous work, as described below. In the present work, we used LiNO₃ as the Li salt, which has been known to form high-quality solid-electrolyte-interphase (SEI) layer on the negative electrode^{20,21}. This allows the use of amide solvents, which are generally unstable to lithium^{22,23}. However, amides with CF₃ moiety do not dissolve LiNO₃ salt. To address this, we mixed them with *N,N*-dimethylacetamide (DMA) that has high solubility of LiNO₃. The mixing ratio was set at 1:1 vol% unless otherwise specified. Table 2 summarizes the electrolyte compositions used and their abbreviations.

Table 1 List of solvent abbreviations.

Abbreviations	Name of the solvent	Molecular structure of the solvent
G4	Tetraglyme	
DMA	<i>N,N</i> -Dimethylacetamide	
DMTFA	2,2,2-Trifluoro- <i>N,N</i> -dimethylacetamide	
DEA	<i>N,N</i> -Diethylacetamide	
DETFA	<i>N,N</i> -Diethyl-2,2,2-trifluoroacetamide	
CH ₃ CON(Me)(iPr)	<i>N</i> -Methyl- <i>N</i> -(1-methylethyl)acetamide	
CF ₃ CON(Me)(iPr)	2,2,2-Trifluoro- <i>N</i> -methyl- <i>N</i> -(1-methylethyl)acetamide	
CH ₃ CON(nPr) ₂	<i>N,N</i> -Dipropylacetamide	
CF ₃ CON(nPr) ₂	2,2,2-Trifluoro- <i>N,N</i> -dipropylacetamide	

Table 2 Given names of the electrolytes.

Given names	Electrolyte composition
G4	100 vol% Tetraglyme + 1M LiNO ₃
DMA	100 vol% DMA + 1M LiNO ₃
DMTFA-50	50 vol % DMTFA+ 50 vol% DMA + 1M LiNO ₃
DEA-50	50 vol % DEA+ 50 vol% DMA + 1M LiNO ₃
DETFA-50	50 vol % DETFA+ 50 vol% DMA + 1M LiNO ₃

CH ₃ CON(Me)(iPr)-50	50 vol % CH ₃ CON(Me)(iPr) + 50 vol% DMA + 1M LiNO ₃
CF ₃ CON(Me)(iPr)-50	50 vol % CF ₃ CON(Me)(iPr) + 50 vol% DMA + 1M LiNO ₃
CH ₃ CON(nPr) ₂ -50	50 vol % CH ₃ CON(nPr) ₂ + 50 vol% DMA + 1M LiNO ₃
CF ₃ CON(nPr) ₂ -50	50 vol % CF ₃ CON(nPr) ₂ + 50 vol% DMA + 1M LiNO ₃

Figures 1a and b show the cycle test results at a current density of 0.2 mA cm⁻² and an electrolyte volume of 31.4 μ L cm⁻² using DMA and DETFA-50 electrolytes, respectively. The DETFA-50 electrolyte exhibited a notably sustained low voltage plateau, in contrast to the DMA electrolyte. Figure 1c shows the average charge voltage plotted against the number of cycles for both electrolyte systems, where a reduction in charge voltage of approximately 0.3 V was observed with DETFA-50. In this study, where the cut-off voltages for discharge and charge were set to 2.0 V and 5.0 V respectively, the number of cycles in DETFA-50 was 16.

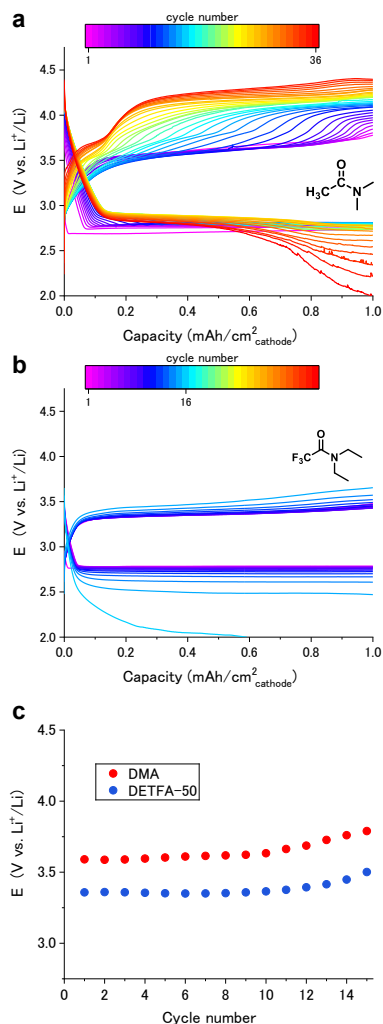


Figure 1 (a,b) Discharge–charge cycles under current-controlled conditions at 0.2 mA cm^{-2} with a fixed capacity of 1.0 mA h cm^{-2} in (a) DMA and (b) DETFA-50 electrolyte. (c) plots depicting the average charge voltage vs. cycle number constructed from the charging profiles. KB-based porous carbon was used as the positive electrode.

To elucidate the impact of the CF_3 moiety, we compared CF_3 -containing DETFA (Figure 2a) and CF_3 -free *N,N*-Diethylacetamide (DEA) (Figure 2c), both having ethyl groups adjacent to the amide group. (The behavior under the same conditions in G4-based electrolyte, which is one of

the standard electrolytes in LOB studies²⁴, is shown in Figures 1b, 1c, and S1 in reference 18.) In these tests, the current density was increased to 0.4 mA cm^{-2} and the capacity was raised to 4 mAh cm^{-2} , resulting in a slight increase in the charge voltage for DETFA-50 compared to Figure 1b. The effect of the CF_3 -moiety was confirmed even at the larger discharge capacity of 10 mAh cm^{-2} (Figure S1). This test condition is to evaluate the feasibility of achieving the expected gravimetric energy density of 500 Wh kg^{-1} for LOBs^{25,26} (Table S1). CF_3 -containing DETFA-50 maintained the charging voltage around 3.5 V for more extended period compared to CF_3 -free DEA-50 even under these relatively severe conditions. This fact can be clearly seen in the dQ/dV plot obtained from the charging profiles (Figures 2b and d). DETFA-50 has large peaks around 3.5 V . The above trend for charging voltages was more pronounced for higher ratio of DETFA mixed in the solvents (Figure S2). These findings revealed the role of the CF_3 moiety in DETFA as an electrolyte solvent in establishing the low-charging voltage plateau.

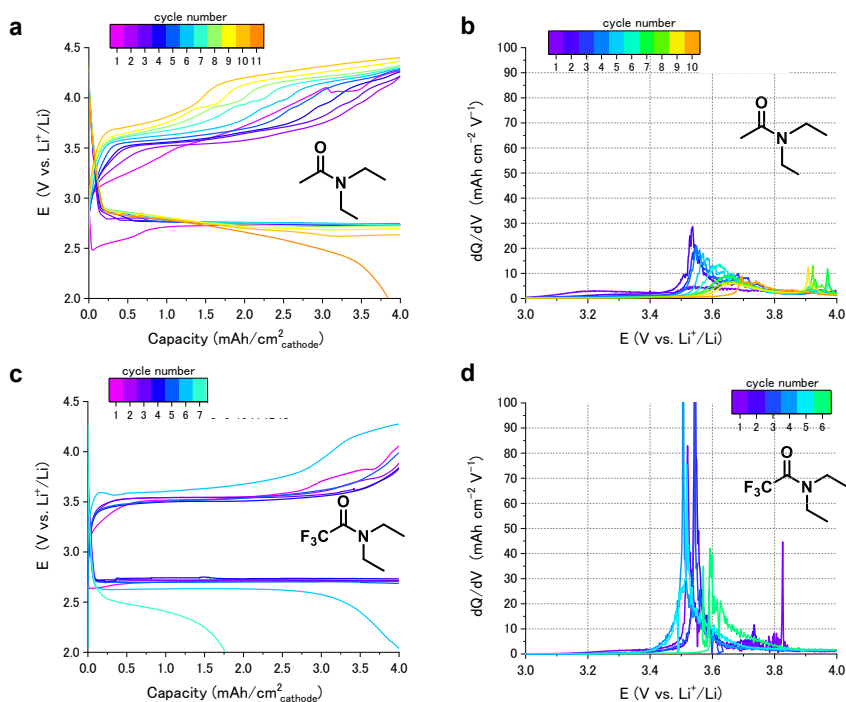


Figure 2 (a, c) Discharge–charge cycles and (b, d) the corresponding dQ/dV plots constructed from the charging profiles under current-controlled conditions at 0.4 mA cm^{-2} with a fixed capacity of 4.0 mA h cm^{-2} in (a,b) DEA-50 and (c, d) DETFA-50 electrolyte. KB-based porous carbon was used as the positive electrode.

Next, to verify whether such phenomena occur with other fluorine-containing molecules as well, we synthesized several fluorine-containing amides (Figure S3) and their corresponding CF_3 -free amides (Figure S4). Generally, amides are synthesized by condensing an acyl molecule with an amine. However, since amines with fluoroalkyl groups are unstable, synthesizing a diverse range of amides with fluoroalkyl groups presents a challenge²⁷. Therefore, we made comparisons among molecules where a fluorine group was introduced into the amides in the form of a trifluoroacetyl group. Same trend for charging voltages was also observed in other CF_3 -containing electrolytes

except for DMTFA. These results clearly indicate that CF₃-containing amides generally lead to long-lasting plateaus of low-charging voltage. The lack of a charging voltage plateau in DMTFA is attributed to the electrochemical instability of the molecule in the voltage range of 2.4–4.0 V, which will be elaborated on later.

As it is known that even trace amounts of water can significantly affect the morphology and composition of discharge products²⁸, it is important to investigate the potential impact of water contamination. Our experiments were conducted in a tightly sealed system, and we have confirmed that the water content in the electrolyte is less than 50 ppm. In fact, the cycle characteristics remained unchanged even when the sealed cell was placed in an argon-filled glove box with a dew point of –80 °C or lower, suggesting that our sealed cell setup provides a high level of isolation from external conditions.

Characterization of the electrolytes

As mentioned above, CF₃-containing amides exhibited significantly lower charge voltages. Understanding the characteristics and properties of the electrolyte is essential for further examining the reasons behind this lower charge voltage. Therefore, we first evaluated the electrochemical stability of various electrolyte solvents through cyclic voltammetry under argon-atmosphere using the same LOB cells with same electrolyte volume as all other experiments (Figure S5). For DETFA-50, CF₃CON(Me)(iPr)-50, and CF₃CON(nPr)₂-50, clear redox peaks were not observed except for a small oxidation peak at around 3.6 V. This small peak can be assigned to oxidation of trace amount of NO₂[–], which can be generated by reduction of NO₃[–] by lithium during cell assembly²⁹. Thus, the electrolytes are electrochemically stable at in the range

of 2.4–4.0 V at levels where their decomposition is not detected in cyclic voltammetry. However, an oxidation peak was clearly observed at around 3.5 V for DMTFA-50. Therefore, the absence of a charging plateau during cycle tests with only DMTFA-50 among the CF₃-containing amides, as illustrated in Figure S2a, is thought to be due to the electrochemical oxidative decomposition of DMTFA. Since the other CF₃-containing amides demonstrated electrochemical stability within the charging voltage range where a plateau was observed, it is unlikely that the observed lower charging voltage plateau results from the electrochemical instability. It should be noted here that the NO₂[−] species constitutes a redox pair NO₂[−]/NO₂ with a redox potential approximately in the range of 3.6 to 3.8 V²⁹. While it can function as a redox mediator if its concentration is sufficiently high²⁹, the observed redox peak near 3.6–3.8 V are significantly small and sometimes absent (Figure S5). The above results clearly demonstrate that the concentration of the NO₂[−]/NO₂ pair is sufficiently low that its influence as a redox mediator can be neglected.

Table 3 shows the physical properties of the four main electrolyte solvents used. Generally, when the viscosity is low and the solubility of lithium salts is high, the ionic conductivity of the electrolyte increases. High-rate O₂ diffusion is also important to achieve large discharge current densities. CF₃-containing molecules are expected to have high O₂ transport properties due to their low polarizability^{30,31}. Indeed, as expected, DETFA with CF₃ moieties exhibited a larger diffusion coefficient (*D*_{O₂}) and Henry's law solubility constants of O₂ than those for DEA, which is the corresponding CF₃-free amide. Although the *D*_{O₂} became smaller with longer alkyl chains as reported previously using glyme-based solvents³¹, we found that introducing CF₃ moieties into the amides reduces such negative effects. Table S2 shows the properties of electrolytes prepared using the solvents, in which it can be seen that. Ionic conductivity, viscosity, and salt dissociation of

DETFA-50 were poorer than those of DMA with the simplest structure, while O₂ transport in DETFA-50 was comparable to that in DMA.

Table 3 Physical properties of the electrolyte solvents.

Solvent	Boiling point / °C	Viscosity / mPa s (25°C)	Density / g cm ⁻³ (25°C)	D_{O_2} / 10 ⁻⁵ cm ² s ⁻¹ (25°C)	Henry's law solubility constants of O ₂ / mmol L ⁻¹ bar ⁻¹ (25°C)
DMA	165 ³²	0.919 ³²	0.936	8.03	4.8
DEA	185	1.485	0.905	7.00	4.7
DETFA	65-67 (24 mmHg) ³³	1.372	1.145	10.8	12.9
G4	275 ³²	3.255 ³²	1.071	3.0 ³⁴	5.2 ³⁴

O₂ evolution efficiency during charging

To further verify that the electrode reactions underlying the charging plateau in Figures 1b and 2c originate from the ideal oxidative decomposition of discharge products, we quantitatively investigate the O₂ evolution efficiency by differential electrochemical mass spectrometry (DEMS) (Figure 3). We also evaluated the O₂ evolution efficiency in DMA and G4 electrolytes, which are the standard electrolytes in LOB studies²⁴, for comparison. First, each cell was discharged at a constant capacity for 4.0 mAh cm⁻² using G4, DMA, and DETFA-50 electrolytes. Linear sweep voltammetry was then conducted at a positive sweep rate of 0.05 mV s⁻¹. The overlaid *I*–*V* curves obtained in these experiments are shown in Figure S6. Consistent with the fact that a low-voltage plateau was observed, it was confirmed that the oxidation current flows from the lowest voltage in the DETFA-50 electrolyte. Notably, simultaneous DEMS measurements confirmed that this oxidation current was accompanied by O₂ evolution. Thus, it was clearly shown that the discharge

products are oxidatively decomposed from lower voltages in the DETFA-50 electrolyte. Based on these results, it is concluded that the low charging voltage obtained with CF₃-containing DETFA is due to the formation of highly decomposable discharge products.

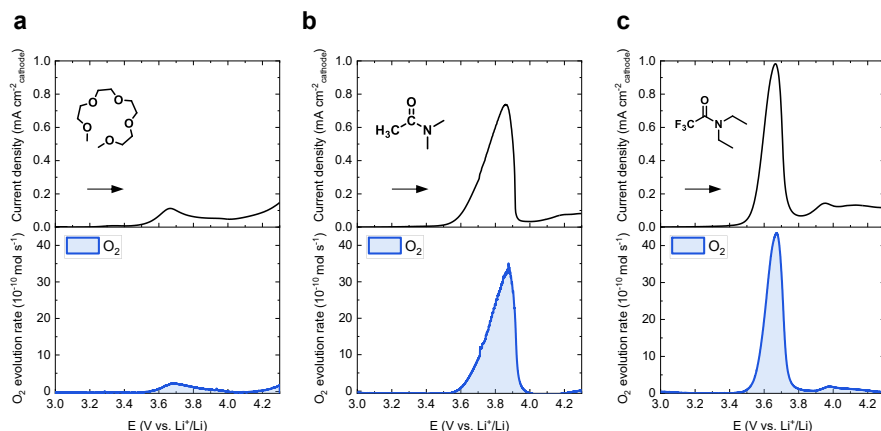


Figure 3 DEMS analyses during the linear sweep voltammetry at a positive sweep rate of 0.05 mV s⁻¹. Prior to the voltammetry, the cells were discharged in (a) G4, (b) DMA, and (c) DETFA-50 at 0.4 mA cm⁻² for 4.0 mAh cm⁻². KB-based porous carbon was used as the positive electrode.

Similar experiments were also conducted under constant current charging conditions (Figure 4). The O₂ evolution efficiencies for the entire charge process was 70.6 % for DEA-50 and 80.0 % for DETFA-50 electrolyte. The overall O₂ evolution efficiencies with CH₃CONMe(iPr)-50, CF₃CONMe(iPr)-50, CH₃CON(nPr)₂-50, and CF₃CON(nPr)₂-50 electrolytes were 51.7, 70.2, 63.2, and 80.0 %, respectively (Figure S7). Thus, the O₂ evolution efficiencies were always higher with the CF₃-containing electrolytes compared to the corresponding CF₃-free electrolytes. When the voltage range was limited to 3.5 V or lower, the O₂ evolution efficiency was 79.0 % for DEA-50

electrolyte and 86.2 % for DETFA-50 electrolytes, indicating that lithium peroxide can be decomposed more easily for the CF_3 -containing electrolyte. The results in Figure S8 further support this result. DEMS measurements tend to have higher charging voltages than those on closed systems¹⁸. This could be due to the high volatility of solvents in the DEMS measurement system, which requires gas flow, resulting in changes in electrolyte volume. Higher charging voltages lead to electrochemical decomposition of the electrolyte, which reduces O_2 evolution efficiency. Therefore, the O_2 evolution efficiency estimated above is an underestimate, and the true O_2 evolution efficiency in the electrolytes should be higher.

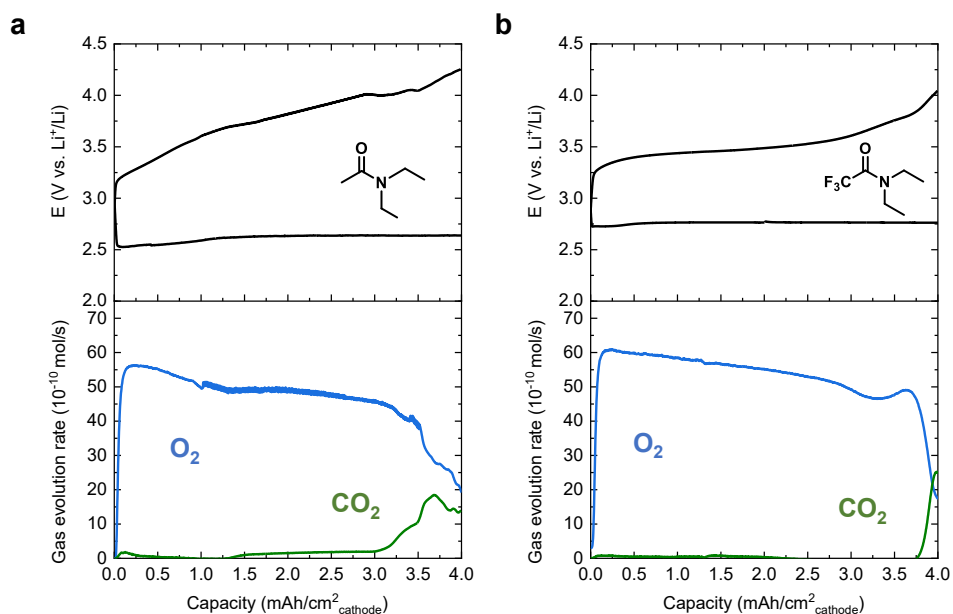


Figure 4 DEMS analyses during charging. The cells were discharged and subsequently charged in (a) DEA-50 and (b) DETFA-50 at 0.4 mA cm^{-2} for 4.0 mAh cm^{-2} . KB-based porous carbon was used as the positive electrode.

Characterization of the discharge products

In order to understand the reason why discharge products formed in DETFA electrolyte are highly decomposable, we conducted a structural analysis of the discharge products. First, we attempted to observe the discharge products through SEM observation. It should be noted that in this experiment, we used a carbon paper electrode to facilitate the observation of individual discharge product particles, thereby distinguishing them from the carbon particles on the porous positive electrode¹⁸. The deposits assignable to lithium peroxide formed in the DETFA-50 electrolyte were smaller in size and less-uniform in shape compared to that formed in the DMA electrolyte (Figure 5). After charge for 1 mAh cm^{-2} , the deposits disappeared from the positive electrode.

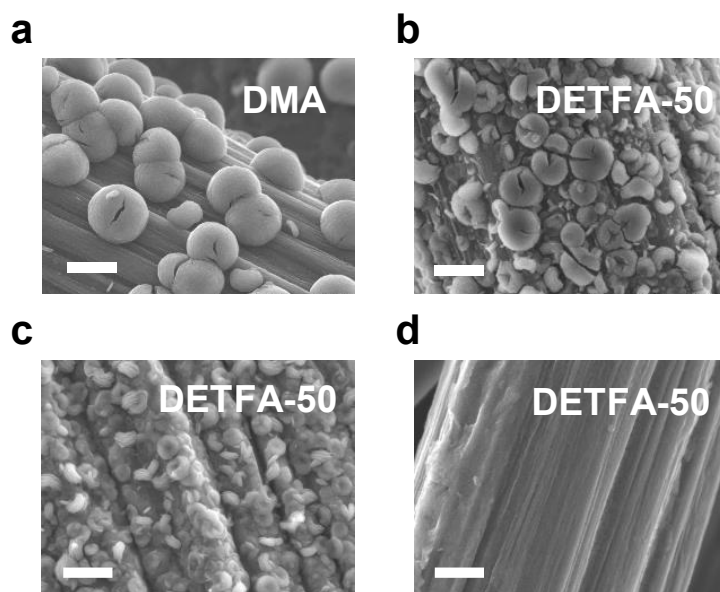


Figure 5 SEM images of CP electrodes discharged at 0.1 mA cm^{-2} for 1.0 mAh cm^{-2} in (a) DMA and (b) DETFA-50, and subsequently charged for (c) 0.5 mAh cm^{-2} and (d) 1.0 mAh cm^{-2} in DETFA-50. Each scale bar indicates $1 \text{ }\mu\text{m}$.

Next, we performed a crystal structure analysis of the discharge products using synchrotron X-ray diffraction (XRD). Figure 6 shows synchrotron XRD patterns of discharge products obtained in the G4, DMA, and DETFA-50 electrolytes. Note that in the XRD measurements, we used porous carbon as the positive electrode to obtain larger peaks originating from lithium peroxide. No essential difference was observed in the XRD patterns between CP and porous carbon electrode (Figure S9). The intensities of the Li_2O_2 -derived diffraction lines are particularly small in the sample obtained with the DETFA-50, even though the discharge capacity was the same for all samples. Compared to the samples obtained in G4 electrolyte, the 101 diffraction line in the DMA sample and both 101 and 100 diffraction lines in the DETFA-50 sample were broader. These results mean that the crystallinity of lithium peroxide is lowest in DETFA-50, followed by DMA and G4.

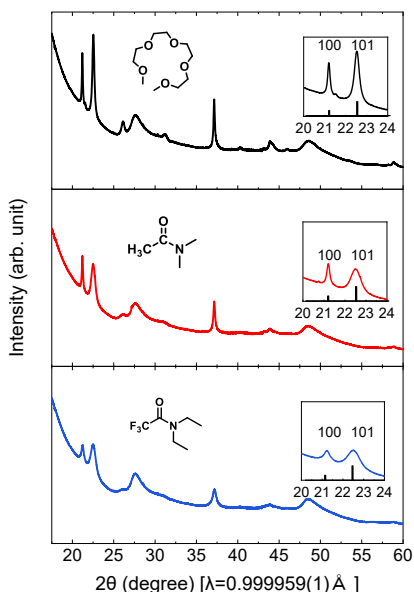


Figure 6 Synchrotron XRD patterns of discharge products after discharge at 0.2 mA cm^{-2} for 2.0 mAh cm^{-2} in G4 (black), DMA (red), and DETFA-50 (blue).

Estimating the Li deficiency (i.e., X value in $\text{Li}_{2-x}\text{O}_2$) is of high interest in previous studies from the perspective of reducing charging overvoltages^{35,36}. Then, we qualitatively estimated the X value by Rietveld analysis of the XRD patterns, following the protocol described in previous reports^{37,38}. It is important to note that since Rietveld analysis is conducted under several premises that are difficult to verify experimentally, it is appropriate to limit discussions based on X -values to qualitative rather than quantitative interpretations. The crystal structure of lithium peroxide is assumed to be hexagonal, the $P6_3/mmc$ (#194) space group (Figure S10a). Li(2a), Li(2c), and O(4f) represents Li at site 2a, site 2c, and O, respectively. In our analysis, the Li(2a) site was assumed to be deficient according to previous reports^{35,36}, and fitting was conducted using the degree of vacancy X at the Li(2a) site as a parameter. See the supporting information for details on the analysis protocol and the reliability of the fitting. Tables S3 and S4 present the optimized structural parameters for each scenario, both with and without the consideration of anisotropy parameters. As shown in these tables, the X values are highest in descending order for DETFA-50, followed by DMA and G4, suggesting that lithium peroxide formed in the DETFA-50 has the highest Li deficiency.

To confirm the rationality of the crystal structure suggested by the Rietveld analysis, the stable atomic configuration of the crystal lacking Li(2a) was investigated by structural optimization using the first-principles calculations based on the density functional theory (DFT) framework (See the Experimental Section for details of calculation). Specifically, one Li(2a) was removed from a

2×2×2 supercell of Li₂O₂ (*P6₃/mmc*), in which the *X* value corresponds to 0.0625. Utilizing DFT calculations to analyze the cell constant and atomic positions of the lithium-deficient structure pre- and post-structural optimization, it was observed that the interatomic distance between two opposite Li(2c) atoms adjacent to the vacant Li(2a) site decreased from 5.2976 to 5.0452 Å (Figure S10d), while that between two opposite oxygen atoms adjacent to the site increased from 4.3108 to 4.4959 Å (Figure S10e). This is qualitatively consistent with the results of the Rietveld analysis of the experimentally obtained XRD patterns (*z* values in Tables S3 and S4).

Possible origins of the long-lasting plateau of low-charging voltage

Why are highly decomposable discharge products formed in the DETFA-50 electrolyte? A possible explanation is the incorporation of fluorine from the electrolyte into the crystal lattice of the discharge products. The presence of fluorine in the discharge products is suggested by energy-dispersive X-ray spectroscopy (EDX) (Figure S11), and it is conceivable that doping with the larger ionic radius of F could lead to increased lithium deficiency and reduced crystallinity. Indeed, it is known that the doping with hetero-elements like sodium can promote defective lithium peroxide formation and reduce overpotential during charging^{16,39}. SEM observations confirmed that the discharge products formed in DETFA-50 have smaller particle sizes and different morphology (Figure 5), which can also contribute to the reduction of charging voltage⁴⁰. Additionally, changes in the physical properties of the electrolyte caused by the introduction of CF₃ moiety might lead to lattice defects and strains in the discharge products. More specifically, as indicated in Table 3, the incorporation of CF₃ moiety affects not only the diffusion coefficient (*D*_{O₂}) and Henry's law solubility constants of O₂ but also the self-diffusion coefficient of Li⁺. This

suggests a change in the balance of O₂ and Li⁺ supply at the growth interface of the discharge products, impacting their formation and structure. In fact, it has been observed that modifying the nanopore structure of the positive electrode to adjust the balance of mass transportation can lead to the formation of discharge products with varied morphologies and degrees of crystallinity, even while using the same electrolyte^{41,42}.

Determining factor for the cyclability.

Regarding the cycle performance in the CF₃-containing DETFA-50 electrolyte, despite the significantly low charging voltage achieved, the desired cycle performance was not attained. This limitation is thought to be due to the volatility of DETFA. For the cycle tests shown in Figures 1 and 2, we applied the small electrolyte volume of 31.4 $\mu\text{L cm}^{-2}$ because the electrolyte amount is the largest weight fraction in the entire battery. For the tests with low electrolyte volume, the effective electrode area is reduced via volatilization of the CF₃-containing solvent with a lower boiling point, resulting in an increase in charging voltage and, in turn, premature cease of the discharge-charge cycle. In fact, longer cycle life was obtained when the electrolyte volume was increased (Figure S12). Furthermore, previous reports have indicated that lithium peroxide is stable in organic solvents⁴³, meaning it does not decompose the electrolyte. Therefore, it is unlikely that electrolyte decomposition by lithium peroxide is the cause of shorter cycle life. Thus, the low cycle performance in DETFA-50 is attributed to physical rather than chemical factors. Therefore, it is believed that this issue can be avoided by developing selective membranes, for example, that prevent the leakage of volatile electrolyte components while allowing the taking O₂ from the outside.

CONCLUSIONS

In the present study, we found that the fluorine-containing amide-based electrolytes are able to form lithium peroxide, which is decomposable at lower voltages than DMA or G4 electrolytes, with a long-lasting plateau of charging voltage at around 3.5 V. Notably, the persistence of the low charging voltage plateau obtained in this study significantly exceeds that obtained with alternative approaches, such as using additional redox mediators^{44–46} under test conditions which can verify the feasibility of large gravimetric energy densities. Low charging voltage is also desirable to minimize the potential impact of singlet oxygen, which can be significant in voltage regions greater than 3.5 V^{47–49}. (It should be noted that there is currently a debate about whether a significant amount of singlet oxygen is being generated⁵⁰.) In the fluorine-containing electrolytes, both amorphous lithium peroxide and Li-deficient $\text{Li}_{2-x}\text{O}_2$ were formed. Furthermore, the size of the discharge products in DETFA-50 was smaller than that in DMA, and their morphology was inhomogeneous. Although the physicochemical modification of the positive electrode has been the main approach to form structurally disordered discharge products^{14–17}, we found that the selection of an appropriate electrolyte can also induce the formation of such highly-decomposable lithium peroxide. The reason why the Li-deficiency level can depend on the kind of electrolyte remains veiled. We expect that continued research in this direction will significantly contribute to the development of novel electrolyte molecular systems for LOBs.

EXPERIMENTAL SECTION

Cell configuration.

The electrochemical cell employed in this study was previously described elsewhere⁵¹. Li foil (25 mm diameter, 400 μm thick, Honjo Metal) was used as a negative electrode. Porous carbon (20 mm diameter, 270 μm thick, porosity 91 %, 5.4 mg cm^{-2} -carbon) or carbon paper (CP, 20 mm diameter, 190 μm thick, porosity 78 %, TGP-H-060, Toray) was used as a positive electrode. The porous carbon electrode is a self-standing sheet consisting of carbon fiber and Ketjenblack (KB)⁵². Polyacrylonitrile was used as the binding polymer material. For the porous carbon, a mixture slurry was prepared using 65 wt% of KB, 12 wt% of carbon fiber, and 23 wt% of polyacrylonitrile. The prepared membrane was dried and heat treated, and finally calcinated at 1,050 $^{\circ}\text{C}$ in an inert atmosphere⁵². CP was prepared by immersing pristine CP in hot acid ($\text{H}_2\text{SO}_4\text{:HNO}_3 = 3\text{:}1$) for 2 h, as described in the literature⁵³. The free-standing graphene mesosponge was prepared following the procedures in the literature⁵⁴ and exclusively employed as a positive electrode for synchrotron XRD measurements. A polyolefin-based separator (20 mm thick, 22 mm diameter) was used after vacuum drying when using the KB-based porous carbon electrode. When the CP electrode was used, a glass-fiber filter (GF/A, 22 mm diameter, Whatman) was used as the separator after vacuum drying at 110 $^{\circ}\text{C}$ overnight. DMA (Wako) and DETFA (TCI) was used as the main solvent for the electrolyte. In addition, DMTEFA(TCI), DEA (TCI) and tetraglyme (G4, Japan Advanced Chemicals) were used. $\text{CF}_3\text{CON}(\text{Me})(\text{iPr})$, $\text{CH}_3\text{CON}(\text{Me})(\text{iPr})$, $\text{CF}_3\text{CON}(\text{nPr})_2$, $\text{CH}_3\text{CON}(\text{nPr})_2$ were synthesized through the procedure described below and used as electrolyte solvents. LiNO_3 (Kishida, Japan), LiTFSa (Kishida, Japan), and LiBr (Sigma-Aldrich) were used as the salt. The electrolytes were prepared by stirring the salt and solvent overnight. The water content of the electrolytes was confirmed to be under 50 ppm by Karl Fischer titration after mixing the salts. The cells were assembled in an Ar-filled glovebox. O_2 (>99.99% purity) was supplied by attaching a small cylinder (50 mL, 0.25 MPa) except in the case of DEMS measurements. The proportion of

oxygen gas consumed in the reaction is approximately 1.2% and 4.6% of the total amount of oxygen in the cylinder connected to the cell when capacities of 1 mAh cm⁻² and 4 mAh cm⁻² are applied, respectively. Only when DEMS measurements were conducted, the lid of these cells was replaced to make them a flow-type cell.

Electrochemical measurements.

Electrochemical measurements were performed using a VMP3 electrochemical test unit (Bio-Logic, France) or a battery measuring apparatus (HJ1020mSD8, HOKUTO DENKO) in a thermostatic chamber kept at 25 °C. All electrochemical tests were conducted after the cells were maintained at open-circuit voltage for 12 h or more.

Characterization of the electrolyte solvent.

The viscosity of the electrolyte solvents was determined using a viscometer (Lovis 2000 ME, Anton Paar). Self-diffusion coefficients of the electrolytes were measured at constant each temperature using pulsed gradient spin-echo nuclear magnetic resonance (PGSE-NMR) with a JOEL tunable pulsed-field gradient (PFG) probe. To minimize convection effects, each sample was prepared in an NMR microtube (BMS-005J, Shigemi, Tokyo) with a height of less than 5 mm. The PFG was calibrated using H₂O (¹H resonance), and the same PFG intensity was applied for each nuclide, ensuring consistent values were obtained with different irradiation times for accurate self-diffusion coefficients measurements. The ionic conductivities of the electrolytes were determined using a conductivity meter (S230 SevenCompact, Mettler Toledo). Measurements were conducted after allowing the electrolytes to equilibrate at each temperature for a minimum of 1 h.

The diffusion coefficients of oxygen were determined through gas uptake measurements using a thin film cell, described in the literatures^{30,31}. It was connected to a gas reservoir of approximately 26 mL via a Swagelok ball valve, with a pressure sensor directly attached. For each measurement, 1 mL of solvent was introduced into the thin film cell. The container was connected to a vacuum pump, and the solvent was degassed prior to the experiment. Subsequently, gas was supplied to the gas reservoir, and the setup was transferred to a climate chamber set at 25 °C. The ball valve between the gas reservoir and thin film cell was swiftly opened and closed, allowing for gas uptake. The pressure decay during the process was measured, and the diffusion coefficient was subsequently calculated. At least three measurements were conducted for each solvent. Henry's law solubility constants were determined using gas uptake measurements, following the procedures described in the literatures^{30,31,55}.

Characterization of the positive electrodes.

SEM measurements were conducted using a field-emission scanning electron microscope (JSM 7800F, JEOL). Prior to these measurements, the samples were treated with anhydrous acetonitrile and handled in an environment devoid of air exposure. The electron acceleration voltage of SEM images was set at 5 kV. XRD measurement was conducted with an X-ray diffractometer (SmartLab, Rigaku). The pattern was measured within $30^{\circ} \leq 2\theta \leq 60^{\circ}$ with a step size of 0.1° without exposure to the atmosphere.

DEMS.

The gas evolution efficiency was investigated with a DEMS system consisting of a quadrupole mass spectrometer (PrismaPlus QMG220, Pfeiffer Vacuum, Germany) connected to a flow-type cell via capillary tubing (56712-U, Sigma). Prior to discharge tests, the cell interior was filled with

either $^{16}\text{O}_2$ (0.3 MPa, >99.99% purity) or $^{18}\text{O}_2$ (0.3 MPa, including 2% or less $^{16}\text{O}_2$, TAIYO NIPPON SANSO) and subsequently sealed. When switching gases during discharge, measurements were paused, and the cell was purged with another gas. During the charging process, a continuous flow of helium was employed as a carrier gas at a rate of 3 mL min^{-1} . For DEMS analyses, a gas flow of approximately 1 mL min^{-1} was introduced into the mass spectrometer. The quantity of gas evolved in each trial was determined based on the instrument's signal and calibrated using a gas sample of known concentration.

Synchrotron XRD and its Rietveld analyses.

Synchrotron XRD measurements were carried out on the BL5S2 beamline of the Aichi Synchrotron Radiation Center to obtain PXRD patterns suitable for comprehensive crystal structure analyses using the Rietveld method. Each sample was carefully packed into a glass capillary tube with a diameter of 0.7 mm (WJM-Glas Müller, Germany) and sealed with epoxy resin to prevent exposure to air. Two-dimensional detectors (Pilatus 100 K, Dectris, Switzerland) were employed to collect PXRD patterns over a 2θ range of 5° to 95° . The incident X-ray wavelength (λ) was calibrated to $0.999959(1)\text{ \AA}$ using Si standard powders (NIST 640d). Rietveld analyses were performed using the RIETAN-FP program following the protocol described in previous reports^{37,38}, while crystal structure visualization was carried out using the VESTA software. Regarding the crystal structure of lithium peroxide, the thermodynamically most stable hexagonal form, the space group $P6_3/mmc$, was assumed (Figure S10a). Here, Li in the 2a site is denoted as Li(2a), Li in the 2c site as Li(2c), and O as O(4f). Following the initial fitting of the background and peak positions, we executed partial profile relaxation for the peaks originating from the (100) and (110) crystallographic planes. Subsequently, data fitting was conducted through sequential adjustment of parameters pertaining to the background, half-width, and atomic positions

within the crystal structure. In assessing the reliability of the analysis results, we adhered to the general practice: an analysis result was considered satisfactory if the reliability factor (R factor), specifically the S value ($S = R_{wp}/R_e$), was less than 1.3⁵⁶. Note that the reliability factors R_{wp} , R_e , and S are represented by the following formulas.

$$R_{wp} = \left\{ \frac{\sum_i \omega_i [y_i - f_i(\mathbf{x})]^2}{\sum_i \omega_i y_i^2} \right\}^{1/2}$$

$$R_e = \left(\frac{N - P}{\sum_i \omega_i y_i^2} \right)^{1/2}$$

$$S = \frac{R_{wp}}{R_e} = \left\{ \frac{\sum_i \omega_i [y_i - f_i(\mathbf{x})]^2}{N - P} \right\}^{1/2}$$

Here, ω_i represents the statistical weight, y_i the observed intensities, $f_i(x)$ the theoretical diffraction intensities, N the total number of data points, and P the number of refined parameters. Additionally, due to the tendency of standard uncertainty values in Rietveld analysis to underestimate the actual error, we considered a value threefold the standard uncertainty as the error margin. Any variations in analysis results that persist even after accounting for this adjusted error margin were considered significant.

DFT calculations.

We performed DFT calculations using the projector augmented wave (PAW) method as implemented in the Quantum ESPRESSO (QE) code⁵⁷. The exchange-correlation interaction was approximated by the Generalized Gradient Approximation (GGA) based on the Perdew-Burke-Ernzerhof (PBE) functional. In these calculations, we used the kinetic energy cut-off at 78 Rydberg

(Ry), the convergence threshold for the self-consistent field at 2×10^{-7} Ry, a Monkhorst-Pack grid with parameters of $5 \times 5 \times 5$, and a Methfessel-Paxton smearing with a degauss value of 0.01.

For the structure optimization, we used the vc-relax calculation where the relaxation of atom positions was calculated by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm with a force convergence threshold of 5×10^{-4} Ry/Bohr. Specifically, the structural optimization was performed through the following steps. First, the lattice parameters of the unit cell of Li_2O_2 ($P6_3/mmc$) (Figure S10a) were obtained from the Materials Project database⁵⁸, specifically, $a = b = 3.10$ and $c = 7.57$ Å. Next, a $2 \times 2 \times 2$ supercell was constructed by stacking this unit cell twice along each of the a-axis, b-axis, and c-axis directions (Figure S10b), and relaxation calculations were performed to obtain optimized cell constants of the supercell ($a = b = 6.3176$ and $c = 15.3680$ Å), which are in good agreements with a previous calculation⁵⁹. Finally, the cell constants and atomic positions of the structure with one Li(2a) atom removed from this supercell (Figure S10b and c) were optimized. The cell constants of the Li-deficient supercell were $a = b = 6.3176$ and $c = 15.3680$ Å before the optimization and $a = b = 6.3300$ and $c = 15.3863$ Å after the optimization, indicating that the removal of Li(2a) increased the cell size in all axial directions.

To ensure the reliability of the parameters and computational method, we calculated the formation energy of Li-vacancy (E_v) using the following definition⁶⁰:

$$E_v = E_{\text{defect}} + E_{\text{Li-bcc}} - E_{\text{perfect}}$$

where E_{defect} and E_{perfect} are the total energies of the $2 \times 2 \times 2$ supercell with and without a Li-vacancy, respectively. $E_{\text{Li-bcc}}$ is the energy of one Li atom in the body-centered cubic (bcc) structure. For the calculation of $E_{\text{Li-bcc}}$, the lattice constants of a unit cell of Li bcc structure were optimized under the same calculation conditions as described above except that a Monkhorst-Pack grid of $20 \times 20 \times 20$ was used. The formation energy of Li(2a)-vacancy ($E_{\text{Li(2a)-v}}$) and Li(2c)-vacancy ($E_{\text{Li(2c)-v}}$)

_v) was 3.372 eV and 3.249 eV, respectively, and the difference between them ($\Delta E_v = E_{\text{Li(2a)-v}} - E_{\text{Li(2c)-v}}$) was 0.123 eV. These results were in good agreement with the previous calculations ($E_{\text{Li(2a)-v}} = 3.46$ eV, $E_{\text{Li(2c)-v}} = 3.36$ eV, and $\Delta E_v = 0.10$ eV)⁶⁰, ensuring the reliability of the calculation.

ASSOCIATED CONTENT

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

Discharge–charge cycles, dQ/dV plots, Cyclic voltammograms under an Ar atmosphere, linear sweep voltammograms, DEMS analyses during charge, SEM images of discharged positive electrodes, XRD patterns, structures for DFT calculations, EDX mapping images, discharge profiles under current-controlled conditions, Walden plots, Self-diffusion coefficients, viscosities, and ionic conductivities of the electrolytes, and crystal structure parameters of samples discharged with various electrolytes determined through Rietveld analyses.

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Author Contributions

K. Nishioka and S. Nakanishi proposed the concept and wrote the manuscript. K. Nishioka and M. Tanaka, performed the battery tests and gas analyses. R. Haas, A. Henss S. Azuma, and M. Saito characterized the electrolytes. T. Goto, S. Matsuda, W. Yu, and H. Nishihara prepared the carbon positive electrodes for this study. H. Fujimoto and M. Tobisu synthesized the electrolyte solvents. K. Nishioka, M. Tanaka and Y. Mukouyama analyzed the experimental data. All authors discussed the results and reviewed the final version of the manuscript before submission.

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Notes

The authors declare no competing financial interest.

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