Fluorinated Amide-Based Electrolytes Induce a Sustained Low-Charging Voltage Plateau under 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 charging 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 a benchmark energy density value of 500 Wh kg–1. Notably, the achievement of the low-voltage plateau was accomplished solely by 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 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 superoxide 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 electrolyte depletion within the porous electrode, resulting in a reduction of the effective electrode surface area. These factors cause an increase in charging voltage. (6−10) The increase in charging voltage consequences for 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 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 peroxide. (18) 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 a 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 interface. (19) 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 those in the previous work, as described below. In the present work, we used LiNO3 as the Li salt, which has been known to form a 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 a CF3 moiety do not dissolve the LiNO3 salt. To address this, we mixed them with N,N-dimethylacetamide (DMA) that has a 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.

To elucidate the impact of the CF3 moiety, we compared CF3-containing DETFA (Figure 2c) and CF3-free N,N-diethylacetamide (DEA) (Figure 2a), both having ethyl groups adjacent to the amide group. (The behavior under the same conditions in the G4-based electrolyte, which is one of the standard electrolytes in LOB studies, (24) is shown in Figure 1b,c and the S1 in ref (18).) In these tests, the current density was increased to 0.4 mA cm–2 and the capacity was increased 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 CF3-moiety was confirmed even at a 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). CF3-containing DETFA-50 maintained a charging voltage of around 3.5 V for a more extended period compared to CF3-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 (Figure 2b,d). DETFA-50 has large peaks around 3.5 V. The above trend for charging voltages was more pronounced for a higher ratio of DETFA mixed in the solvents (Figure S2). These findings revealed the role of the CF3 moiety in DETFA as an electrolyte solvent in establishing a low-charging voltage plateau.

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 CF3-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 challenge. (27) Therefore, we made comparisons among molecules where a fluorine group was introduced into the amides in the form of a trifluoroacetyl group. The same trend for charging voltages was also observed in other CF3-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 products, (28) it is important to investigate the potential impact of water contamination. Our experiments were conducted in a tightly sealed system, and we 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 glovebox 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 examination of the reasons behind this lower charge voltage. Therefore, we first evaluated the electrochemical stability of various electrolyte solvents through cyclic voltammetry under an argon atmosphere using the same LOB cells with the 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 a trace amount of NO_2^-, which can be generated by the reduction of NO_3^- by lithium during cell assembly. (29) Thus, the electrolytes are electrochemically stable 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 S3a, 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 NO_2^- species constitutes a redox pair NO_2^-/NO_2 with a redox potential approximately in the range of 3.6–3.8 V. (29) While it can function as a redox mediator if its concentration is sufficiently high, (29) the observed redox peaks near 3.6–3.8 V are significantly small and sometimes absent (Figure S5). The above results clearly demonstrate that the concentration of the NO_2^-/NO_2 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 O_2 diffusion is also important for achieving large discharge current densities. CF3-containing molecules are expected to have high O_2 transport properties due to their low polarizability. (30,31) Indeed, as expected, DETFA with CF3 moieties exhibited a larger diffusion coefficient (D_{O_2}) and Henry's law solubility constants of O_2 than those for DEA, which is the corresponding CF3-free amide. Although the D_{O_2} became smaller with longer alkyl chains as reported previously using glyme-based solvents, (31) 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 O_2 transport in DETFA-50 was

comparable to that in DMA.

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 studies (24) for comparison. First, each cell was discharged at a constant capacity of 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 an 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.

Similar experiments were also conducted under constant current charging conditions (Figure 4). The O2 evolution efficiencies for the entire charging process were 70.6% for DEA-50 and 80.0% for the 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 those of 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 the DEA-50 electrolyte and 86.2% for DETFA-50 electrolytes, indicating that lithium peroxide can be decomposed more easily for the CF3-containing electrolyte. The results in Figure S8 further support this result. DEMS measurements tend to have higher charging voltages than those on closed systems. (18) This could be due to the high volatility of solvents in the DEMS measurement system, which requires gas flow, resulting in changes in the electrolyte volume. Higher charging voltages lead to electrochemical decomposition of the electrolyte, which reduces O2 evolution efficiency. Therefore, the O2 evolution efficiency estimated above is an underestimate, and the true O2 evolution efficiency in the electrolytes should be higher.

Characterization of the Discharge Products

In order to understand the reason why discharge products formed in the DETFA electrolyte are highly decomposable, we conducted a structural analysis of the discharge products. First, we attempted to

observe the discharge products through a 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 electrode. (18) The deposits assignable to lithium peroxide formed in the DETFA-50 electrolyte were smaller in size and less uniform in shape compared to those formed in the DMA electrolyte (Figure 5). After charging for 1 mAh cm–2, the deposits disappeared from the positive electrode.

Next, we performed a crystal structure analysis of the discharge products using synchrotron X-ray diffraction (XRD). Figure 6 shows the 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 the porous carbon electrode (Figure S9). The intensities of the Li2O2-derived diffraction lines are particularly small in the sample obtained with DETFA-50, even though the discharge capacity was the same for all samples. Compared to the samples obtained in the 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.

Estimating the Li deficiency (i.e., X value in Li2–xO2) is of high interest in previous studies from the perspective of reducing charging overvoltages. (35,36) Then, we qualitatively estimated the X value by the Rietveld analysis of the XRD patterns, following the protocol described in previous reports. (37,38) It is important to note that since the 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, with the P63/mmc (#194) space group (Figure S10a). Li(2a), Li(2c), and O(4f) represent 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 Experimental Section 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 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 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 poststructural 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 doping with heteroelements 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 morphologies (Figure 5), which can also contribute to the reduction of charging voltage. (40) Additionally, changes in the physical properties of the electrolyte caused by the introduction of the 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 (DO2) and Henry's law solubility constants of O2 but also the self-diffusion coefficient of Li+. This suggests a change in the balance of the supply of O2 and Li+ 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 μL cm–2 because the electrolyte amount is the largest weight fraction in the entire battery. For the tests with a 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 extinction of the discharge–charge cycle. In fact, a 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 solvents, (43) meaning it does not decompose the electrolyte. Therefore, it is unlikely that electrolyte decomposition

by lithium peroxide is the cause of the 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 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 generated. (50)) In the fluorine-containing electrolytes, both amorphous lithium peroxide and Li-deficient Li2–xO2 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 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.