ACS APPLIED MATERIALS & INTERFACES

Research Article

Cite This: ACS Appl. Mater. Interfaces 2019, 11, 39715−39721

www.acsami.org

Bifunctional Lithium Carboxylate for Stabilizing Both Lithium-Metal Anode and High-Voltage Cathode in Ether Electrolyte

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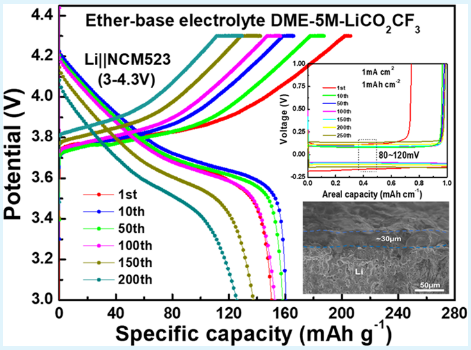
Supporting Information

ABSTRACT: Lithium-metal batteries have attracted extensive attention due to the increasing demand for storage devices with high energy density. For the modification of lithium-metal battery, how to effectively inhibit the growth of lithium dendrites has become a key challenge. Ether electrolytes have been widely used owing to their good compatibility with lithium metal. However, they are still difficult to be applied in high-voltage battery systems because of the poor cathodic stability. In this work, we have dissolved the lithium carboxylate, $LiCO_2CF_3$, into a dimethyl ether-based ether solvent to achieve a relatively outstanding performance in both positive and negative electrodes. Using this dilute ether electrolyte (1 mol L^{-1}), the Li||Cu half-cells retain a Coulombic efficiency of 98.5% after 100 cycles at the current density of 1 mA cm^{-2} and lithium deposition amount of 1 mAh cm^{-2} for each cycle. Meanwhile, the Li||NCM523 full-batteries also realize a capacity retention of nearly 80% after 100 cycles in the voltage range of 3.0−4.3 V. Moreover, when the concentration increases to 5 mol L^{-1}, the Coulombic efficiency of the half-cells stabilizes at around 99.0% after 250 cycles under the condition of 1 mA cm^{-2} current density along with the average Coulombic efficiency of as high as 98.4% and the capacity retention rate of the full-batteries is nearly 95.4% after 100 cycles and over 83.8% after 200 cycles.



KEYWORDS: *$LiCO_2CF_3$, Li-metal battery, high voltage, high concentration, ether electrolyte*

1. INTRODUCTION

As we all know, lithium metal is regarded as the “holy grail” among the battery anodes due to its ultralow electrode potential (−3.04 V, versus standard hydrogen electrode) and ultrahigh theoretical specific capacity (3860 mAh g^{-1}).[1] However, the huge volume change during the cycling process, easy pulverization, and growth of lithium dendrite may cause a decrease in the utilization rate of active materials, a short battery life, and even a safety problem, which has greatly limited its further application.[2] In recent years, a variety of efforts have been devoted into the modification of lithium metal,[3] including the construction of an artificial solid electrolyte interface (SEI) film on the surface of lithium anode,[4−7] addition of electrolyte additives,[8−10] use of high-concentration electrolyte,[11−16] and so on. There is no doubt that the electrolyte[17] plays an important role. Within all kinds of electrolytes, the ether electrolytes[18] have unparalleled advantages than the ester electrolytes[19] for suppressing lithium dendrite because they can form a stable SEI layer due to the good compatibility with lithium metal. The ether electrolyte such as lithium bis(fluorosulfonyl)imide (LiTFSI) dissolved in 1,3-dioxolane (DOL)/dimethyl ether (DME) (v/v = 1:1) has unique advantages in Li−S batteries,[20] but it is difficult to be applied in high-voltage systems above 4.0 V, mainly because of the poor oxidation stability of ether solvents under the condition of low concentration and terrible corrosion resistance of LiTFSI to Al current collectors. Even if it is replaced by lithium bis(fluorosulfonyl)imide (LiFSI), which has a higher corrosion resistance potential for Al foil,[21] the overcharge is still inevitable in the high-voltage systems.[22] Jiao et al. have reported a kind of 4 M high-concentration dual-salt ether electrolyte to enhance the stability of the positive electrode,[23] but to some extent, it will lead to the degradation of lithium-metal anode. However, whether it is a single lithium salt or a mixture, it is hard to achieve the effective suppression of lithium-metal dendrite, and a perfect match of high-voltage systems above 4.0 V at the same time.

In our work, we have found a new kind of ether electrolyte by dissolving $LiCO_2CF_3$ in the DME solvent, which can stabilize both lithium-metal anode and 4.3 V high-voltage NCM523 cathode. The Li||NCM523 batteries can remain nearly 80% capacity after 100 cycles with a charge cutoff voltage of 4.3 V even in the 1 mol L^{-1} $LiCO_2CF_3$ DME-based electrolyte. Also, the Coulombic efficiency of Li||Cu cells at a current density of 1.0 mA cm^{-2} can also remain at 98.5% after 100 cycles, which is much better than that of LiFSI with the

Received: May 19, 2019
Accepted: September 30, 2019
Published: September 30, 2019

DOI: 10.1021/acsami.9b08703
ACS Appl. Mater. Interfaces 2019, 11, 39715−39721

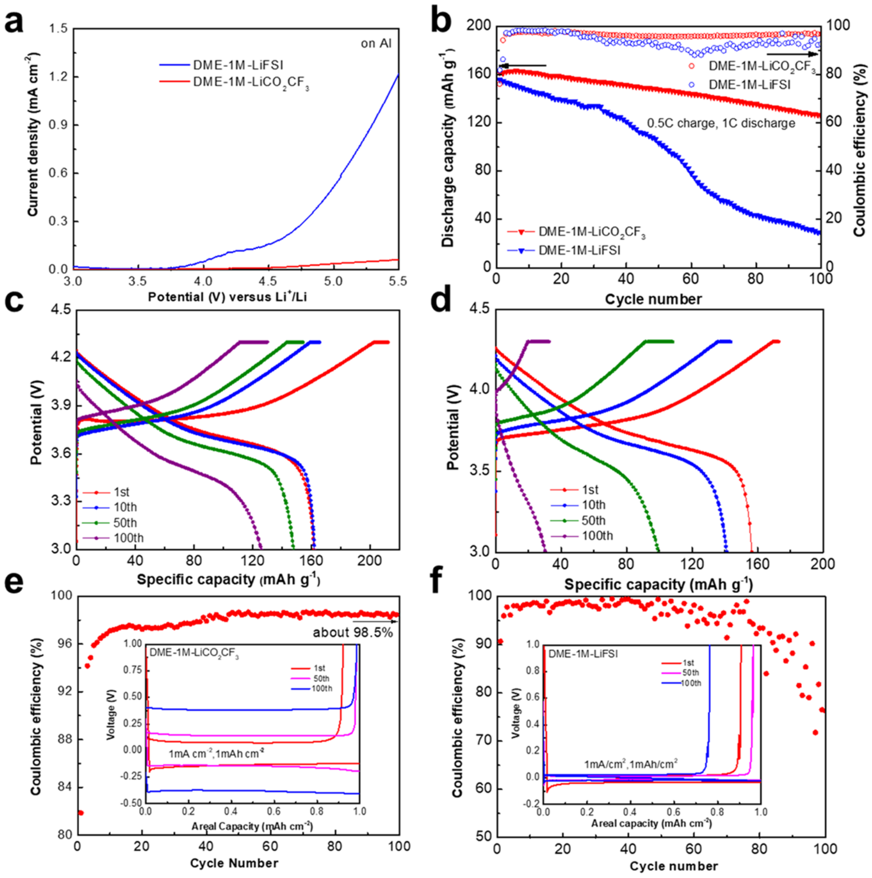


Figure 1. Electrochemical performance of DME-1M-LiCO$_2$CF$_3$ and DME-1M-LiFSI on the Al electrode and in Li||Cu and Li||NCM523 batteries. (a) LSV curves of two electrolytes on the Al electrodes in a three-electrode system under the sweep rate of 1 mV s^{-1}. (b) Discharge capacity and cycling stability at the condition of 0.5C charge/1C discharge (1C = 160 mAh g^{-1}). (c, d) Voltage profiles of Li||NCM523 batteries at the selected number of cycles. (e, f) Cycling performance of Li||Cu cells (the inset is Li plating/stripping profile on a Cu working electrode at a current density of 1 mA cm^{-2}).

same concentration. Moreover, as the concentration of the electrolyte is increased to 5 mol L^{-1}, the Coulombic efficiency of Li||Cu cells can reach nearly 99.0% after 250 cycles, and the average Coulombic efficiency is further improved to 98.4%. Also, the capacity retention rate of Li||NCM523 full-batteries is over 95.4% after 100 cycles and nearly 84.0% after 200 cycles, which shows a better performance. Undoubtedly, this work has provided a new alternative to the commonly used lithium salts, including the sulfonymide lithium salts such as LiTFSI and LiFSI, the lithium borate such as lithium bis(oxalate)borate and lithium difluoro(oxalato)borat, and the most widely used lithium salt LiPF$_6$.

2. EXPERIMENTAL SECTION

2.1. Material Preparation. The LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (NCM523) cathode material was provided by Beijing Easpring Material Technology Co., Ltd. (China) and the laminate of NCM523 electrode was prepared by mixing up the NCM523 cathode powder, acetylene black, and poly(vinylidene fluoride) binder after weighing according to the mass ratio of 8:1:1, using the *N*-methyl-2-pyrrolidone as a solvent and electromagnetic stirring for 6 h. Then, the paste was coated on an aluminum foil, followed by baking on a heating board at 60 °C for 30 min and in a vacuum oven at 80 °C for 12 h. The active material load was about 4 mg cm^{-2}. The elemental sulfur was purchased from Sigma-Aldrich, China, and the preparation of electrodes was nearly same as the method above, just different in the ratio of 6:3:1 and the temperature of vacuum oven at 60 °C. The formula of ether electrolyte is to dissolve lithium salts like LiCO$_2$CF$_3$ into DME or DME/DOL (v/v = 1:1) solvent for obtaining the electrolyte of required concentration. The separator was supplied by the Celgard.

2.2. Material Characterization. The X-ray diffraction (XRD) data were collected by using Rigaku miniflex 600 X-ray diffractometer with Cu K2 radiation from 10 to 90° at 2° min^{-1}. The scanning electron microscopy (SEM) pictures were picked by the field-emission scanning electron microscopy (FESEM, HITCHI 4800). The transmission electron emission (TEM) images were gotten by using the TECANI G2 F30 device. The X-ray photoelectron spectroscopy (XPS) analysis was examined on the PHI Quantum 2000 equipment. The ionic conductivity of the electrolytes was obtained by an conductivity meter (DDS-307).

2.3. Electrochemical Measurement. The linear sweeping voltammetry (LSV) experiment was conducted in a three-electrode cell, which consisted of a working electrode of 1.2 × 1.2 cm^2 aluminum foil and a reference/counter electrode of a lithium wafer (about 1.2 cm in diameter), at a scan rate of 0.1 mV s^{-1}. Both Li−Cu half-cells and Li||NCM523 or Li−S full batteries were assembled in a 2016 coin-type battery including a Cu foil or an active material cathode plate, a piece of Celgard separator, and a lithium chip (1 mm in thickness) with a 25 × 2 μL electrolyte in a glovebox under an argon atmosphere with both oxygen content and water content less than 0.1 ppm. The galvanostatic charge/discharge performance of the cells was tested with a Land BT2000 battery test instrument (Wuhan, China) at 25 °C.

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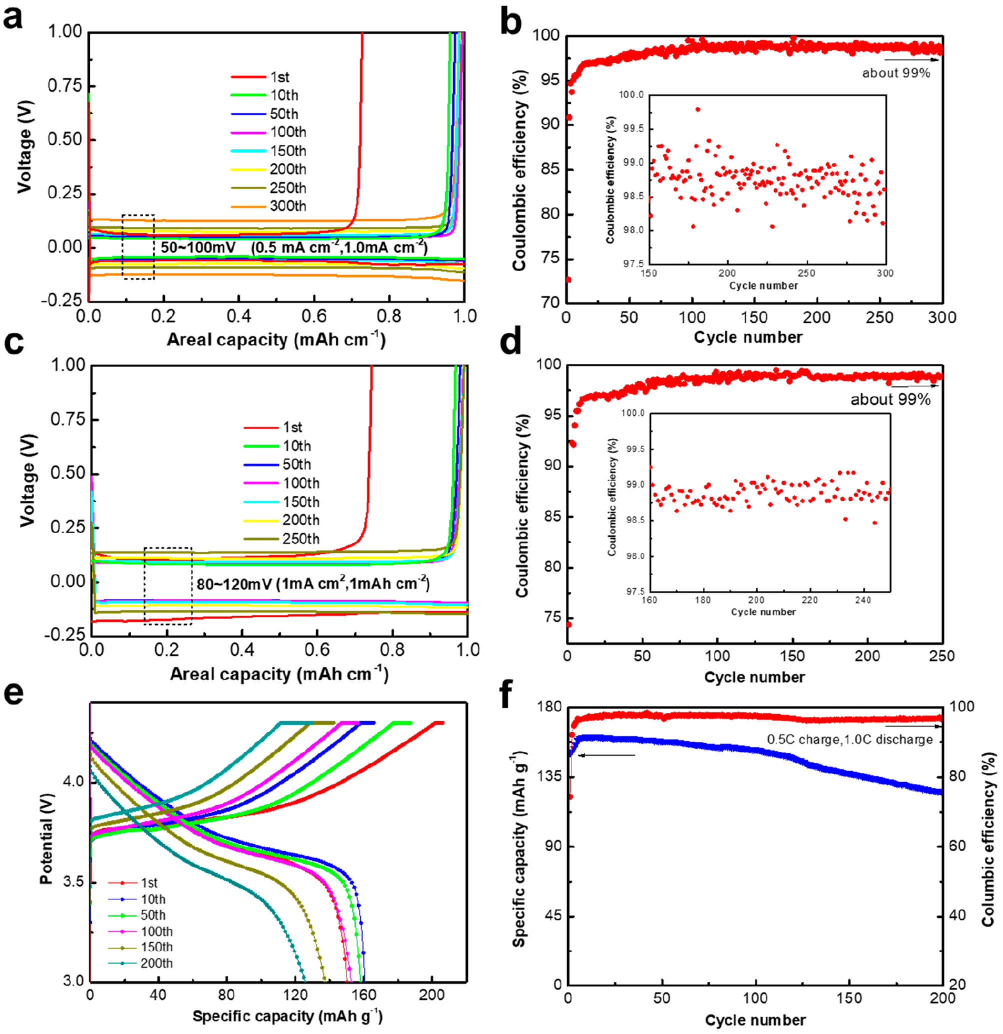

Figure 2. Electrochemical performance of Li||Cu and Li||NCM523 batteries in DME-5M-$LiCO_2CF_3$. (a−f) Li plating/stripping profile on a Cu working electrode and cycling performance of Li||Cu cells at current densities of 0.5 mA cm^{-2} (a, b) and 1 mA cm^{-2} (c, d), respectively. (e) Voltage profiles of Li||NCM523 batteries at the selected number of cycles. (f) Discharge capacity and cycling stability at the condition of 0.5C charge and 1C discharge (1C = 160 mAh g^{-1}).

3. RESULTS AND DISCUSSION

First, we prepared two kinds of dilute DME-based ether electrolytes of 1 mol L^{-1} $LiCO_2CF_3$ and 1 mol L^{-1} LiFSI and then conducted the LSV experiments in a three-electrode cell at the scan rate of 0.1 mV s^{-1}. Apparently, the oxidation potential on the Al electrode in DME-1M-$LiCO_2CF_3$ electrolyte is above 4.3 V (about 4.5 V, Figure 1a), higher than 4.2 V of DME-1M-LiFSI,[21] which indicates its practicality in the high-voltage battery systems. As for the electrochemical performance of Li||NCM523 batteries, there is no obvious overcharge in the 3.0−4.3 V voltage range, which is consistent with the result of LSV. As for the cyclic performance of the batteries, the capacity retention rate in the DME-1M-$LiCO_2CF_3$ can reach nearly 80% after 100 cycles (0.5 charge, 1C discharge, 1C = 160 mAh g^{-1}), whereas the other one (in the DME-1M-LiFSI) almost causes an overcharging. Even if there is no overcharge, the capacity continues to rapidly decline, with only no more than 30% capacity remained after 100 cycles (Figure 1d). The above results fantastically demonstrate that this new type of ether electrolyte with $LiCO_2CF_3$ is antioxidative on the positive electrode, and its resistance to corrosion is the best among the dilute ether electrolytes ever reported.[21] Of course, we can see that the polarization voltage of Li||Cu batteries is relatively high, about 180 mV (Figure 1e, inset), which may be related to the formation of passivation film on the lithium-metal surface caused by the generation of CO_2 from the decarboxylation reaction[24] of $LiCO_2CF_3$, and the Coulombic efficiency still remains 98.5% (Figure 1e) after 100 cycles. However, the DME-1M-LiFSI is less polarized (about 30 mV) but more unstable, which begins to decay after around 50 cycles and decreases to about 70% after the same cycling times (Figure 1f). The results above also seem to indirectly prove that Li_2CO_3 has a better mechanical strength than LiF, which is conducive to the maintenance of interface stability.

Recently, researches on inhibiting lithium dendrites by use of concentrated electrolytes have become more and more extensive. Obviously, the concentrated electrolytes have great superiority in improving the performance of lithium metal. Therefore, we have also increased the concentration of the aforementioned electrolyte to a certain extent, that is, the DME-5M-$LiCO_2CF_3$ high-concentration ether-based electrolyte has been prepared. Then, we have also applied it to the Li||Cu half-cells and carried out the stripping/deposition tests

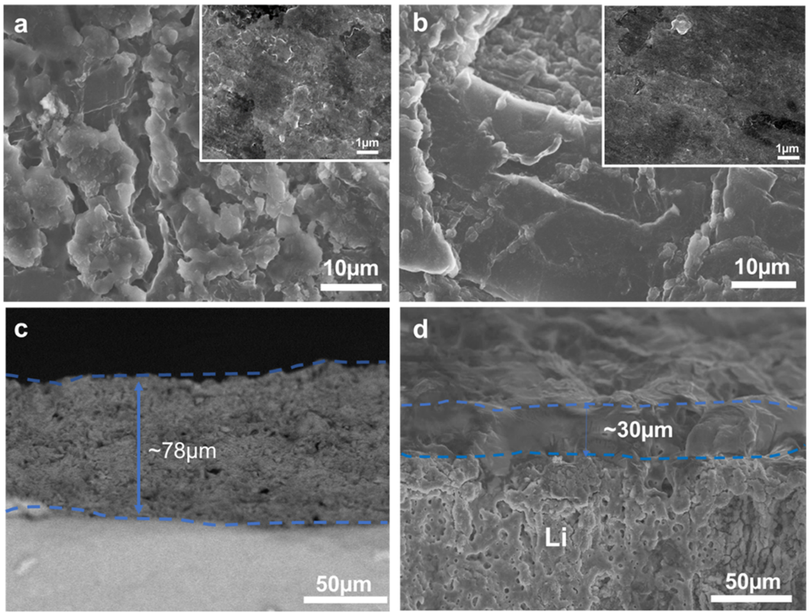

Figure 3. SEM characterization of Li-metal anodes after 50 cycles. (a−d) SEM images of the top view (a, b) and cross section (c, d) for the Li-metal anodes in the two ether electrolytes of DME-1M-$LiCO_2CF_3$ (a, c) and DME-5M-$LiCO_2CF_3$ (b, d).

of lithium metal under the conditions of 0.5 mA cm^{-2} (Figure 2a,b) and 1.0 mA cm^{-2} (Figure 2c,d), respectively. As we expect, the results show that the Coulombic efficiency of the half-cells is around 99% after 250 or 300 cycles under the condition of two kinds of current density. Moreover, the Li||Cu half-cells under the high current density of 0.5 mA cm^{-2} not only maintain the polarization voltage at a relatively lower level (50−100 mV) than the latter (80−120 mV) but also have an average Coulombic efficiency of up to 98.5% for 300 cycles (Figure 2b), which is more advantageous than that of 98.4% for 250 cycles (Figure 2d) of the latter, showing a better cycling stability. At the same time, the full-batteries composed of NCM523 positive electrodes and lithium-metal anodes also achieve an excellent capacity retention rate of over 95.4% after 100 cycles and nearly 84.0% (83.8%) after 200 cycles (Figure 2f), which is much better than that of DME-4M-LiFSI (Supporting Information Figure 1). Clearly, the above-mentioned result also indicates that the cycling stability of positive and negative electrodes is significantly improved under the high concentration conditions and the ether-based electrolyte prepared with this new type of lithium salt is no exception as well.

To investigate the mechanism of the electrolyte on the negative electrode, the cycled lithium foils have been characterized by the scanning electron microscopy. From the morphological point of view (Figure 3a,b), no powdering phenomenon occurred on the surface of lithium metal at either a low or high concentration attributed to the passivation film, which can inhibit the dendrite growth to a certain extent during the deposition/exfoliation process of lithium metal. In contrast, the nonuniform deposition on the surface of the lithium metal under the low concentration condition is more obvious, while it is relatively uniform under the high concentration condition. This indicates that the concentration can effectively alleviate the nonuniform deposition on lithium metal caused by uneven current density due to the concentration polarization, which is also consistent with the cycling performance of Li||Cu batteries. From the cross-sectional view (Figure 3c,d), even in the dilute electrolyte, it can be found that the morphology of SEI is still relatively dense, and the change in the thickness of lithium metal is about 78 μm after 50 cycles of stripping/deposition process, which is obviously better than that in DME-1M-LiFSI (Supporting Information Figure 2b) or that with the thickness of over 100 μm reported by the literature,[23] not to mention that the thickness is further reduced to 30 μm at the concentration of 5 mol L^{-1}, showing an even more outstanding performance.

To further determine the composition of the passivation film formed by the electrolyte on the negative electrode surface, the X-ray photoelectron spectroscopy has been performed. To be specific, the lithium metal cycled after 50 times in the half-batteries is characterized by XPS of three elements including C 1s, O 1s, and F 1s. By combining with the analyses of several spectra, it is found that the SEI film components on the lithium surface at low concentration mainly include the lithium alkoxide (LiOR, about 531 eV, O 1s), lithium fluoride (LiF, about 685 eV, F 1s), lithium carbonate (Li_2CO_3, about 532.5 eV, O 1s), and so on. However, under the condition of high concentration, the proportions of different compositions are greatly changed, namely, Li_2CO_3 is the main component accompanied by a relatively small amount of LiOR and LiF. Based on the above differences, we speculate that it might be attributed to the fact that the decomposition contribution from DME solvent is greater at low concentration, while the proportion of lithium salt decomposition is significantly increased when the concentration is increased. Meanwhile, we have found that the SEI film components in the DME-1M-LiFSI are mainly composed of LiOR, LiF, and S═O species (Supporting Information Figure 3), which suggests that both solvent and lithium salt play a major role in forming a passivation film in the dilute electrolyte. Also, it also demonstrates that the C═O species is quite important to improving the cycle stability of the batteries. Moreover, the passivation film mainly composed of lithium carbonate has a relatively poor ionic conductivity but good mechanical

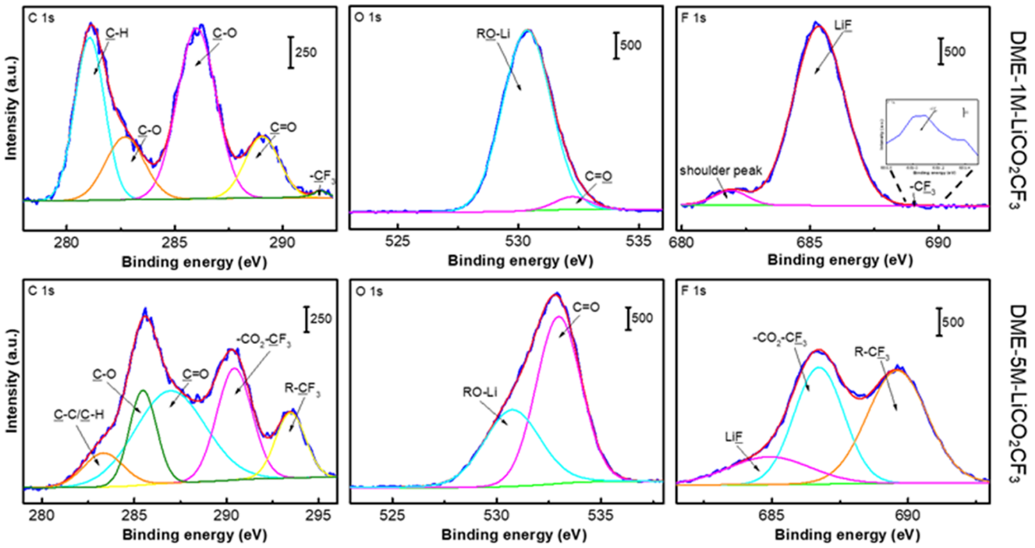

Figure 4. XPS characterization of the SEI components on the Li-metal anodes after 50 cycles. C 1s, O 1s, and F 1s XPS spectra of the Li anodes in the DME-1M-LiCO$_2$CF$_3$ and DME-5M-LiCO$_2$CF$_3$ electrolytes.

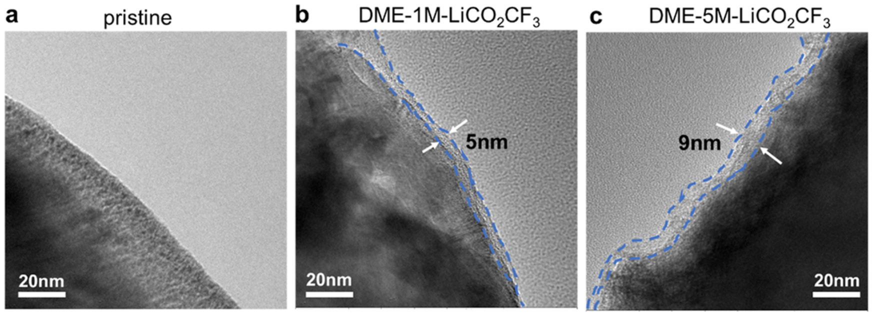

Figure 5. TEM characterization of NCM523 cathodes before and after 50 cycles. (a−c) Pristine NCM523 cathode (a) and the cycled NCM523 cathodes in DME-1M LiCO$_2$CF$_3$ (b) and DME-5M LiCO$_2$CF$_3$ (c).

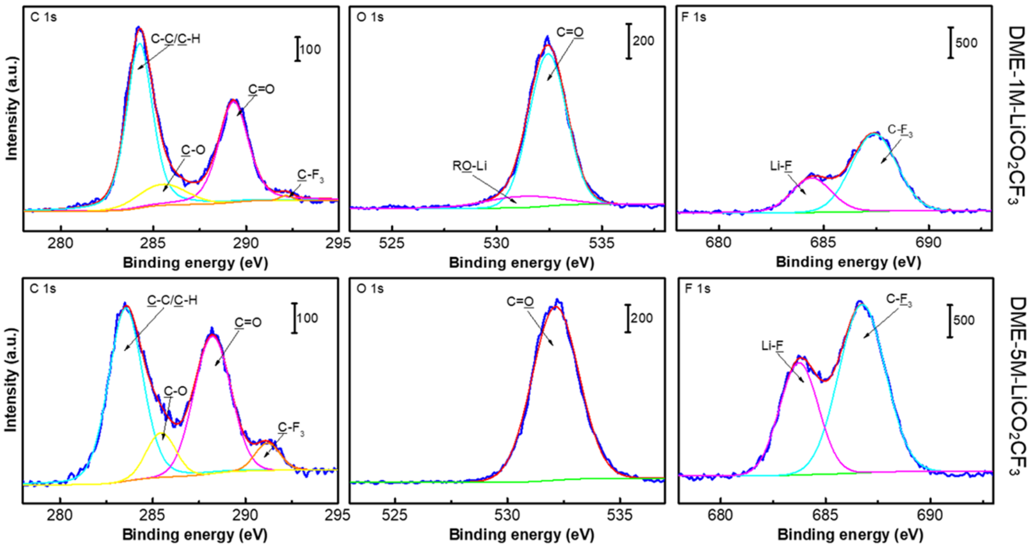

Figure 6. XPS characterization of the CEI components on the NCM523 cathodes after 50 cycles. C 1s, O 1s, and F 1s XPS spectra of the cycled NCM523 cathodes in DME-1M-LiCO$_2$CF$_3$ and DME-5M-LiCO$_2$CF$_3$ electrolytes.

strength, which is also consistent with the performance of Li||Cu batteries in our work. However, in most cases, the SEI membranes formed by commonly used lithium salts, such as LiTFSI, LIFSI, LiPF$_6$, and lithium trifluoromethanesulfonate (LiSO$_3$CF$_3$), mainly comprise LiF and have a relatively excellent ionic conductivity but a relatively poor mechanical strength, which is just opposite to the passivation film in our work. In view of above facts, we hypothesize that mixing these two different types of lithium salts may achieve the effect of complementary advantages; therefore, we have chosen $LiSO_3CF_3$, which can produce the required passivation film components, and carried out some relevant verification experiments. First, a high concentration of 5 mol L^{-1} DME-based ether electrolyte was prepared for the Li||Cu half-cell tests. Just as we envisage, the polarization voltage is indeed small, about 30 mV, but its Coulombic efficiency is only about 80% along with the extremely terrible cyclic stability (Supporting Information Figure 4). On the other hand, after mixing it with $LiCO_2CF_3$, it is surprising to find that the performance of Li||Cu half-cells in a mixed dual-salt electrolyte is obviously different, namely, the polarization voltage is approximately 50 mV and the cycling stability using DME-23M-LSCF, which is a mixed DME-based dual-salt electrolyte composed of 2 M $LiSO_3CF_3$ and 3 M $LiCO_2CF_3$, as the electrolyte is almost comparable to that of DME-5M-LCF electrolyte (Supporting Information Figure 5). The above results not only prove the correctness and feasibility of our previous conjecture but also broaden the application range of such type of lithium salt and provide a practical and effective way to modify lithium-metal anodes (Figure 4).

Of course, the reason why the oxidation stability of this kind of ether electrolyte is improved has also attracted our attention. The passivation mechanism of two different concentrations of electrolytes on the positive electrode surface needs further investigation. Therefore, we have performed the TEM (Figure 5) and XPS (Figure 6) characterizations. The cathode cycled 50 times in Li||NCM523 cells displays that the film is relatively thin with about 5 nm thickness at low concentration (Figure 5b), while it is nearly twice as thick as the former, about 9 nm at the high one (Figure 5c), exhibiting that the high concentration is more beneficial to the passivation of the positive electrode, which is in good agreement with the electrochemical performance of the Li||NCM523 batteries. Furthermore, as the TEM characterization (Supporting Information Figure 6a) result of the cycled NCM523 cathode in DME-1M-LiFSI shows, it is not difficult to observe that the cathode−electrolyte−interface (CEI) layer is irregular and even partly damaged. Also, after analyzing the XPS data (Supporting Information Figure 6b), we can even find the M−O signal, which suggests the electrolyte is not able to effectively suppress the cathode side reactions, and this is also consistent with the electrochemical performance. In addition, we have also compared the XRD results of cathodes cycled 100 times with the pristine cathodes (Supporting Information Figure 7). From the figures, we can see that the cathodes before and after cycling are almost the same under high-concentration conditions, with only a slight decrease in peak intensity probably caused by the surface passivation film. However, at low concentration, there is an obvious difference of peaks that may be due to the relatively thin and inhomogeneous passive films failing to protect the cathode structure from being destroyed during the cycling process, which can also correspond to the differences in the electrochemical performance of the Li||NCM523 batteries. Moreover, based on the good film-forming property of electrolyte on the positive electrode surface, we also try to apply it to Li−S battery system for the performance exploration. Three kinds of ether electrolytes, including DOL/DME-1M-$LiCO_2CF_3$, DOL/DME-1M-LiTFSI, and DOL/DME-1M-LiTFSI with 1% $LiNO_3$ additive, have been prepared, and then the electrochemical properties of lithium-metal battery systems assembled by both Li foil anode and pure S cathode are tested. To our surprise, the cycle stability and capacity retention rate of DOL/DME-1M-$LiCO_2CF_3$ are the most remarkable, even without an additive, as seen from the specific capacity-cycle times curve of 100 cycles (Supporting Information Figure 8), which further manifests the superiority of this kind of lithium salt.

Also, the XPS characterization of several elements, such as C 1s, O 1s, and F 1s, was carried out and the spectra were analyzed to determine the composition of the cathode surface passivation film (Figure 6). We have found that whether in low- or high-concentration condition, the composition of the cathode−electrolyte−interface (CEI) on the positive electrode is basically the same, mainly including Li_2CO_3, LiF, and LiOR, while the content of lithium carbonate is higher under the high-concentration condition, which is in line with our expectation. This suggests that the decomposition reaction of lithium salt has an important effect on the composition of the ingredients.

4. CONCLUSIONS

$LiCO_2CF_3$, one kind of lithium carbonate, is first applied to the DME-based ether electrolyte, which has no obvious corrosion on the surface of Al collectors and enables the capacity retention of 4.3 V high-voltage Li||NCM523 battery systems to approach 80% after 100 cycles even in the dilute solution. On the other hand, the Coulombic efficiency of Li||Cu cells is about 99.0% and the average Coulombic efficiency is 98.4% after 250 cycles at a relatively high current density of 1 mA cm^{-2} along with the concentration of electrolyte up to 5 mol L^{-1}, which is much better than 97.8% of the dilute electrolyte around 100 cycles at same condition. Furthermore, the capacity retention rate of Li||NCM523 batteries is approximately 95.4% after 100 cycles and nearly 84.0% after 200 cycles, exhibiting more excellent improvements as well. Moreover, the salt has been applied to the Li−S battery system, and its performance is also promising. To sum up, these studies have unraveled that $LiCO_2CF_3$ has a great potential to obtain outstanding outcomes in the high-voltage lithium-metal batteries, and its future developments and applications are bound not to be underestimated. Of course, more systematic researches and performance optimizations are still being performed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b08703.

Cycling performance of Li||NCM523 full batteries in DME-4M-LiFSI electrolyte and Li−S full batteries in three kinds of DOL/DME-based ether electrolytes including DD-1M-$LiCO_2CF_3$, DD-1M-LiTFSI, and DD-1M-LiTFSI + 1% $LiNO_3$, XRD of pristine and 100 times cycled NCM523 cathodes in DME-1M-$LiCO_2CF_3$ and DME-5M-$LiCO_2CF_3$ electrolyte, Li||Cu half-cells performance in DME-5M-$LiSO_3CF_3$ and DME-23M-LSCF electrolyte; ionic conductivity of the two electrolytes with different concentrations at 25 °C; SEM, XPS, and TEM characterizations of electrodes cycled with DME-1M-LiFSI electrolyte (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of National Key Research and Development Program of China (2017YFB0102000), National Natural Science Foundation of China (21603179 and 21621091), the Fundamental Research Funds for the Central Universities (20720170021). The authors also thank Prof. Daiwei Liao for his valuable suggestions.

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