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Research Article

Functional Electrolyte of Fluorinated Ether and Ester for Stabilizing Both 4.5 V $LiCoO_2$ Cathode and Lithium Metal Anode

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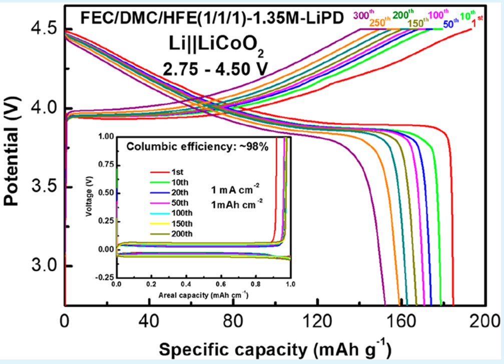
ABSTRACT: In our work, fluoroethylene carbonate (FEC) with higher ionic conductivity and oxidative stability has been used to replace ethylene carbonate along with 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (HFE) added to obtain a trisolvent electrolyte system of 1.2 M $LiPF_6$ in FEC/dimethyl carbonate/HFE (1:1:1 by volume). In addition, on the basis of such an electrolyte, we have also added 0.15 M lithium difluoro(oxalato)borate as a film-forming additive to further stabilize both the cathode and anode, so that a new bifunctional electrolyte of 1.35 M has been obtained. The new electrolyte enables Li||$LiCoO_2$ batteries to maintain nearly 84% capacity after 300 cycles when charged to 4.5 V under the current density of 200 mA g^{-1}. Meanwhile, it can also make Li||Cu half-cells maintain about 98% coulombic efficiency after being charged/discharged 200 times under 1 mA cm^{-2} current density and 1 mAh cm^{-2} lithium deposition amount per cycle, showing an obvious advantage in the stability of lithium metal.



KEYWORDS: *fluorinated solvent, ester electrolyte, high-voltage $LiCoO_2$, lithium metal, LiDFOB additive*

1. INTRODUCTION

Lithium-ion batteries[1−4] have been widely used in portable electronic devices, such as consumer electronics and power tools, and have also been popularized in large-scale energy storage, such as electric vehicles, as a result of their high energy density[5,6] and long cycle life.[7,8] However, as the market share of power lithium batteries increases year by year, higher requirements are placed on their energy density, cycle life, and safety. As we all know, one of the key factors to improve the energy density of lithium-ion batteries is to broaden its voltage range. In addition to the development of high-voltage[9−14] cathode materials, the studies on electrolytes[15,16] with higher oxidative stability are also very important. As far as the current situation is concerned, on one hand, some commercial electrolytes have relatively low electrochemical stability windows, such as carbonate-based electrolytes, with the electrochemical window of <4.3 V (versus Li/Li^+), and are prone to take place with side reactions in the electrode interface and so on, which greatly limits their application as lithium-ion batteries, and on the other hand, the ester electrolyte is difficult to form a stable solid electrolyte interface (SEI) film on the surface of the anode and impossible to suppress the lithium dendrites, which also limits its further development in the lithium metal battery.[17−28] It is well-known that the ether electrolytes[29−31] have a unique advantage in lithium metal modification; that is, they can form a stable SEI film to inhibit lithium dendrite[32] growth, but they also have a poor cathodic stability, with the stable electrochemical window, at only about 3.7 V, still very flawed. Although high-concentration[24,33−38] bis-ether electrolytes in the 4.3 V system has also been reported,[29] their ultrahigh concentration and limited oxidative stability[15] cannot be further applied in higher voltage lithium metal battery systems. Therefore, it is particularly important to realize the good match of electrolytes and electrode materials in a high-voltage lithium metal battery system above 4.3 V.

In our work, we replaced ethylene carbonate (EC) with fluoroethylene carbonate (FEC),[39,40] which owns higher ionic conductivity and oxidative stability. Moreover, we chose fluorinated ether solvent 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (HFE) as a co-solvent, which is not only used as a high-voltage additive[14,41,42] but also widely used as a diluent[34,43−45] for high-concentration electrolytes. In addition, because lithium difluoro(oxalato)borate (LiDFOB)[46−48] can form a relatively stable film on both cathode and anode material surfaces, we added 0.15 M LiDFOB to the 1.2 M $LiPF_6$ trisolvent mixed electrolyte system to obtain a 1.35 M new functional electrolyte. This electrolyte enables the lithium metal battery using $LiCoO_2$ as a cathode material to have a nearly 84% capacity retention rate under the current density of

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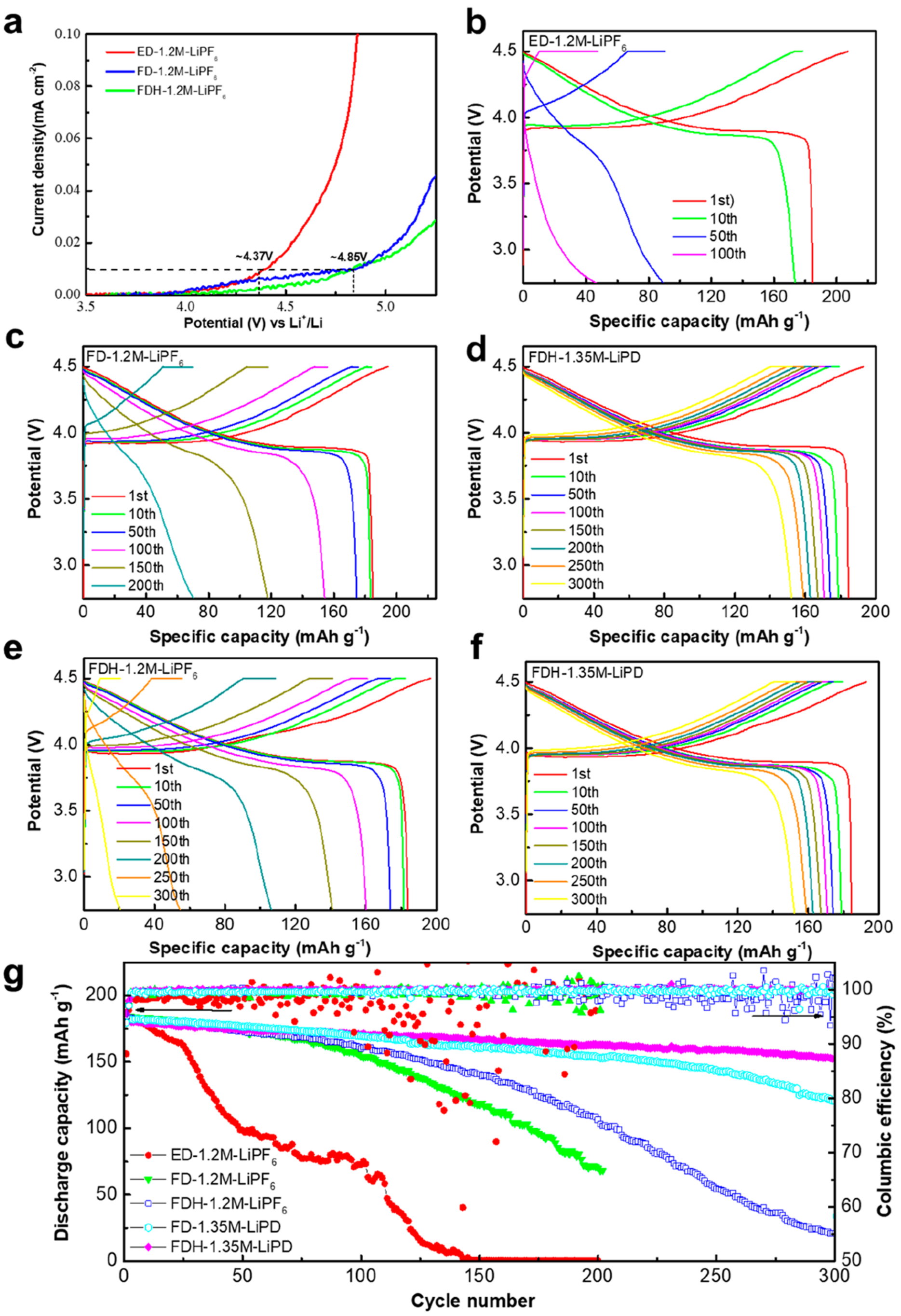

Figure 1. (a) LSV test results of three electrolytes in the three-electrode system of an Al foil working electrode and a lithium sheet for reference/counter electrode at the scan speed of 1 mV s^{-1}. (b–f) Selected cycles of the Li||LiCoO$_2$ battery under five electrolyte conditions. (g) Li||LiCoO$_2$ battery cyclic performance using the five electrolytes within the voltage range of 2.75–4.5 V at the current density of 200 mA g^{-1}.

200 mA g^{-1} along with the 4.5 V cutoff voltage; at the same time, it also makes Li||Cu half-cells maintain about 98% coulombic efficiency after being charged and discharged for 200 cycles under the 1 mA cm^{-2} current density and 1 mA h cm^{-2} lithium deposition amount per cycle, showing a significant advantage in stabilizing lithium metal. By the way, through the comparison of experimental variables, we have a relatively clear understanding of the role of various components of the electrolyte. In detail, the addition of FEC is critical to improve the performance of both the cathode and anode, but that is not enough. With the addition of HFE, on the one hand, it can be used as a high-voltage additive to enhance the performance of the LiCoO$_2$ cathode material, while on the other hand, it still indirectly increases the concentration of the electrolyte as a diluent for a local high-concentration electrolyte, which has a certain effect on the performance improvement of the lithium metal anode. In addition, LiDFOB itself is also a widely used additive, which can not only form a stable cathode electrolyte interface (CEI) film to further improve the cycle stability of high-voltage LiCoO$_2$ but also stabilize the lithium anode with a stable SEI

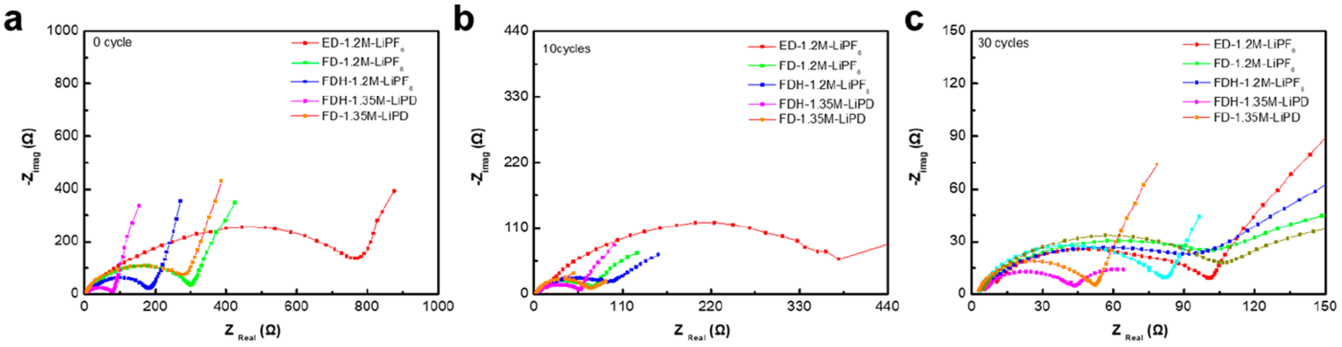

Figure 2. Comparison of EIS characterization results of the Li||LiCoO$_2$ batteries before and after 10 and 30 cycles in the five electrolytes, separately. (a−c) Impedance values (R_{SEI}) of Li||LiCoO$_2$ batteries after (a) 0 cycles, (b) 10 cycles, and (c) 30 cycles in five kinds of electrolytes, separately.

film. Finally, the effect of "1 + 1 > 2" is achieved by an effective and appropriate combination of these components.

2. EXPERIMENTAL SECTION

2.1. Material Preparation. The LiCoO$_2$ electrode laminated pole piece was made up of a blend of LiCoO$_2$ active material, acetylene black conductive agent, and polyvinylidene fluoride (PVDF) binder on the basis of a mass ratio of 8:1:1, with electromagnetic stirring for 6 h with *N*-methyl-2-pyrrolidone (NMP) solvent. Aluminum (Al) foil was used as the slurry carrier, and then it was baked on a 60 °C heating board for half an hour and kept in a 80 °C vacuum oven overnight. The active positive electrode material loading amount was close to 8 mg cm^{-2}. The electrolytes were prepared by dissolving 1.2 M LiPF$_6$ in EC/dimethyl carbonate (DMC) (1:1 by volume), FEC/DMC (1:1 by volume), and FEC/DMC/HFE (1:1:1 by volume) solvents to obtain ED-1.2M-LiPF$_6$, FD-1.2M-LiPF$_6$, and FDH-1.2M-LiPF$_6$, three electrolytes with the same concentration, respectively. FD-1.35M-LiPD was obtained by adding 0.15 M LiDFOB to FD-1.2M-LiPF$_6$. In addition, 0.05, 0.15, and 0.3 M LiDFOB were separately added to FDH-1.2M-LiPF$_6$ to obtain FDH-1.25M-LiPD, FDH-1.35M-LiPD, and FDH-1.5M-LiPD. The electrode piece and the lithium piece were all 12 mm in diameter. The Celgard provided us with the separator.

2.2. Material Characterization. A Rigaku MiniFlex 600 X-ray diffractometer was used to measure X-ray diffraction (XRD) patterns using Cu K$_2$ radiation within the angle range between 10° and 70° under the rate of 2° min^{-1}. Field emission scanning electron microscopy (FESEM, Hitchi 4800) was used to obtain the scanning electron microscopy (SEM) images. JEM2100 equipment was used to pick the transmission electron microscopy (TEM) pictures. A PHI Quantum 2000 device was used to obtain the X-ray photoelectron spectroscopy (XPS) analyses. A DDS-307 conductivity meter was used to acquire the electrolyte ionic conductivity. STA 449 F3 Jupiter was used to measure differential scanning calorimetry (DSC) data.

2.3. Electrochemical Characterization. A three-electrode system composed of a 1.2 × 1.2 cm Al foil working electrode along with a lithium plate reference electrode/counter electrode was carried out for the linear sweep voltammetry (LSV) test to obtain data on a CHI660D electrochemical workstation under the sweep speed of 1 mV s^{-1}. The Solartron equipment was used to pick the electrochemical impedance spectroscopy (EIS) data. Both Li||Cu half-cells and Li||LiCoO$_2$ full batteries consisted of a 2016 coin-type cell, which contained a copper foil or LiCoO$_2$ cathode laminate, a slice of separator and lithium sheet, and a 2 × 35 μL electrolyte. They were assembled in a glovebox full of argon, along with <0.1 ppm water content and oxygen content. The Land BT2000 battery test system was used to conduct the galvanostatic tests after the assembled batteries were allowed to stand for 12 h at room temperature.

3. RESULTS AND DISCUSSION

In the first place, we prepared ED-1.2M-LiPF$_6$, FD-1.2M-LiPF$_6$, and FDH-1.2M-LiPF$_6$, three kinds of electrolytes with the same concentration, and then conducted the LSV experiments to compare their stable electrochemical windows. It can be seen from the test results in Figure 1a that the replacement of EC with FEC increases the oxidative resistance potential of the electrolyte, that is, from about 4.37 to about 4.85 V, which provides the potential of applying it to the 4.5 V high-voltage lithium battery system. In addition, we can also find that adding a certain amount of HFE to the electrolyte as a co-solvent reduces the oxidation current to a certain degree, indicating that it can indeed act as a diluent to indirectly increase the electrolyte concentration. By the way, we also measured the ionic conductivity of the above three electrolytes at 25 °C (Table S1 of the Supporting Information). The results show that the addition of FEC greatly improves the ionic conductivity of the electrolyte, and the introduction of HFE has almost no negative impact. Then, we applied several electrolytes to the Li||LiCoO$_2$ battery system with 200 mA g^{-1} current density along with a voltage range of 2.75−4.50 V. We can see from the results (Figure 1b) that the ED-1.2M-LiPF$_6$ electrolyte causes the battery to rapidly decay after around 20 cycles and the capacity retention rate is less than 80% in less than 50 cycles, while the modified electrolyte FDH-1.35M-LiPD under the same conditions makes the battery maintain a capacity of nearly 84% (83.6%) after 300 cycles, which suggests that the cycling stability is obviously improved. By designing related control experiments, we can also see that it is necessary to use the interactions of components. To be specific, FD-1.2M-LiPF$_6$ is able to maintain a 94.8% capacity retention rate after 50 cycles compared to that of the unmodified electrolyte, with a large degree of improvement, but it only remains 63.9% after 150 cycles, indicating that the simple replacement of EC is still insufficient to meet the performance requirements that we need. Further, by adding a certain amount of HFE, it can be used as a high-voltage additive to improve the cathode performance. When it comes to the optimal ratio of solvent, on one hand, we refer to the relevant literature[48] to know that the three-component system containing FEC has the best effect when it accounts for one-third of the total, while on the other hand, we also compare the experimental results of different contents. In the case where the amount is too small, the performance is not improved well, and when the amount is too large, the solubility is limited (Figure S2 of the Supporting Information). Therefore, in combination with the above analyses, it can finally maximize the effect when the three components are uniform. Of course, in comparison to the battery performance of FDH-1.2M-LiPF$_6$, the cycle stability is indeed improved to remain 76.7% after 200 times cycling,

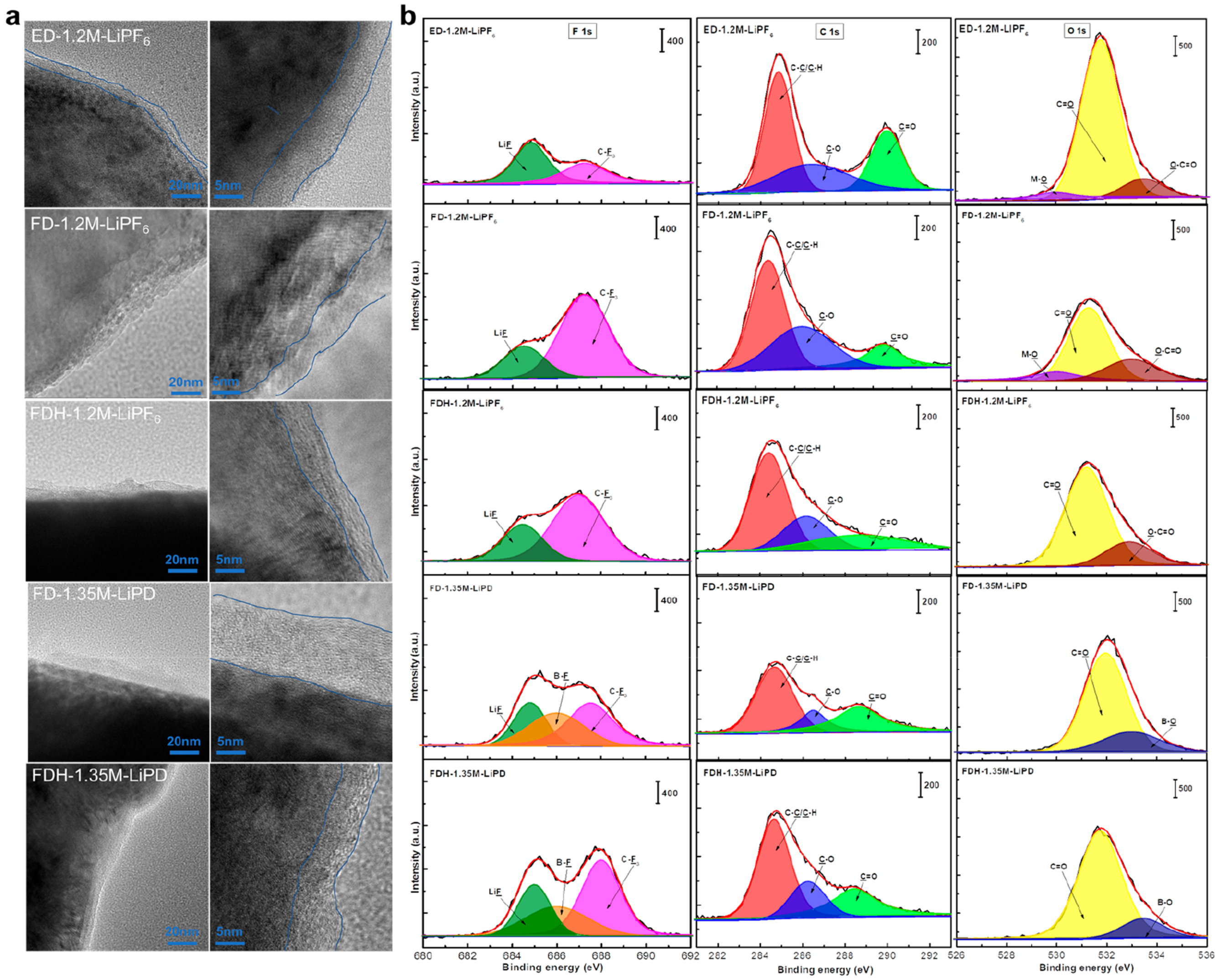

Figure 3. TEM and XPS characterization results of the cathode materials of Li||LiCoO$_2$ batteries after 10 cycles in five electrolytes. (a) TEM images of LiCoO$_2$ cathodes cycled 10 times in five kinds of electrolytes, separately. (b) XPS characterization analyses of C 1s, O 1s, and F 1s on cycled 10 times LiCoO$_2$ cathode surfaces in five kinds of electrolytes, separately.

better than that without HFE, but there is still much room for improvement. Furthermore, on the basis of the above modified electrolyte, we tried to add a certain amount of LiDFOB additive to further improve the performance. Similarly, we did some comparison experiments on dosage (more details can be obtained from Figure S2 of the Supporting Information) and finally chose 0.15 M as the optimal amount. Meanwhile, to prove the necessity of the addition of HFE, we carried out a control experiment to prove it. In terms of the cycle performance, the electrolyte containing no HFE but with LiDFOB makes the battery contain only 11.3% of the capacity left after 300 cycles; however, the other electrolyte maintains as high as 83.6% after 300 cycles, suggesting that various components are indispensable. Additionally, we performed a comparison of the impedance values of the batteries in the high-frequency range before and after the cycle in different electrolytes (Figure 2). The results are also basically consistent with our conjecture and related electrochemical experiments; that is, the modified FDH-1.35M-LiPD mixed electrolyte makes the battery have the smallest interface impedance (R_{SEI}) among all.

To further understand the mechanism of the electrolytes on the cathode, we carried out XRD, TEM, and XPS characterization tests. First, from the XRD of the cathode material in different electrolytes before and after cycling (Figure S1 of the Supporting Information), it can be found that the structure of the LiCoO$_2$ cathode material is obviously greatly damaged after using the unmodified electrolyte for 200 cycles, while there is a significant improvement in structural integrity with the modified electrolyte, which is also in accordance with the electrochemical performance. Besides, by comparison of the TEM results of the cathode material of Li||LiCoO$_2$ batteries after 30 cycles of using different electrolytes (Figure 3), it can be seen that the passivation film is also formed on the cathode surface using the electrolyte without any modification, whose morphology is obviously loose and vulnerable, which is unfavorable for the maintenance of battery cyclic stability. However, the uniformity and compactness of the CEI film have also changed significantly after optimization. Furthermore, by characterization of the XPS of the elements of F 1s, C 1s, and O 1s on the surface of the LiCoO$_2$ cathode after 10 cycles, it can be seen that the passivation film component without

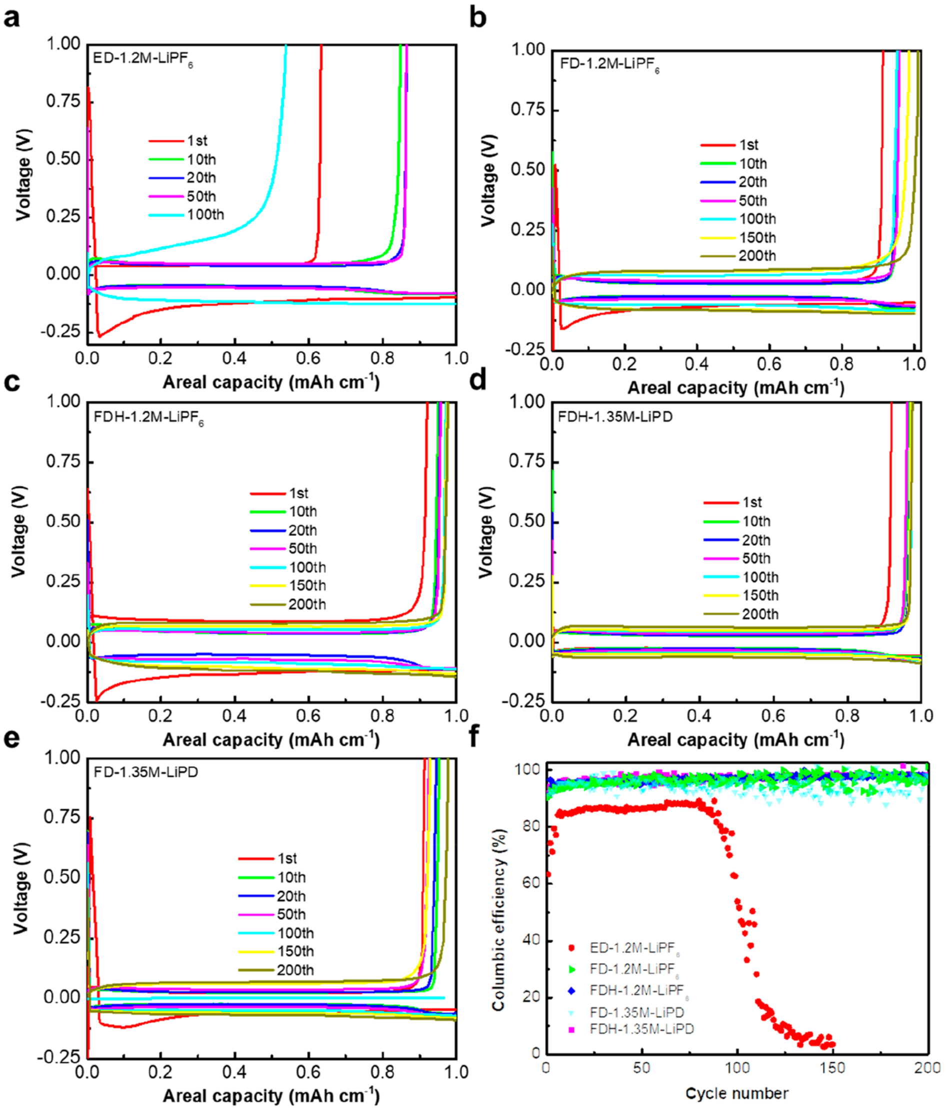

Figure 4. Electrochemical performance of Li||Cu half-cells. (a−e) Specific Li depositing/exfoliating curve in Li||Cu half-cells with a Cu working electrode using five different electrolytes under the current density of 1 mA cm^{-2}. (f) Cycling performance of Li||Cu half-cells using five electrolytes.

modification mainly includes lithium fluoride (LiF; 684.9 eV, F 1s), lithium carbonate (Li_2CO_3; 288.5 eV, C 1s; 532 eV, O 1s), and lithium alkoxide (LiOR; 530.9 eV, O 1s). However, the content of LiF does not significantly increase after EC is replaced by FEC, indicating that the fluorinated solvent makes little contribution to the CEI layer. M−O (530 eV, O 1s) can also be observed on the cathode surface with the above two electrolytes, which may imply a small amount of dissolution of the cathode material during the cycle. On the other hand, FDH-1.2M-$LiPF_6$ with the addition of HFE makes a slight increase in the content of LiF, which shows its function as a high-voltage additive. The presence of M−O is not detected, suggesting that the electrolyte has a certain effect to protect the structural integrity of cathodes. Further comparison of the two electrolytes with the LiDFOB additive reveals that the additive not only increases the B-containing components, such as B−F and B−O, but also increases the content of LiF and Li_2CO_3. These changes are the important determinants for maintaining stability under a high-voltage condition of 4.5 V. As a consequence, our optimized modified FDH-1.35M-LiPD electrolyte makes good use of the synergistic complementation of different components, leading the Li||$LiCoO_2$ batteries to own an excellent electrochemical performance in 4.5 V high-voltage cycling, which is also what we want.

On the other hand, we applied the five electrolytes to Li||Cu half-cells (Figure 4). The results show that the ED-1.2M-$LiPF_6$ electrolyte fails to form a stable SEI passive film, and then the columbic efficiency of the half-cells is just close to 87%, along with poor stability. With the replacement of EC with FEC, the coulombic efficiency and cyclic stability of the half-cells are significantly improved, indicating that the addition of FEC has a great advantage for improving the lithium anode performance. In addition, what we hope that the fluorinated ether is added to the electrolyte as a diluent to modify lithium metal performance has not been greatly achieved in FDH-1.2M-$LiPF_6$. However, when we continued to add 0.15 M LiDFOB additive, the electrolyte makes Li||Cu half-cells remain with about 98% coulombic efficiency after lithium deposition/exfoliation for 200 times and the polarization voltage is also stabilized at about 60 mV, showing relatively great electrochemical performance. To further prove the effect of HFE, we prepared FD-1.35M-LiPD, an electrolyte without HFE but still

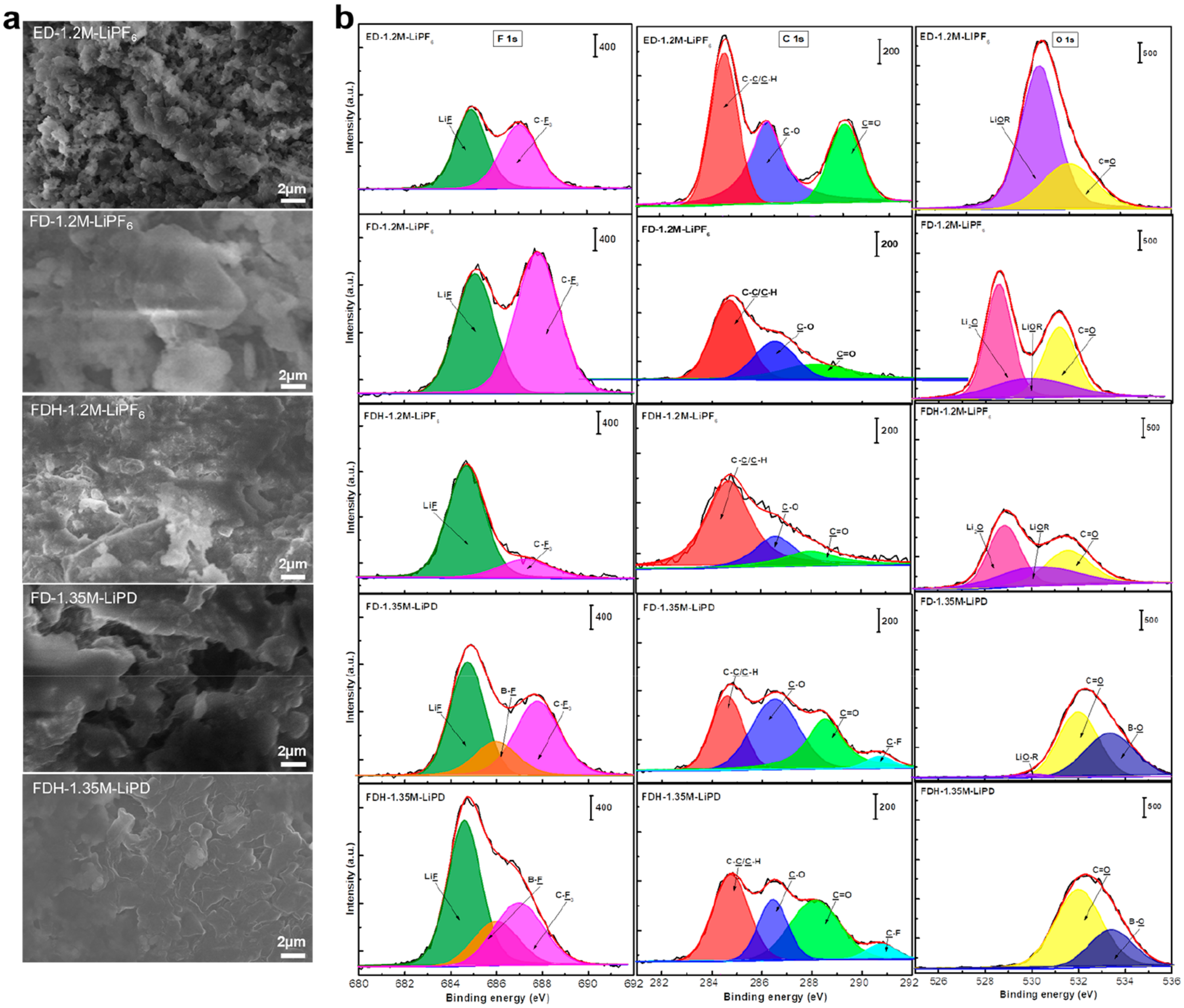

Figure 5. SEM and XPS characterization results of the lithium anode surface of Li||Cu half-cells after 50 cycles in five electrolytes. (a) SEM images of Li anodes after 50 cycles in five kinds of electrolytes, separately. (b) XPS characterization analyses of F 1s, C 1s, and O 1s on cycled 50 times Li anode surfaces in five kinds of electrolytes, separately.

containing 0.15 M LiDFOB, and conducted a control experiment. From the results, we can see that the cycling performance of the half-cells is still inferior to that of the former, which indicates the necessity of HFE. The above controlled experiments also well illustrate that different substances need to complement each other to achieve the best results.

To further prove our point of view and reveal its mechanism, we conducted the characterization tests, such as SEM and XPS. At first, the characterization results of SEM (Figure 5) show that the cycled lithium anode surface shows a high degree of loose powdering in the ED-1.2M-LiPF$_6$ electrolyte, indicating that it has been severely damaged. Meanwhile, in combination with the characterization of XPS, including the elements of F 1s, C 1s, and O 1s, it can be seen that the content of the LiOR component on the lithium surface is the highest and the contents of LiF and Li$_2$CO$_3$ are relatively low. In fact, the SEI film composed of the above components does not benefit for inhibiting lithium dendrite growth. As for FD-1.2M-LiPF$_6$ with FEC, the surface of the lithium metal anode is obviously dense and flat. The contents of LiF and Li$_2$CO$_3$ are obviously increased in combination with XPS characterization results, and it is the increase of these two components that greatly improves the ionic conductivity and structural stability of the SEI film, which is also consistent with the electrochemical performance. When it comes to the lithium surface cycled in FDH-1.2M-LiPF$_6$, its state does not change as much as that of FDH-1.2M-LiPF$_6$; however, it can be found that the LiF and Li$_2$CO$_3$ contents are slightly decreased. We guess that HFE used as the diluent can indirectly increase the concentration of the electrolyte and also reduce the amount of FEC, which can form a large amount of LiF passivation film components. However, the overall result is that the stability of half-cells is improved. When we compare the morphology of the lithium metal anode after cycling in the two electrolytes with the LiDFOB additive, it can be seen that the electrolyte containing HFE makes the lithium metal exhibit a dense and smooth sheet-like morphology, while the electrolyte without HFE is also very dense but not so flat. The comparison of XPS results shows that both of them increase the content of B-containing components, such as B−F and B−O, but there is still a difference in the contents of LiF and Li$_2$CO$_3$. The latter two components greatly affect the performance of the half-cells. On the basis of the above results, our optimized design of the FDH-1.35M-LiPD electrolyte not only has excellent electrochemical performance for $LiCoO_2$ at 4.5 V high voltage but also improves the performance of the lithium metal anode. All of these good results actually benefit from the proper interaction with different components.

4. CONCLUSION

By making the most of the existing electrolyte components in an appropriate combination, we have designed a functional electrolyte FDH-1.35M-LiPD, which is beneficial to both high-voltage $LiCoO_2$ cathode material and lithium metal anode. It allows Li||$LCoO_2$ batteries to realize a capacity retention rate of approximately 84% under the 200 mA g^{-1} current density, along with 4.5 V cutoff voltage. At the same time, it also makes coulombic efficiency of the Li||Cu half-cells maintain 98% or so after charging and discharging for 200 times under 1 mA cm^{-2} current density and 1 mAh cm^{-2} lithium deposition amount per cycle. It is noted that, although there is no introduction of new substances in our work, we have also achieved relatively excellent performance of the relevant battery systems, which also inspires us to obtain unexpected results through reasonable use of the common and available materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b21679.

> XRD patterns of pristine and cycled $LiCoO_2$ cathodes in five kinds of electrolytes (Figure S1), cycling performance and voltage profiles at the specific times of Li|| $LiCoO_2$ batteries in three kinds of electrolytes (Figure S2), XPS spectra of B 1s on the cycled $LiCoO_2$ cathodes (10 cycles) and lithium anodes (50 cylces) in two electrolytes (Figures S3 and S4), ionic conductivity, density, and thermal stability of five kinds of electrolytes at 25 °C (Table S1), and performance comparisons of Li||$LiCoO_2$ batteries in five kinds of electrolytes (Table S2) (PDF)

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Notes

The authors declare no competing financial interest.

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