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Article

# An Effective Electrolyte Strategy To Improve the High-Voltage Performance of LiCoO<sub>2</sub> Cathode Materials

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Supporting Information

ABSTRACT: According to the theoretical calculations and combining the advantages of different solvents, an effective electrolyte capable of effectively improving the high-voltage performance of LiCoO<sub>2</sub> (LCO) cathode materials has been designed. The electrolyte utilizes dimethyl sulfone, which can be preferentially oxidized and form a stable protective layer on the surface of the positive electrode material during the cycles. Compared with the conventional electrolyte, by use of our designed electrolyte, the capacity retention rate increases from the original 38.1% up to 87.1% after cycling for 300 times at 4.45 V, and the capacity retention rate is also effectively promoted from the previous 21.0% up to 74.9% after 300 cycles under a higher voltage of 4.55 V. The experimental results show that use of this electrolyte can



effectively inhibit the dissolution of transition metal ions in  $LiCoO_2$  materials, thereby ensuring the structural stability of the cathode material and greatly improving the electrochemical performance. As can be seen from a series of tests, the effective electrolyte system we designed is very promising.

**KEYWORDS:** LiCoO<sub>2</sub>, high-voltage performance, electrolyte, cathodes, lithium-ion batteries

# 1. INTRODUCTION

The high energy density lithium-ion batteries are becoming more and more important in life today.<sup>1-4</sup> To adapt to the promotion and product upgrade of smartphones, electric vehicles, hybrid vehicles, and so on, we must find ways to improve the working voltage of existing lithium-ion batteries and thus increase their energy density for meeting the products' demand.<sup>5,6</sup> In the 1990s, the  $LiCoO_2$  has been used as one of the earliest positive electrode materials for the commercial lithium-ion batteries. As a cathode material with high volume and mass energy density, the layered LiCoO<sub>2</sub> material is highly competitive and has been studied for a long time.<sup>7-9</sup> It is worth noting that after more than 20 years the LiCoO<sub>2</sub> still occupies an important position in the cathode material of consumer lithium-ion batteries. To achieve higher energy density, the charge cutoff voltage of commercial LiCoO<sub>2</sub> batteries has been increased from the original 4.2 to 4.3 V and will continue to move toward higher 4.45 and 4.55 V in the future. However, to date, the LiCoO<sub>2</sub> currently still has many problems in high- voltage cycling, mainly because the material undergoes deep lithium-ion intercalation and extraction when it is circulated under a high-voltage condition, which will lead to dramatic structural damage with the increase of cycle numbers.<sup>10-12</sup> It is understandable that the cracking of the LiCoO<sub>2</sub> material has a very serious impact on the electrochemical performance of the battery. To overcome these problems, in the past few decades, many researches and

optimizations have been performed on the LiCoO<sub>2</sub> material itself, such as atomic doping and protective layer coating.<sup>13–17</sup> Although the stability of the structure can be enhanced by modifying the LiCoO<sub>2</sub> material, this method cannot suppress the oxidative decomposition of the electrolyte at a high voltage, which will still largely limit the high-voltage electrochemical performance of the LiCoO<sub>2</sub> material. Therefore, in addition to solving the problem of structural collapse of the LiCoO<sub>2</sub> material itself under a high voltage,<sup>18</sup> it is also important to reduce the oxidative decomposition of the electrolyte at high voltages.<sup>19-22</sup> A large number of the high-voltage solvents previously published are almost beneficial to the positive electrode materials, but many of them do not form a stable solid electrolyte interface (SEI) film on the graphite surface,<sup>23</sup> resulting in lack of real commercial application possibility.

The research goal of this work is to design a kind of highvoltage electrolyte that can improve the cycle performance of LiCoO<sub>2</sub> at 4.45 V or even 4.55 V and to make it compatible with the graphite anode. The main method is to screen different components through theoretical calculations and make rational use of the advantages of each component. On the basis of careful design and screening, the fluoroethylene dipropyl ether (HFE) and fluoroethylene carbonate (FEC)

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have been chosen as the components to improve the oxidation resistance of the electrolyte. Moreover, the FEC has good film forming properties to ensure this electrolyte compatible with the graphite anodes. In addition, the dimethyl sulfone (MSM) has been selected as a positive film-forming additive to form a stable passivation layer on the surface of the positive electrode, and the dimethyl carbonate (DMC) has been added to reduce the viscosity of the entire electrolyte. According to the above design, a kind of high-voltage electrolyte (the MSM electrolyte) with DMC/HFE/FEC/MSM as a solvent has been prepared, and the chemical structures of four solvents are shown in Figure S1. Through a series of tests, the MSM electrolyte has been proven to greatly improve the cycle performance of Li/LCO cells at 4.45 and 4.55 V, and this electrolyte is well compatible with the graphite anodes.

# 2. EXPERIMENTAL SECTION

**2.1. Density Functional Theory Calculation (DFT).** The DFT calculations were executed by the Gaussian 09 package using the B3PW91 functional in DFT. The B3PW91/6-311++G(d,p) basis set was employed to analyze natural bond orbital (NBO) charge distribution and the equilibrium structures for the steady state and transition state.<sup>24</sup> To explore the effect of the solvent, the equilibrium structure was optimized by using the conductor-variant polarized continuum model (CPCM). The value 46.4 was selected as the dielectric constant of the entire electrolyte, which is the average value of the dielectric constants of ethylene carbonate (EC, 89.6) and DMC (3.1).

**2.2.** Preparation of Electrode and Electrolyte. The conventional electrolyte (LB-301) used was offered by Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. The LB-301 electrolyte was produced by dissolving 1 M LiPF<sub>6</sub> in a mixture of EC/DMC (1:1, m/m).

The designed electrolyte consists of LiPF<sub>6</sub>, DMC, FEC, and HFE (Shanghai Mingxu Electronic Technology Co., Ltd.). After continuous trial and proportional optimization, considering the electrochemical performance and viscosity, the electrolyte was prepared as follows. In the Ar gas-protected glovebox, 1 M LiPF<sub>6</sub> was dissolved in a mixture of DMC/FEC/HFE (30%:35%:35%, m/m/m). When the mixture was stirred evenly, 10 wt % of MSM was added therein. After shaking evenly and standing for 12 h, a high-voltage electrolyte became available, for convenience of description, hereinafter termed MSM electrolyte.

The commercial LiCoO<sub>2</sub> powder was mixed with the conductive agent acetylene black and the binder poly(vinylidene fluoride) (PVDF) at a mass ratio of 94%:3%:3% and then thoroughly stirred and mixed with N-methylpyrrolidone (NMP). Then, the slurry was evenly coated on an aluminum foil and dried in a vacuum oven at 80 °C overnight to prepare the positive electrode. The commercial graphite powder was mixed with the conductive agent acetylene black and the binder PVDF at a mass ratio of 90%:5%5% and then thoroughly stirred and mixed with NMP. The mixture was spread on a copper foil and dried in a vacuum oven at 80 °C overnight to prepare a negative electrode.

**2.3. Electrochemical Measurements.** To evaluate the oxidative decomposition behavior of the LB-301 and MSM electrolytes, the linear sweep voltammetry (LSV) was performed on the electrolyte with a scanning interval from open circuit voltage (OCV) to 6 V at sweep rate of 0.1 mV s<sup>-1</sup>. The LSV test was performed using a three-electrode electrolytic cell with the platinum electrode was the working electrode (WE), and the lithium plate was the counter electrode (CE) and the reference electrode (RE).

The commercial  $LiCoO_2$  material was used as the positive electrode, the lithium plate was the negative electrode, and the Asahi Kasei polyethylene porous membrane was used as the separator. The prepared LB-301 or MSM electrolyte was added dropwise and assembled into the Li/LCO CR-2016 coin cells in the Ar gas-protected glovebox. The 2016-type coin cells were used to detect the

effect of MSM electrolyte on the high-voltage performance of LiCoO<sub>2</sub>. At the same time, the commercial graphite was used as the positive electrode, and the negative electrode, separator, and electrolyte were the same as used above. The graphite/Li 2016-type coin cells were assembled in an argon-filled glovebox to study the impact of MSM electrolyte on cycling performance of anode materials.

The charge and discharge behaviors were tested on the LAND CT-2001 test system. The Li/LCO half-cell cycle tests at room temperature were based on the protocol below: the first cycle of the battery was first charged at a current density of 0.01 C for 1 h as an activation step and then subjected to a cyclic test at a current density of 1 C at a voltage range of 2.75–4.45 V/4.55 V (CC/CV charge–CC discharge, the off current of the constant voltage charging was 1/10 of the constant current charging current value, 1 C = 200 mA g<sup>-1</sup>). The Li/graphite half-cell cyclic tests at room temperature were based on the agreement below: the first cycle of the battery was charged and discharged at a current density of 0.1 C for two cycles as a precycle step. After the precycle treatment, the cycle test was performed at a current density of 0.2 C in a voltage range of 0–3 V (CC discharge–CC charging, 1 C = 370 mA g<sup>-1</sup>).

The ac impedance test was performed in the following manner: the 300 times cycled battery was fully charged by CC/CV in the voltage range of 2.75-4.55 V and then placed on the Solartron for the ac impedance test. The frequency test range was 100 kHz–0.1 Hz, the ac perturbation voltage amplitude was 10 mV, and the electrochemical impedance spectroscopy (EIS) equivalent circuit was fitted by using Zview software.

2.4. Morphology and Composition Analysis. The recycled Li/ LCO battery was disassembled in a glovebox, and the LCO electrode and the lithium piece were rinsed four times with anhydrous DMC to clean the remaining EC and decomposition products of LiPF<sub>6</sub> on the surface of the electrode piece. The electrodes were placed in a glovebox and dried at room temperature. The scanning electron microscope (SEM) was used to observe the surface topography of the LCO electrode, X-ray diffraction (XRD) was performed to measure the crystal structure of the material, X-ray photoelectron spectroscopy (XPS) was executed to determine the deposition of electrolyte decomposition products on the surface of the electrode, transmission electron microscopy (TEM) was applied to observe changes in the microstructure of material particles, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was employed to detect the amount of transition metal ions from the electrode, and differential scanning calorimetry (DSC) was utilized to observe the heat release of different electrolytes with LiCoO<sub>2</sub> materials.

#### 3. RESULTS AND DISCUSSION

**3.1. Orbital Energy Calculation Results and LSV.** The HOMO and LUMO levels of the solvent determine the properties of oxidation and reduction: if the HOMO level of a substance is higher, its oxidation potential is lower, and the more easily it is oxidized; if the LUMO level of a substance is lower, the higher its reduction potential is and the more easily it is reduced. The Gaussian 09 software package has been used to calculate the HOMO and LUMO levels of the material, as shown in the Table 1 and Figure 1. It turned out that the HOMO level of HFE and FEC is very low, which can greatly improve the oxidation resistance of the electrolyte. At the same

# Table 1. Calculated HOMO/LUMO Energies (in eV) of DMC, HFE, FEC, and MSM

molecule	HOMO (eV)	LUMO (eV)
DMC	-8.47	0.06
HFE	-9.67	0.073
FEC	-9.10	-0.026
MSM	-8.43	-0.019



Figure 1. Diagram of the HOMO and LUMO energy levels of FEC, EC, DMC, HFE, and MSM.



Figure 2. Linear sweep voltammograms of different electrolytes from OCV to 6 V vs  $Li/Li^+$  at a scan rate of 0.1 mV/s: (a) is the overall result of the LSV test, and (b) is the amplified portion of 3.8–5.0 V.

time, the FEC has the lowest LUMO energy level; thus, it will be preferentially reduced, and its excellent film forming performance will benefit the compatibility with graphite anode in the high-voltage electrolyte. The MSM has the highest HOMO level; thus, it is preferentially oxidized to participate in the positive film formation. The DMC, as a solvent to reduce the viscosity of the electrolyte, has a moderate HOMO and LUMO level; thus, it does not participate in the film formation reaction at the interface between the positive and negative electrodes.

To verify that the MSM electrolyte has the desired oxidative decomposition behavior, the LSV has been performed with an inert platinum electrode as the working electrode. As can be seen from the Figure 2 (Figure 2b is a partial enlargement), as we have envisaged, the oxidation potential of the LB-301 electrolyte is obviously higher than that of the MSM electrolyte, indicating that the components in the MSM electrolyte are preferentially oxidized. According to our design, it should be that the component with the highest HOMO energy level (dimethyl sulfone) is first oxidized, and its oxidation product participates in the positive electrode film formation, thereby reducing the oxidative decomposition of the electrolyte at high voltage and improving the high-voltage performance of battery. To more strongly demonstrate that MSM is the preferred oxidizing component in the electrolyte, the LSV test of the electrolyte without the MSM component and the second LSV test of the electrolyte with the MSM component were also performed. The test results are shown in Figure S2. It is obvious from the test results (Figure S2a) that

the electrolyte with 10% MSM showed a higher oxidation current during the LSV test, but the corresponding current did not appear in the LSV test of the electrolyte without MSM. When the second LSV test (Figure S2b) of the MSM electrolyte was performed, the higher oxidation current disappeared. This also indicated that the preferential oxidation of the electrolyte was due to MSM.

3.2. Electrochemical Performance. At present, the mainstream anode material for commercial lithium-ion batteries is still the graphite-based carbon anode. To verify whether the designed electrolyte has good compatibility with graphite anode materials, both the LB-301 and MSM electrolytes have been tested in the Li/graphite batteries at 0-3 V. The cycle results are shown in Figure S3a, and the coulomb efficiency is shown in Figure S3b. It is found that the coulomb efficiency of the first cycle for the Li/graphite battery using the MSM electrolyte is slightly lower than that for the battery using the LB-301 electrolyte. This is mainly because the FEC in the MSM electrolyte has better film forming properties on the negative electrode surface than the EC, which will preferentially undergo a reduction reaction to participate in the SEI film formation. Despite a lower initial coulomb efficiency, the batteries with different electrolytes both have similar cycle performances, and the capacity and coulomb efficiency are generally consistent. This indicates that the MSM electrolyte as a high-voltage electrolyte has good compatibility with graphite negative electrode and has prospects for commercial applications.

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Figure 3. Electrochemical performance (a–d) and EIS analysis (e, f) after 300 cycles of Li/LCO cells with different electrolytes under a voltage range of 2.75–4.55 V at 25 °C with 1 C charge/discharge.

According to the test results of LSV, the MSM component in the designed electrolyte will preferentially oxidize after the first cycle, and a protective layer will be formed on the surface of the positive electrode material, thereby achieving the effect of improving the cycle performance of the battery under high voltage. To confirm this point, the EIS test after the first cycle of the battery was carried out, and at the same time, the XPS test of the positive electrode material after the first cycle was also performed. It can be seen from the EIS result (Figure S4) that the battery impedance using the MSM electrolyte ( $R_{all}$  = 19.76  $\Omega$ ) is slightly larger than that of the battery using LB-301  $(R_{\text{all}} = 18.5 \ \Omega)$ , which is mainly due to the difference in SEI impedance ( $R_{SEI}$ ).  $R_{SEI}$  of the battery using MSM electrolyte is 8.08  $\Omega$ , while the  $R_{\rm SEI}$  of the battery using LB-301 is 6.35  $\Omega$ . This also shows that the MSM electrolyte will form a protective film on the surface of the positive electrode during the first cycle. The XPS result (Figure S5) shows that the positive electrode showed a very pronounced peak of S 2p in the XPS test with MSM electrolyte, which is a good proof that film formation by dimethyl sulfone appeared in the first cycle.

The LB-301 and MSM electrolytes have been used to assemble Li/LCO batteries separately, and the batteries have been cycled at voltages of 2.75-4.45 V under room

temperature (the loading density of the positive electrode material is ~12.4 mg cm<sup>-2</sup>). The cycle results are shown in Figure S6a, the coulomb efficiency is shown in Figure S6b, and the data of capacity are listed in Table S1. Compared to the conventional electrolyte, the cycle performance of Li/LCO in MSM electrolyte is significantly improved at a high voltage of 4.45 V. The coulomb efficiency is higher than 99.8% after the second cycle, the capacity is still as high as 149.4 mAh g<sup>-1</sup> after 300 cycles, and the capacity retention rate is 87.1%. In comparison, the battery capacity using the LB-301 electrolyte is rapidly attenuated, the capacity is only 65.9 mAh g<sup>-1</sup> after 300 cycles, and the capacity retention rate is N1%. This shows that the designed high-voltage electrolyte, MSM electrolyte, does greatly improve the cycle performance of LCO at a higher voltage.

Because the MSM electrolyte has been proven to improve the electrochemical performance at 4.45 V cutoff voltage, an additional test is performed at a cutoff voltage of 4.55 V. The cycle performance is shown in Figure 3a, the coulomb efficiency is displayed in Figure 3b, and the specific data of the test are enumerated in Table S2. It is obvious that the initial discharge capacities of the both batteries using LB-301 and MSM electrolytes are significantly higher than that of 4.45 V after the voltage is increased to 4.55 V, but the cycle stabilities reduce to a different extent than that of 4.45 V. The capacity of the battery with LB-301 electrolyte is attenuated more rapidly, the capacity is reduced from 198.7 to 41.7 mAh  $g^{-1}$  after 300 cycles, and the capacity retention rate is only 21.0%. On the contrary, the battery using the MSM electrolyte still has a better cycle performance at 4.55 V. The coulomb efficiency is higher than 99.7% after the second cycle, the capacity is still as high as 147.3 mAh g<sup>-1</sup> after 300 cycles, and the capacity retention rate reaches 74.9%. This means that the high-voltage electrolyte, MSM electrolyte, still has a good cycle performance under the cutoff voltage of 4.55 V. At the same time, the rate performances of the batteries with two different electrolytes were also studied. The two batteries were tested at the different rates of 0.2 C/0.5 C/1 C/2 C/5 C under the voltage of 4.55 V at room temperature. From the test results (Figure S7), we can clearly see that the battery using the MSM electrolyte has better rate performance, especially at higher rates. This may be related to the slightly higher ionic conductivity of the MSM electrolyte than the LB301 electrolyte; the ionic conductivity of the two electrolytes at different temperatures was measured by an ionic conductivity meter (DDS-307A, INESA Scientific Instrument Co., Ltd.). The conductivity behavior was analyzed with the VTF equation

$$\sigma = \sigma_0 \exp\left[\frac{-B}{T - T_0}\right] \tag{1}$$

where B is the activation energy,  $\sigma_0$  is the pre-exponential factor,  $T_0$  is the theoretical glass transition temperature, and T is the absolute temperature.<sup>25</sup> The respective VTF diagrams are displayed in Figure S8, and the VTF fitting parameters are shown in Table S3. According to the test results, at the temperature of 25 °C, the conductivity of the LB-301 electrolyte is  $11.51 \text{ ms cm}^{-1}$ , and the conductivity of the MSM electrolyte is 12.49 ms  $cm^{-1}$ . In addition, the cycling performance of Li/LCO in DMC/FEC/HFE electrolyte without 10% dimethyl sulfone is tested (Figure S9). Compared with the MSM electrolyte, the electrolyte exhibits significantly worse electrochemical cycle performance, and it can be seen that the MSM can form a good protection for the positive electrode material at high voltages. Moreover, the charge and discharge curves of different turns change dramatically (Figure 3c). As the loop progressed, the slope of the baseline cell charging curve increases sharply, the discharge capacity of the battery reduces rapidly, and the discharge platform attenuates. By contrast, the charge and discharge curves of the MSM cell maintained good stability (Figure 3d).

The electrochemical impedance of the fully charged state after 300 cycles (Figure 3e,f and Table 2) has been obtained by the Zview software. The Nyquist plot consists of the electrolyte body impedance ( $R_s$ ), SEI impedance ( $R_{SEI}$ ), electron transfer impedance ( $R_e$ ), and charge transfer impedance ( $R_{ct}$ ).<sup>26–29</sup> We found that  $R_s$ ,  $R_{SEI}$ , and  $R_e$  are similar for both the LB-301 and the MSM, but the charge transfer impedance  $R_{ct}$  has an

 Table 2. Fitted Resistance Values for the Cells with

 Different Electrolytes after 4.55 V Cutoff Cycling

fitted resistance (ohm)	R <sub>s</sub>	$R_{\rm SEI}$	R <sub>e</sub>	R <sub>ct</sub>	$R_{\rm all}$
LB-301	25.0	20.8	7.9	766.1	819.8
MSM	20.5	17.2	2.8	13.6	54.1

obvious difference. Because of the continuous oxidative decomposition of the electrolyte, the SEI film on the surface of the positive electrode will become thicker and thicker, which will cause the charge transfer of the battery circulating in the LB-301 electrolyte to become more and more difficult, resulting in a large charge transfer impedance ( $R_{\rm ct} = 766.1 \Omega$ ), but the battery using the MSM electrolyte has a significantly reduced charge transfer resistance. Therefore, the total battery resistance  $R_{\rm all}$  (equal to the sum of  $R_{\rm s}$ ,  $R_{\rm SEI}$ ,  $R_{\rm e}$ , and  $R_{\rm ct}$ ) by using the LB-301 electrolyte is significantly larger than that of the battery using the MSM electrolyte.

3.3. Characterization of LCO Electrode at High Voltage of 2.75-4.55 V. To further study the mechanism of MSM electrolyte to improve battery performance, we have conducted a more in-depth study of the electrode sheet after circulation. Figure 4a-c shows the SEM images of the fresh LCO electrodes and the electrodes after 300 cycles at 4.55 V high voltage. It can be seen that the fresh LCO surface is very smooth, and the surface becomes very rough with sediment after 300 cycles of high-voltage cycling in the LB-301 electrolyte. These deposits are caused by the oxidative decomposition of LB-301 electrolyte on the surface of the positive electrode during high-voltage cycling.<sup>30</sup> After circulating 300 times in the MSM electrolyte, the surface of the positive electrode remains in a smooth state. It is mainly because the MSM electrolyte can significantly suppress the oxidative decomposition of the electrolyte on the surface of the positive electrode at a high voltage.

At the same time, the TEM technology has been also used to microscopically characterize electrode materials after electrochemical cycling. From the transmission electron micrograph (Figure 4d-g), it can be clearly seen that the electrodes cycled with the LB-301 electrolyte generates a layer of deposit of about 10-20 nm around the positive electrode material particles. However, the surface of the LCO electrode material particles is relatively flat compared with that using the MSM electrolyte, and no visible sediment can be found around the particles. This shows that the MSM electrolyte helps to inhibit the oxidative decomposition of the electrolyte compared to the LB-301 electrolyte, which is consistent with the results of the previous part of the SEM test.

In addition, from the results of the XRD test (Figure 5a), it can be seen that the peaks of the fresh LiCoO<sub>2</sub> material, and the LiCoO<sub>2</sub> circulating under the electrolytes of LB-301 and MSM electrolyte, respectively, are all consistent with the standard PDF card of LiCoO<sub>2</sub> (LCO-PDF #75-0532). At the same time, after amplification of the peaks from  $64^{\circ}$  to  $68^{\circ}$ (Figure 5b), it is obvious that the (018)/(110) splitting diffraction peaks of the electrode using the LB-301 electrolyte become less noticeable than the original materials. However, the corresponding splitting peaks of the electrode that circulated under the MSM electrolyte are well maintained. For the layered structure cathode materials, the more obvious the separation between (018) and (110) peaks, the more complete the layered structure of the material is.<sup>31,32</sup> It can be seen that the use of MSM electrolyte helps to maintain the stability of the LiCoO<sub>2</sub> material circulating at high voltage, which is consistent with the results of previous SEM and TEM tests. Other than this, well known to everyone is that as the cycle progresses the repulsive forces between slabs and the average oxidation state of the transition metal ions will increase and thus bring the contracted *a*-axis and extended *c*-axis lattice parameters.<sup>33–35</sup> After accurate calculations, the lattice



Figure 4. SEM images of the fresh LCO cathode (a) and 4.55 V high-voltage cycled LCO cathodes with the LB-301 electrolyte (b) and MSM electrolyte (c). TEM images of the high-voltage cycled LCO cathodes with LB-301 electrolyte (d, e) and the MSM electrolyte (f, g).



Figure 5. XRD images of the fresh LCO cathode and 4.55 V high-voltage cycled LCO cathodes with the LB-301 electrolyte and MSM electrolyte (a, b). ICP images of cobalt ion eluted from the surface of the LCO electrode with different electrolytes (c). XPS profiles of the surface elements on the LCO cathode after 300 cycles at a high voltage of 4.55 V with LB-301 electrolyte and MSM electrolyte (d-f).

parameters of the  $LiCoO_2$  material in different states have been obtained, as shown in Table S4. As we expected, the shrinkage of the *a*-axis and the expansion of the *c*-axis are significantly inhibited when using the MSM electrolyte compared to the LB-301 electrolyte, which further illustrates the advantages of the designed electrolyte in maintaining structural stability of the material.

To further investigate the influence of MSM electrolyte on the LCO cathode, the ICP-AES has been used to measure the number of cobalt ions dissolved from LCO cathode pieces (the number of cobalt ions measured includes all cobalt ions eluted from the positive electrode material into the separator and the negative electrode material). From the ICP test results (Figure 5c), it can be clearly seen that when the MSM electrolyte is used, the amount of metal cobalt ions eluted is less than onethird of the amount of metal cobalt ion eluted when the LB-301 electrolyte is used. This shows that the  $LiCoO_2$  material is less damaged when the MSM electrolyte is employed, which brings less metal cobalt ion dissolution.

To better explore the effect of electrolyte on the surface of the cathode material after high-voltage cycling, XPS has been used to determine the composition of the surface of the cathode material. Panels d, e, and f of Figure 5 respectively show the XPS F 1s, P 2p, and S 2p spectra of LCO electrode surface after 300 cycles at 4.55 V high voltage with the LB-301 electrolyte or MSM electrolyte. In the spectrum of F 1s (Figure 5d), the main peak corresponding to 685.0 eV belongs to the peak of LiF,<sup>36</sup> and from the test result, it is apparent that the

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intensity of the LiF peak is definitely stronger for the LCO with the LB-301 electrolyte than that with the MSM electrolyte. LiF is mainly caused by the decomposition of LiPF<sub>6</sub> in the electrolyte, and it may cause an increase in battery impedance,<sup>37</sup> which is also consistent with the impedance test results mentioned in the previous article. In the P 2p spectra (Figure 5e), the peaks at 136.3 and 133.7 eV can be assigned to  $\text{Li}_{x}\text{PF}_{y}$  and  $\text{Li}_{x}\text{PO}_{y}\text{F}_{z}^{-38}$  which are also due to  $\text{Li}\text{PF}_{6}$ decomposition on the cathode surface. By comprehensively observing the F 1s and the P 2p spectra, it can be seen that the intensities of LiF,  $Li_x PF_{y}$  and  $Li_x PO_y F_z$  are much weaker on the cathode surface when the MSM electrolyte is used than that of the LB-301 electrolyte, which also proves that the MSM electrolyte can significantly inhibit the decomposition of LiPF<sub>6</sub> in electrolyte at a high-voltage cycling. The S 2p peak (Figure 5f) intensity in the XPS spectra of the cathode with MSM is higher than that for the control sample. The S element is a characteristic element in the designed electrolyte. Because there is a strong peak of S 2p on the surface of the positive electrode material, it is indicated that the MSM actually decomposed on the surface of the positive electrode and formed a film, which is consistent with our previous design ideas.

In addition, the safety performance is also an important indicator of whether the electrolyte can be commercialized.<sup>39</sup> Therefore, the DSC tests of the delithiated LCO material in two different electrolytes have been carried out. The curve is shown in Figure S10. It can be clearly seen from the comparison that after using the MSM electrolyte, although the heat flux value of the first small exothermic peak slightly increases, the exothermic temperature of the second main exothermic peak extends from 247.1 to 262.9 °C. More importantly, its maximum heat flow value decreases from 5.378 to 1.306 mW/mg. The above data show that our MSM electrolyte can improve the safety performance of the battery to a certain extent, not only delaying the peak temperature of its main exothermic peak but also significantly reducing its maximum heat flow value, thereby greatly reducing the severity of the heat release of the battery.<sup>2</sup>

#### 4. CONCLUSIONS

In summary, we have designed an effective type of high-voltage electrolyte based on the guidance of theoretical calculations combined with the advantages of different solvents. The electrolyte is composed of the fluoroethylene dipropyl ether, which is excellent in antioxidation and antireduction, the fluorinated ethylene carbonate, which is excellent in antioxidation and has a better film forming property on the negative electrode surface, the dimethyl sulfone, which preferentially oxidizes on the positive electrode and participates in positive electrode film formation, and the lowviscosity dimethyl carbonate as a solvent. This designed electrolyte can not only greatly improve the cycle performance of Li/LCO battery at 4.45 and 4.55 V but also has a good compatibility with graphite anode. At the same time, it also has a certain improvement on the safety performance of the battery, not only delaying the peak temperature of its main exothermic peak but also significantly reducing its maximum heat flow value. Therefore, the designed high-voltage electrolyte made of such a mixed solvent has good prospects for future application to actual battery production.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.9b00149.

Chemical structure of the four solvents DMC, HFE, FEC, and MSM, LSV test of electrolyte with and without MSM component and the second LSV test of the electrolyte with the MSM component, electrochemical performance of Li/graphite cells with different electrolytes under a voltage range of 0-3 V, EIS analysis of first cycle of Li/LCO cells with different electrolytes under a voltage range of 2.75-4.55 V at 25 °C, XPS profile of the sulfur element on the surface of LCO cathode after first cycle at a high voltage of 4.55 V with LB-301 electrolyte and MSM electrolyte, electrochemical performance of Li/LCO cells with different electrolytes under a voltage range of 2.75-4.45 V after 300 cycles, rate performance of Li/LCO cells with different electrolytes under a voltage range of 2.75-4.45 V at 25 °C, VTF plot of conductivity of LB-301 and MSM electrolytes, cycle performance after 300 cycles of Li/ LCO cells with and without MSM component in electrolytes under a voltage range of 2.75-4.55 V at 25 °C, DSC curves of delithiated LCO with LB-301 and MSM electrolyte, comparative cycle performances data of Li/LCO cells under a voltage range of 2.75-4.45 V with different electrolytes, comparative cycle performances data of Li/LCO cells under a voltage range of 2.75-4.55 V with different electrolytes, VTF fitting parameters of conductivity of LB-301 and MSM electrolytes, calculated lattice parameters of LiCoO<sub>2</sub> under different conditions (PDF)

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### Notes

The authors declare no competing financial interest.

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